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3.091SC Introduction to Solid State Chemistry, Fall 2010
Transcript – Session 8

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PROFESSOR: OK. OK. Settle down. Settle down. Settle down. So the weekend doesn't begin until after the 3.091 lecture.

OK. A couple of announcements. Tuesday, Quiz 3 based on Homework 3. The final exam has been scheduled. In fact, all the finals are scheduled now, so please consult the Registrar's listing. The celebration of celebrations, the 3.091 final exam, will be Tuesday, 15th of December in the morning, 9:00 am to 12:00 noon over in the Johnson Athletic Center. So I urge you to go through the final exam schedule and then make your travel plans when you know what your last obligation is. And book them soon, because we've got about a quarter of a million students in the Boston area and the semesters all come to a close within a very narrow time window, and everybody's trying to get through a wormhole called Logan Airport. So you want to be ready. Do not try to leave town before you've met all of your obligations. You can't leave before you've finished all of your finals. But you know what they are now, so call your travel agent or make your internet booking.

And an announcement for Professor Paul's section. Owing to the holiday on Monday, he's going to have office hours from noon to 1:30 today. So if you're in Professor Paul's section, you'd like to catch up with him, noon till 1:30 today.

All right. Let's get to the lesson. The last day we started looking at octet stability, and we looked at octet stability and what it means in terms of shell filling and some sweet spot in energy with respect to reactivity. And a filled shell leaves us with this electron configuration, ns^2np^6 for n greater than 1. In the case of n equals 1, there's just ns^2 for helium. Otherwise, ns^2np^6 . 2 plus 6 is 8. There's the octet stability. It's observed trivially in noble gases. And then we saw that it can also be observed in certain ions.

And how do we get to octet stability? Electron transfer. And here's the prototypical reaction. I like this. This is very iconic. It puts it in broad terms. The marriage of an electron donor with an electron acceptor leads to the formation of a cation and an anion, thanks to electron transfer from the donor to the acceptor. It doesn't end there, though. You have cations and anions in the gas phase and they're attracted to one another by coulombic forces, or electrostatic forces, and that leads to ionic bonding. And today I want to go deeper into it and study the energetics of ion-pair formation.

So let's do it. And what I'm going to do is study this with reference to an example of sodium chloride. So we will go through the energetics of sodium chloride, which we know is going to exist as Na plus and Cl minus-- sodium being the electron donor and chlorine being the electron acceptor.

So what I'm going to do is show you a plot of energy as a function of separation. So you're going to have to be pluralistic here in your ideas. So, for example, if I wrote this word by itself you don't know if I'm saying lead or I'm talking about the metal lead. The only way you know is in context. And so you have to know in context here. So r is not the radius of the atom. In this case it's the symbol. And I'm using this symbol not to confuse you. This is what professionals use. So if you go to the text and the literature you'll see r . This is the interionic separation, and it's determined nucleus to nucleus. So I'm going to put a sodium ion at the origin. This is the origin. Energy is on the ordinate. So I'm going to model this as a hard sphere. So this is sodium ion, Na plus, and it's got some finite radius. And its radius, I'm going to call it r_{+} . That's the radius of the cation.

And next to sodium I'm going to put the chloride anion. And it's bigger. It's bigger. It's not to scale, but it's bigger. So this is chloride, the Cl minus, and it has its radius, r_{-} . And then the interionic separation is measured from the sodium nucleus to the chloride nucleus, and it's given the symbol r_0 . That's the interionic separation. And we could we write that r_0 , in fact, is strictly $r_{+} + r_{-}$ because we're using a hard sphere model. So there's no shrinkage when the two touch. So that makes sense.

Now what I want to do is calculate the energy here. The only energy that we have here is electrostatic. So we're going to start and say, imagine if we had these two ions separated by infinite distance and we brought them to a separation of r_0 . How much electrostatic energy would be stored there? So I can write that as E , and I'm going to call it attractive. There's a force that attracts these two ions together, and that's given by Coulomb's Law. So that's the product $q_1 q_2$ over $4 \pi \epsilon_0 r$, in general. I'm making this as a function of r and then we're going to figure out how to get to r_0 .

Let's put a little ledge in here. So q_1 , I'm going to make that the sodium just for grins and chuckles. So q_1 is equal to the z , the valence on the sodium, times the charge, the elementary charge. So the charge on the sodium is plus 1-- so it's plus $1e$ -- and q_2 is going to equal the charge on the chloride times e . And in this case the chloride ion is negative 1, so q_2 is minus e , q_1 is plus e . Now if instead I were doing magnesium oxide, magnesium would be plus 2, oxide would be minus 2. So that's where the charge on the ion comes into play.

So we can put that in here and will make this $z_{+} e$, $z_{-} e$. So there's $q_1 q_2$ over $4 \pi \epsilon_0 r$. And in this case, for sodium chloride, this is plus 1 times minus 1 is minus 1 e^2 over $4 \pi \epsilon_0 r$. So this is a function of r . This e is $1/r$. That's the hyperbole, and I can draw that here. So it's going to look something like this. All right? It's going to be a right like this. Good. So that's the attractive force.

Now how do we avoid the ions just blending together? Why do they stop at r_0 ? What puts the brakes on the coulombic force? Ah! For that we have to look at the fine structure of sodium. So let's look at the fine structure of sodium.

So sodium is net charge plus 1. But sodium more properly, if I go to the next level of structure, is really 11 protons in the nucleus and it's got electrons around it-- in total, 10 electrons. So it's net charge is plus 1, all right? Now if I'm way over here and I look at sodium I just see something of charge plus 1. And, in fact, I could

model sodium as just a point charge, a plus 1, and do all the electrostatics and I would be perfectly accurate in my estimation. But as I get closer I see there's fine structure. It's like so many other things in life. You know, from a distance it looks really good, and you get up close you go, eww.

[LAUGHTER]

PROFESSOR: I'm not going to mention any names, all right? But it's Friday. Be careful. So as I get up closer I realize that it's plus 1, but the plus 1 is plus 11 mediated by minus 10. So when things start getting close together this exterior of negative charge becomes manifest, palpable.

So let's look at the chlorine. The chlorine's coming, sees plus 1, plus 1. It starts getting closer and closer. And now what happens? The negative electronic configuration on the outside of sodium is interacting with the negative electronic configuration on chlorine, and the result is you have electron-electron repulsion. And we've got an equation for that, and that's given by $E_{\text{repulsion}}$ is equal to some constant b over r to the n . And this n is called the Born exponent. It's not the quantum number. So r today means interionic separation, n means Born exponent. And you have to determine it by experiment and the value lies between 6 and 12. And we have to determine b by experiment.

So let's say this thing's got a-- pick a number in the middle. Say it's 8. So let's plot r to the eighth. So that's going to hug the abscissa, and it's going to come in really, really close. And then somewhere around this distance here, where the electron-electron repulsion starts to be felt, this thing takes off. But 1 over r to the 8 goes way, way up fast. So instead of being a gentle curve it's more like a hockey stick shape here.

And so now the net energy is the sum of the negative attractive energy and the positive repulsive energy. And if we sum the two what are we going to get? Well, way out here 1 over r to the 8 is negligible. And the net value-- so E_{net} , in red-- is essentially equal to $E_{\text{attractive}}$. And at very, very low values of r , r to the 8 dominates r . So we have this as the net value. And the two sum-- and I can't quite do it because of the way this is drawn, but I think you can see. These two eventually equilibrate and go through a minimum. So I'm going to cheat a little bit here and I'm going to add these two in such a way as to go through a minimum value of energy at r equals r_0 , which is the sum of $E_{\text{attractive}}$ and $E_{\text{repulsive}}$.

So we can sum those two and let's see what we get. At r equals r_0 , E_{net} is equal to its minimum value. So how do you find a minimum in a function? You take the derivative. I'm going to put some math to work here. So we'll take dE by dr and set it equal to 0. And the value of r at which it equals 0 is termed r_0 . OK?

So we'll just go through and take the derivative of that thing. And I'm not going to go through all the math but just show you the set-up here. What's the other thing that we know? dE by dr represents what? That's force. So I could say that at r equals r_0 the net force is 0, which is what you'd expect. Because if the net force isn't 0 it's going to either push the ions farther apart or draw them closer together. So this is mathematics imitating reality. What a concept. Math working for you instead of you working for math.

So what do I have? I have everything in these equations except the value of b . I'm assuming we know the value of n from experiment. We don't know the value of b . And so you can solve to get the value of b , and once you've got that you can put everything together and give an expression for the energy of the system at r equals r_0 . When you plug everything in you get this: z -plus, which is the net charge on the cation, times z -minus, which is the net charge on anion, divided by $4\pi\epsilon_0 r_0$. $1 - 1/n$, where n is the Born exponent. And this is valid at r equals r_0 only. If you're not at r equals r_0 then you can get the value of b and then put it into this expression, where E_{net} will equal $E_{\text{attractive}}$ plus $E_{\text{repulsive}}$. So there it is.

And so this represents-- this is the energy of a single ionic bond, because that's all the energy that's there. It's the single ionic bond. And the second thing that we realize is plus times minus is net minus, so this means that it's negative quantity, as it should be. It has to be a negative quantity.

All right. So what do we have here? What we've seen by going through this derivation is the recognition that the ionic bond is electrostatic attraction mediated by electronic repulsion. It's the balance of the two. And those words sound so good to me that I'm going to write them down. Electrostatic attraction mediated-- another lovely word-- mediated by electronic repulsion. So that's how you get to the final setting here of the interionic separation.

So what are the characteristics? What does this lead to in terms of characteristics of this bond? Characteristics of the ionic bond. First of all, it's omnidirectional. This is a concept based on the fact that the electric field radiates in all directions uniformly. So the negative field coming from the chloride ion is uniform in all directions. There's no preferred direction. Omnidirectional. OK? E field-- oh, I better not say that. Electric field, not the energy field, radiates in all directions uniformly. And that's going to have consequences. I'm not just telling you this because we like cataloguing things. This isn't a bookkeeping class. So we're going to come back, use this fact.

And the second thing is that the bond is unsaturated, which is a chemical way of saying that a given ion can bond to more than one other ion. In other types of bonds that's not the case. A given atom can only bond once and then it's done. Whereas in this case the ion can bond to a plurality of other ions. So ions bond to more than one. OK? Plurality of bonds is formed. They're polygamous, if you like.

So what does that mean? That means that here is what happens. We've got the blues as the sodiums, and for any given sodium it forms bonds without limit until the number of bonds is stopped by physical limitations-- not because the E field was saturated. It's unsaturated. You just can't jam any more chlorides physically around the sodium. That's why the sodium is only bonding to the number of chlorides that it bonds to. There's no intrinsic limitation.

So what happens when you get to this situation where you have omnidirectional forces, unsaturated bonds, and ions that you can model as hard spheres of constant radius? All the sodiums have the same radius, all the chlorides have the same radius. You make a 3-dimensional ordered array. So you can make an infinite atomic ordered array, which we use the simple Anglo-Saxon word last day to describe: crystal. You form a crystal. And as a result ionics have to be solid at room temperature, because if you've got thousands and thousands of atoms together in one aggregate they're not going to float. They're going to settle. Put another way, the strength of the bond, the amount of energy in here, is so great that the thermal

energy of the room isn't great enough to disrupt this bond. It's a combination of unsaturated, omnidirectional, and high energy. So we form solids at room temperature.

OK. Now I want to show the energetics of that one because this is good. You know, I promised you I wouldn't do derivations, so I'm not going in detail on this. I'm giving you just enough so that I can introduce the characters here. You know, how else am I going to introduce the Born exponent? Am I'm just going to say, there's this exponent n , the Born exponent. We're going to introduce it in context. So now you know what the energetics are.

So now I want to prove to you energetically along this line that crystals will form. So let's imagine-- we're going to do this thought experiment. We're going to take three ion-pairs of sodium chloride. So here's three ion-pairs of sodium chloride. And I want to compare these three ion-pairs. So this is an ion gas. And the distance between ion-pairs is great enough that one pair doesn't affect the other. The electrostatics are only strong within the pair. So we'll just label this infinity with quotation marks around it. They're very far apart. When a physicist says they're very far apart, very is code for infinity.

So this one doesn't interact with this one, which doesn't interact with this one. And I want to compare the energetic state of the ion dispersion to what would happen if I were to put all of those in a single line. Plus, minus, plus, minus, plus, minus. So then this has a certain energy state, it's the energy of the ion line. And I want to show you that there's an energy decrease in collecting all of these and ordering them into a line. So there's more energy in a line dance than in ballroom dancing. That's what we're going to say ultimately. OK?

So let's compare the energies. That's all we're going to do. So what's the energy of this? Well, we're not going to do 3 versus 3. Let's think big. It's Friday. So let's take Avogadro's number of pairs, shall we? So the energy of the ion dispersion would then equal-- that's the energy of one pair, and they're infinite distance apart, so there's nothing to be gained by putting them in the same chamber. So it's just going to be N Avogadro, if that's the number, times the energy evaluated at r equals r_0 . So we're done. And we know what that is. I don't have to rewrite it for you.

OK. So now what I have to do is get an estimate of the energy of the line and show you that the line is at a lower energy state. Well, let's see. Jocelyn, take the top one and the middle one, please, but not the bottom one. Thanks.

OK. So now let's look at the energy of a line. So we're going to do-- here's my line. I'm going to get the colored chalk. Green and blue. You know, some people think being a professor is so cool because you get to travel, you get to research, and so on. It's the colored chalk.

[LAUGHTER]

PROFESSOR: It's the colored chalk. All right. So there's a sodium. And on each side of the sodium we'll put a chloride. All right? And I'm going to just keep going this way. Here's a sodium and here's a chloride. All right. And now what I'm going to do, I'm going to start here at this sodium and I'm going to count the energy, electrostatic energy, that's in this system. So we're going to count to the left, we're going to count to the right, and then we're going to multiply it by the total number of

ion-pairs. And I know that the ones on the end aren't the same, but the number of ends over N Avogadro, that's peanuts. The edge effects are negligible because there's such a giant middle. That's how you model this stuff. You don't obsess over the fact that the last ion doesn't see anything on that side. You just do it and forget about it, because you know you wouldn't do it for 5. This would be a big problem. But if you have Avogadro's number, who cares? It's called risk assessment.

All right. So let's look at the energetics here. So what we've got is the energy of the ion line. OK? So let's start with this central one. And separated by distance r_0 is the chloride, and there's an attractive energy here. So that's going to equal minus e squared over $4\pi\epsilon_0 r_0$. Now I'm going to keep going, because the field is unsaturated and goes in all directions. So this sodium, that's a distance $2r_0$ away. It's got a repulsive force exerted on this sodium. So let's add that. So that's going to be plus. A repulsive force raises the energy of a system. That's e squared over $4\pi\epsilon_0$ times $2r_0$.

And let's keep going. So now let's go $3r_0$ away. So 3 times r_0 , that gets me out to the chloride over here. Let's put $3r_0$. Now that will take me from the center of the sodium to the center of the next chloride. And that's going to be attractive. So that'll be minus e squared over $4\pi\epsilon_0$ times $3r_0$ plus, et cetera. So you see how this goes. So you go all the way out, you add them all up, and you go the other way. And so on and so forth.

So that's how the derivation goes. You might say, hey wait a minute. What happened to the Born exponent and the repulsive energy term? Well, where's the repulsive energy term going to be felt? It's called electron-electron repulsion. Axiomatically, the electrons here are nowhere near these electrons. See, you only have to count it for the nearest neighbor. So we can patch that in at the end. And we do. I haven't forgotten. But I'm not going to spend a whole day trying to derive this thing. I'll show you how it starts to evolve. At some point you end up with something that looks like this. e squared over-- in fact, I'll put the minus sign up here. Minus e squared over $4\pi\epsilon_0 r_0$. And you're going to double it, because you're going to go one side and the other side, and you're going to get a series that looks like this: $1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \text{blah, blah, blah}$. Yeah. OK.

So what does this look like? I've really broken this into two pieces. So this coefficient out in front here, you should now be able to repeat this in your sleep: e squared over $4\pi\epsilon_0 r$. This is electrostatics, isn't it? Electrostatics. This is the consequence of Coulomb's law.

What's this second term here? What's this all about? Geometry. This is dictated by atomic arrangement. So I could calculate this if I took, instead of a line, what if I put them in a sheet subject to the constraints of those sizes and plus 1 and minus 1? So what would be? I'd start at the sodium and count how many chlorides? If I'm on a plane there'd be one, two, three, four. And then how many sodiums? Well, they'd be on the backside of each of the chlorides. And I'd add them all up in 2-space and I'd end up with another coefficient here. All right? And we compress all of this into a coefficient which we call the Madelung constant. And it's a function of the atomic arrangements. So different crystal structures have different Madelung constants. It's named after a German professor, Madelung.

In 1910, he published calculations for the energy of a system of point charges-- just abstract theoretical paper. And then about 10 years later another German professor

by the name of Paul Ewald-- he did his PhD for Sommerfeld-- he published a paper in which he actually made the calculation for ion crystals, and he came up with this constant. And to show you the class of the guy, instead of naming the constant after himself he named it after Madelung. Now that's class. So Madelung did the first calculation so he gets named.

So now what we're going to do is we're going to multiply by the N Avogadro, because I've got N Avogadro of these things, and we're going to put in the Born exponent patch and so on. And here's what the final expression looks like for the line. There are a few algebraic tricks that I'm not willing to do in class because I don't think that's a profitable use of our time in a chemistry class. But if you want to try the derivation I have it in full and we can compare notes.

So once we get the patch in it's going to look like this. It'll be minus. There'll be the Madelung constant times N Avogadro e squared-- and this is already assuming it's plus 1, minus 1. If this were magnesium oxide there'd be a 4 in here. $4 \pi \epsilon_0 r_0$ times $1 - 1/n$, where n is the Born exponent. So compare this to this one here. What's the only difference? The only difference is the Madelung constant, right? It's the only difference. So E of the pair dispersion is really equal to E of the line divided by the Madelung constant. So what I'm trying to prove to you is that E line is more negative than E of the dispersion. So it all hinges on the magnitude of M . If M is greater than 1 we win. If M is less than 1 I've just proved to you that water runs uphill, so that's a bad day. All right?

So let's calculate the value of M . And you can go to your algebra books. And you've got this series natural log-- and engineers write natural log "ln." I know the mathematicians write "log." Uh-uh. Engineers-- uh. That's $1 + x$. OK? Natural log, $1 + x$. You can expand this as $x - x^2/2 + x^3/3 - x^4/4 + \dots$, dah, dah, dah. You know, look that one up. Set x equal to 1, which is what we've got, right? Because we've got $1 - 1/2 + 1/3 - 1/4 + \dots$, dah, dah, dah, dah. Go through it and you'll get the value that M , according to this, will give you 2 times the natural logarithm of 2, which is 1.386-- which is greater than 1. And so we're golden. That means that the energy of the line is lower, more negative, than the energy of the dispersion.

So I'm going to do this pictorially. Let's make an energy level diagram. And the energy level diagram will look like this. So up here the energy is 0 and everything is negative. So if I put this as minus 1 unit. All right? These are all negative values increasing in this direction. So this is the dispersion of ion-pairs. So all we've done is take a cation and put it to the anion. We've just seen that if we do the calculation for the line it's 1.386 times whatever this is. So that gives us-- this is for the ion line, which I'm going to take the liberty of calling a 1-dimensional crystal. It's a 1-dimensional ordered array. And what I can do is go to the 3-dimensional array, start at the lower right-hand corner with that chloride. Calculate the distance to each of the nearest neighbor sodiums. Go through the geometry. The next nearest neighbor chlorides, the next nearest neighbor sodiums. And you'll build an infinite series and you'll evaluate it. And in three dimensions it's even lower. It's 1.7476. So this is for the 3-dimensional crystal. This is for the ionic crystal. All right? 3-D crystal.

So what this is showing is that the system keeps making more and more bonds. Why does it make bonds? Because the more nearest neighbors it has the lower the energy goes. So making a 3-dimensional crystal is energetically favored.

Now there are different Madelung constants for different crystal structures. You say, well wait a minute. How do you get different crystal structures? Suppose instead of sodium it's potassium. What's the only difference? Potassium is plus 1. What's the difference? Size. Potassium is larger. They're not going to pack quite the same. And so depending on the relative ion sizes-- I mean what if I have something like silver iodide? Iodide is huge. Silver is so small it'll fit into the interstices between touching iodines. So it's going to have a different crystal structure, and the different crystal structure will give us a different Madelung constant. And there it is.

So we've come a long way with that little assumption of octet stability. So now let's take a look at what the properties are of these things. They're solid at room temperature because we've got strong bonds. High melting points. Bonding is related to melting point. Now think point is dictated by bonding, because now you're comparing thermal energy versus the cohesive energy of the crystal. So tightly bonded substances melt at high temperatures, weakly bonded substances melt at low temperatures.

Transparent to visible light. How do I know that? Because I'm the professor. No. How do I know that? How do we think about it when someone says to you is something transparent, in this case to visible light. Well, what I do is I say, here's the solid. This is the ionic solid and here is visible light, $h\nu$. And I'm going to write 2 to 3 electron volts per photon. And what happens when I want to decide whether this is transparent to visible light? Now look at the modeling here. Photon is a squiggle. I don't know if that's Cartesian space. This is like a crystal, right? I'm speaking California. It's like a crystal. So now if I go inside I want to make the energy diagram. So what's the energy diagram look like? All right?

So now the question is how does-- if this is the energy diagram of the crystal and I make this the energy of the photon of visible light, I'm going to compare how much energy the photon has versus how much energy it takes to excite electrons all the way to a new state. Because if you don't excite them all the way to a new state-- they can't go part way, so nothing happens. And if nothing happens the photon goes through and that's transparent. Now what do I know about the binding energy and the energy level diagram of Na plus? Well, it's isoelectronic with neon. And I know that neon has an average valence electron energy of about 20 electron volts. So my guess is the visible light is not going to do anything. And so it just passes right on through. See, we got all that.

Electrical insulator. How do I know that? Well, all that glitters is not gold, but it must have free electrons. And these electrons are all bound, and they're tightly bound.

Hard and brittle. If it's going to be ductile the atoms need to be able to slide over one another. Well, there's no way these can slide over one another because to slide over one another requires that at some point the two sodiums are going to be nearest neighbors, and the repulsive forces are so high the crystal fractures. So if you try to deform an ionic solid you will get it moving in accordance to the elasticity. So force will be proportional to the extension-- Hooke's Law-- but if you try to plastically deform it, you shear it.

Soluble in water. We'll come back to that later.

Melt to form ionic liquids. And good for electrolytic extraction of metals. I showed you magnesium last day. Today I'll talk a little bit about aluminum. But that comes later.

OK. So where do we find elements that are going to form ionic solids? Well, you go back to the beginning of the lecture. What do you look for? You've got to find the box of really good electron donors and the box of really good electron acceptors. That's where you go. So the good electron donors are at the left side and the good electron acceptors are at the right side. So if you take sodium plus chlorine you get sodium chloride. If you get calcium plus fluorine, calcium fluoride. Magnesium plus oxygen, and so on. OK? Yeah, this shows. Yeah. Aluminum plus oxygen, yeah.

There's Max Born. Max Born, he got a Nobel Prize. And so did Fritz Haber, but we're going to come to him in a minute. All right.

So now I want to do this energetic calculation one more way, because right now we've been operating with ion gas but sodium isn't found normally in the form of an ion gas. So let's do something that starts with elements found in nature. So we want to form an ionic crystal from elements in their natural state. And what's going to happen is en route we're going to be able to define a few more terms. So that's going to make everybody happy because we get more definitions. And this is called the Born-Haber Cycle, named after Born and Haber.

And what we're going to do is we're going to-- pardon me, there's a C in there-- we're going to invoke Hess's Law. And Hess's Law is sort of like Kirchhoff's law for electric circuits. Hess's law says that the energy of a chemical change is path independent. So energy change in a chemical reaction is path independent. It's sort of like potential energy in Newtonian mechanics. It doesn't matter if you take the elevator to the top of the Hancock Tower or if you walk up the stairs, the change in potential energy is the same when you express it from the top of the Hancock Tower, although you might be somewhat more exhausted having walked the steps instead of taking the elevator. But you don't get any credit in terms of the potential energy.

So let's use Hess's Law in order to describe the formation of sodium chloride. So I'm going to start with sodium as it's found in nature, and I'm going to talk about room temperature. So sodium is a solid at room temperature, and I'm going to react it with chlorine gas. Chlorine's a gas at room temperature and it's a diatomic molecule. And we're going to react it to form sodium chloride, which is a solid and a crystal. Now you might say, well isn't that kind of redundant? No, because later on I'm going to teach you about a form of solid matter that does not consist of atoms in a regular array-- disordered solids. So we're specifying, I want to form crystal and solid sodium chloride, because that's the reaction that would occur if we were to do it in the lab.

And what have we calculated so far? What we've calculated so far is this. We've calculated chloride ion in the gas phase plus sodium ion in the gas phase reacting to form the crystal. And we've called this the energy of crystallization. That's this Madelung stuff. This is the Madelung energy here. All right? I'll even put M here. Madelung energy. And why am I using H? Because that's what the books use. H is enthalpy, and for condensed matter the difference between enthalpy and energy doesn't amount to much. So H, just for the record, is enthalpy. And we've been operating with E as energy. It's almost equal to E, which is energy for condensed matter. For the gas phase it gets hairy.

OK. So I want to get us from sodium solid, chloride solid over to here. So how am I going to do that? Well, first of all, I know how to make sodium ion gas. I start with sodium gas and then by ionization I make the electron plus sodium ion. So this is called the ionization energy, isn't it? This is the ionization energy. Sodium gas goes to that.

And now how do I get sodium gas from sodium? Well that's just called sublimation. So this I'm going to need ΔH of sublimation. Sublimation is the conversion of solid to vapor. And you can look that up on the Periodic Table. I'll show you how to get that in a second.

And now how do I get chloride gas? Well chloride gas is going to start with atomic chlorine gas, but instead of losing an electron I've got to acquire an electron. And this action of adding an electron is sort of an inverse ionization, and this is called electron affinity. And there are tables of electron affinity. So each element has the ability to lose an electron, it has the ability to gain an electron. Losing an electron is ionization energy, acquiring an electron is electron affinity. And just as with ionization energies, if you have multiple electrons you have a first electron affinity, second electron affinity, and so on.

And now how do I get to atomic chlorine? I've got to dissociate diatomic chlorine. So this is called dissociation.

So that's the whole thing. And I'm going to now put some numbers on here. Let's see. I'm going to call sublimation step one, dissociation step two, ionization I've got here is step three, electron affinity is step four, and crystallization or Madelung is step five. And so working off of Hess's law we can say that the total energy required for the formation of the crystal-- ΔH for the reaction. What's the reaction? The reaction of sodium plus chlorine to make sodium chloride-- is going to be the sum of all of the constituent components. The sum of all the ΔH 's. Not ΔH 's. ΔH 's, like attorneys general. All right?

So now let's add these up. So we go number one. Number one I can look up on the Periodic Table. Where is it? There's Fritz Haber. So that's given here. If you look on the Periodic Table that'll give you the number. And for sodium it's 108 kilojoules per mole. Number two, get that from tables. It's 122. Number three is just the first ionization energy. You look it up on the Periodic Table. First ionization energy of sodium is about 5.3 electron volts, which turns out to be 496 kilojoules per mole.

But look, these are all positive energies and we're trying to make a net negative energy. So these three steps are all raising the energy of the system. Finally, acquiring an electron by chlorine is going to decrease the energy of the system, because chlorine is a good electron acceptor. So that's minus 349. But watch this people. The energy in forming the crystal from the discrete ion-pairs is 787 kilojoules per mole, which gives us a net value of minus 410 kilojoules per mole. So what this is showing you is what the relative contributions are of the different components of that thing.

So here it is in graphical form. There's the vaporization of sodium. This is the dissociation of chlorine. This is the ionization of sodium. All positive energies. And now electron affinity. And look at this contribution from the Madelung energy. So

when things crystallize a lot of heat's given off. In fact, we can use that in cooling and moderating climate if we're clever about it.

All right. Now just to show you what the different values are here that you're going to go in and get the lattice energies, you need to know the various r values, you see. The r_0 is simply going to be the r -plus and the r -minus. So lithium fluoride, there it is. There's the lattice energy and it's based on the combination of lithium cation and fluoride anion. So they've gone through and calculated these values. So there's sodium chloride is 787. And, you know, you even get things like the boiling points, melting points. So sodium chloride, for example, melts at about 800 degrees Celsius. Now if you take magnesium oxide, magnesium oxide is, look, 3,700 versus 700. And the melting point of magnesium oxide is 2,800 degrees C.

Look at aluminum. Aluminum plus oxygen, look at the end binding energy there. It's phenomenal, which means it might be useful for-- I'm standing underneath the shuttle here. This is the tiles underneath the shuttle, and they're made of aluminum oxide because the Madelung energy is so high so it's got the thermal shock resistance. So now you know how to go and design things for thermal ablation resistance. All you need is this table. That's all. No, you need a little more than that, but this is a good place to start. If you don't understand this table I don't want you working on the project. OK? What else? All this shows you-- yeah, we're going skip that.

All right. So now we've got a few minutes here. What I want to do is last day I talked about magnesium, today I want to talk about aluminum. And it is also made in an electrochemical process. In this case the electrodes are horizontal. We feed aluminum oxide in and we pass current-- and huge currents. This thing typically runs at 300,000, 400,000 amperes and about 4 volts.

So with the cathode we are running-- remember, we're running nature in reverse. Instead of the electron donor that aluminum is, we're shoving electrons onto aluminum ion and converting it back to aluminum. Unfortunately, on the anode side we have to use carbon, and the carbon itself is consumed. So we consume about a half a ton of carbon to make a ton of aluminum. So aluminum smelters generate a lot of greenhouse gases.

So you can see this is like a drafting pencil: it's constantly being fed. And to give you a sense of scale this is probably about 10 feet across, and this gap is about 2 inches, and this is about, I don't know, a foot and a half deep. It's going to get about 1,000 degrees Centigrade-- liquid aluminum and liquid salt.

So this is what a smelter looks like. What's the sound of electric current? Yeah. The only sound you hear is the fans on the top that keep the place clean. There's the busbars that are bringing in the current. And all of these various posts are these things. So all of the magic is occurring below the floor here.

It was invented simultaneously in the United States by Charles Martin Hall and in France by Paul Heroult. In the same year they filed patents independently and eventually crossed license when they collided at the World Court. So this is what happens. We dissolve aluminum oxide in a molten fluoride called cryolite, which originally came from Greenland, make liquid aluminum carbon dioxide. Now if we wanted to make this truly green, we want to eliminate greenhouse gas emissions, you need to find an inert anode. So on an inert anode aluminum oxide would be

converted into aluminum and oxygen. So not only would you not produce greenhouse gases but you'd produce tonnage oxygen, which is marketable. So some of the work that goes on in my lab is in advanced materials with a view to trying to find an inert anode that would then make this process very, very clean and justify substituting aluminum for steel in cars.

By the way, when you have the field, even though it's a DC current it's a divergent field. And this is me in a magnesium smelter just in Utah. There is the busbar for the magnesium cell. So I'm about, oh, two meters away from the edge of the busbars. The magnetic field is so high I've got one, two, three, four, five paper clips standing against gravity. And I asked them for paper clips and there was no office there. They managed to find a few. I wanted to see how many would go. I'm willing to bet I could probably have about seven or eight paper clips up before the gravity would cause them to collapse. That's the intensity of magnetic fields in these smelters. So when you drive up to the smelter for the tour you park a fair distance away, you leave your wallet with the credit cards in it, because this is the biggest bulk demagnetizer you can imagine. If you've got a watch that's got hands that move they're going to be going like this.

[GESTURING]

PROFESSOR: Yeah. This is the shuttle. This is forged aluminum wheels. The shuttle lands on Centerline racing wheels. They're forged at a place in California. They're made of aluminum alloy. And I don't know if you can read on the side here, it's a little bit light, but these are special tires. They're made by Michelin

So, anyways, the whole message here is learn the lessons here in 3.091 and then we can work together to make metal in an environmentally acceptable way.

And just before I send you on your way for the weekend I thought I'd tell a little joke related to the uncertainty principle. So the joke goes like this. Heisenberg is racing down the Autobahn and he gets pulled over by the state trooper who comes to the car and says, where's the fire buddy? Do you know how fast you were going? And Heisenberg looks at him he says, no, but I know where I am.

[LAUGHTER]

PROFESSOR: All right. Get out of here. Have a good weekend.

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