3.091SC Introduction to Solid State Chemistry, Fall 2010
Transcript – Session 12

Let's go to the lesson. So the last day we studied VSEPR, which allowed us to infer the shapes of molecules, covalent molecules. Today I want to talk about the state of aggregation. What do I mean by state of aggregation? Is something a solid, a liquid or a gas at a particular temperature? So 3.091 is introduction to solid state chemistry. One of the things we need to know is, under what conditions is the solid state stable? And the state of aggregation, when it applies to covalent molecules, is going to lead us to a discussion of secondary bonding. So today's lecture is state of aggregation or secondary bonding.

Now let's just reflect upon what we've learned up until now. We studied ironic bonding and we knew that ionic bonding necessarily leads to crystal formation because we have unsaturated bonds. And that leads to an ion array of unlimited size until you run out of reagent. And something honking big made of ions is going to be a solid at room temperature.

Last day we appreciated with covalent bonding we have two options. We can either make discrete molecules such as HCl. And HCl as a discrete molecule, depending on a number of factors that I'm going to show you today, could be a solid, liquid or gas. And we're going to understand more deeply how to sort out between the three of them. Or, I showed you at the end of the last lecture, you can make a three-dimensional network and diamond was one example. If it's a three-dimensional network that is a large array of solid then that means that you're going to end up with a formation of a crystal, which is going to give you a solid. Diamond is solid at room temperature, graphite is solid at room temperature.

So let's now go to the one case that we haven't dealt with, and that's the formation of discrete molecules. So let's look at discrete molecules. And what we want to understand is whether they're going to be solid, liquid or gas at room temperature and what's the relevant physics here in order to make that determination? The relevant physics is the following. We're going to compare two forces. We're going to compare the cohesive force between molecules versus the disruptive force. And the disruptive force in 3.091 is always going to be thermal. It's thermal energy. We know this. As we heat things they go from solid to liquid to vapor as temperature increases. So thermal energy plays the role of the destructive force whereas the bonding is something that is the cohesive force.

So let's go back to HCL. Last day we looked at HCl. So here's one HCl molecule. We have a covalent bond. It's a covalent bond within the molecule. We know this is a polar covalent molecule, with the chlorine having greater electronegativity and pulling the electrons towards its end. And furthermore, this bond I want to categorize as within the molecule so I'm going to call it intramolecular. Intramolecular.

Now if I want to answer the question, is hydrogen chloride going to be a solid, liquid or gas at room temperature, I don't have the information on the board. The only way I can answer that question is to put another hydrogen chloride. This simply forms the bond between hydrogen and chlorine. To determine whether hydrogen chloride is a solid, liquid or gas, I need to look at how one hydrogen chloride molecule bonds to another hydrogen chloride molecule. So now this end is the delta plus this end is delta minus. And we have again an intramolecular bond.

So the question is, how does one hydrogen chloride bond to another hydrogen chloride? This is the intermolecular bond. Intermolecular bond. So intermolecular bonds govern the state of aggregation. And I'm going to show you the different types of intermolecular bonds. This intermolecular bond isn't the primary bond. The primary bond is here inside the molecule. So the intermolecular bond is known as a secondary bond.

And there three types of secondary bonds. We're going to look at them in turn. So the first one is depicted here on the board. And it's called dipole-dipole interactions. And these obviously occur only between polar molecules. Operative and polar molecules. Not in. Between. Take out in. Operative between polar molecules. So we've made something covalent and now how does one stick to the other?

Alright and I think I've got a cartoon here that shows this. There we go. That's taken from an old book that I had. So you see the H and the Cl and we have a dipole moment and the negative end of one dipole attracted to the positive end of another dipole. So we have a net dipole moment here and we can measure the distance between the center of the dipole-- center to center spacing and call it r. Center to center dipole spacing. And say that the energy in dipole-dipole interaction-- I don't expect you to know this by heart and do anything with it, but I just want you to realize that it's a weak force. This is very weak. It's proportional to the magnitude of the dipole moment. You'd expect that. Weak dipole moment, weak energy. Strong dipole moment, strong energy. Turns out it goes as the fourth order of the dipole moment. And it's inversely proportional to the separation. Only it's not coulombic, it goes as 1 over r cubed.

And there's a temperature factor. 1 over t. As temperature goes up, this energy goes down. And these are very weak forces on the order of about 5 kilojoules per mole. You remember what the crystallization energy of sodium chloride was? 787 kilojoules per mole. So this is very, very weak. It's operative at, between, at low temperatures. At very low temperatures.

So for example, hydrogen chloride, in the case of hydrogen chloride, the melting point of hydrogen chloride is minus 115 degrees C and the boiling point is minus 85 degrees C. You can see at very low temperatures we already have enough thermal energy to disrupt. So if we have solid hydrogen chloride, the forces between the hydrogen chloride molecules in the solid are these very weak dipole-dipole interactions.

And I think there's a couple more cartoons here. This is taken from your text. So there we go. There it is. That's the soup that might be HCl liquid. OK so that's the first type of secondary bond. Dipole-dipole interaction.

Let's look at the second one. The second one is called induced dipole-induced dipole. And it's operative in non-polar species. Dominant in non-polar species. Why am I using the word, species? I'm trying to be a pedant and use fancy words? No. Because I'm going to make it generic. I'm going to show it works in atoms and in compounds.

So as examples, what are some non-polar species? Well how about something like argon? Argon if you look on the periodic table it'll show you that it has a melting point of 84 kelvin and a boiling point of 87 kelvin. So if I cool argon to below 84 kelvin, I get argon ice. So what are the bonds between one argon atom and another argon atom? It can't be this. There's no net charge. It can't be ionic. It doesn't form a covalent network the way diamond does. How do you justify the existence of solid argon? It's just so cold that it just sits there and freezes? I mean, how does it bond? There needs to be some kind of bonding.

And other non-polar species. So for example, the molecule iodine. Iodine melting point is above room temperature. It's a solid crystal at room temperature. Well there's a strong covalent bond inside iodine. But how does one iodine bond to another and to another and to another? And we can even go to polyatomic species, such as methane.

You know there was data from the Cassini Probe. Look at this. This is an image from the Cassini Probe. This is an island group. The yellow is an island group. The blue is a methane sea. A sea of liquid methane on the moon of Saturn, Titan. So there's liquid methane. How does liquid methane form? What causes one methane to bond with another methane? That's the question that we're wrestling with.

So let's look at it first in a simpler context. Let's look at it with argon. So I put argon here. It's a spherical atom. And the question we had before says, how does one argon bond to another argon, as has to be the case in the solid or liquid argon. So we know that this has a lot of electrons and the atom is net neutral. But the electrons are in motion. If I had an attosecond camera and I went in here and I went, snap, I could catch a freeze frame where the electrons aren't symmetrically distributed around the nucleus. This nucleus, the atom is in constant fluctuation. But net neutral. Time average it's symmetrical. So at some moment I might have a preponderance of electrons over here at around three o'clock. So this end of the argon is a little bit delta minus. Which means the other end is delta plus.

Now what happens if this is delta minus, this is delta plus? Can you see that the positive end of this argon atom will then pull on the electron distribution of the adjacent argon atom rendering it delta minus at three o'clock and delta plus? So this is the dipole in one, induces a dipole in another. And why does it occur in the first place? It occurs because the electrons are in motion. Electrons in motion lead to time fluctuating dipoles. They're time fluctuating.

Time average, there's no net dipole moment. I'm not going back on what I said before. There's no net dipole moment here, but this is time fluctuating dipole. Time fluctuating dipole.

So who was the first to explain this? The first to explain this was Fritz London in 1930. In 1930 Fritz London gave us the explanation because this troubled people for a long time. And he did so in a quantitative manner. And the mathematics of the treatment are identical to the mathematics for the dispersion of light under certain

conditions. This has nothing to do with the dispersion of light. The mathematical formulation imitates the formulation of the dispersion of light and hence the force here is known as the London Dispersion Force.

So people will say that solid argon is held together by London Dispersion Forces. Or the bond is known by the name van der Waals. We either call them van der Waals bonds or London Dispersion Forces. Van der Waals was Dutch. I know how to spell the word wall. This is the dutch spelling. W A A L S. Van der Waals.

So in this system here, the London Dispersion Force or the van der Waals bond is in fact not the secondary bond. It's the primary bond, isn't it? It's the only bond. So by definition it must be the primary bond. But can you see that in every compound, including diamond, we have time fluctuating dipoles in all of the atoms? It's not just argon that has time fluctuating dipoles. Every atom in you and me has time fluctuating dipoles. But we're held together by much greater forces. So that's why I say that in this case this is the dominant force. But it's operative in everything. Because wherever we have electrons, they're in motion. So this is the dominant one.

Alright so we can look at it in a few other instances. So for example we can look at it in the case of iodine. We can look at it in the case of methane. All the same. Time fluctuating dipoles. And this is a very, very weak force. So the energy in London Dispersion Forces, or van der Waals bonds, is proportional to a quantity called the polarizability. The polarizability is-- and this was defined by London-- polarizability is the measure of how easy it is to induce this dipole. A measure of the ease of electron displacement within an atom. And it depends on, it's influenced by the size and it's influenced by the number of electrons in the atom.

So what do I mean by that? Well let's take two systems. Suppose I've got argon and I'll go up two members in the same series and I've got helium. So what are the forces that hold helium together? Same thing. But the boiling point here is 87 kelvin. The boiling point here is 4.2 kelvin. Why does this have such a low boiling point? Well, polarizability. Size-- helium is smaller. So the degree, the corral in which the electrons can roam is smaller. So the extent of electron displacement is smaller. And secondly there are only two electrons. And they're in 1s, so they're tightly held. And so the delta minus delta plus capable of being created in helium is tiny compared to the delta minus delta plus that can be created in argon. So the energy goes as polarizability squared and divided by r to the sixth, where this is the separation. Not the radius but this is separation. Dipole separation. And this is a font issue. This is proportional to alpha. So you can tell the difference. This is a proportional that's to alpha.

Of course you can't tell the difference. This is contextual. If I just wrote this by itself, you don't know what it is. My goodness you're nervous. So nervous.

All right let's take a look at-- here's the cartoons. Induced dipole. And here's London's paper. Here's London's paper as it first appeared in 1930. Theory and System of Molecular Forces. And here's some cartoons from your book. This is helium, showing helium. It's kind of funny how the artist shows. Like there's these two helium atoms and they're absolutely immobile and all of a sudden one of the helium atom starts jiggling and then it induces a dipole moment in the other one. That's not how it happens, but anyway.

Alright this is hydrogen. Same thing as iodine. All right so there's delta plus, delta minus. Because the electrons are moving even though there's a strong covalent bond inside. So let me just make the point, I want to make sure people are very clear about primary versus secondary bonding. So if I look at iodine. I2. This is a covalent bond. It's homonuclear. This covalent bond, there's no net dipole moment. Here's another iodine. But then we have time fluctuating dipoles. So this delta minus isn't because this is the bond here. This is the primary bond. This is the primary bond and it's covalent. And this is the secondary bond. And the secondary bond is London Dispersion Force or van der Waals bond because this is induced dipole.

So now let's look at-- oh here's another one. This one gets on my nerves. Oh actually this is good. This is this the bad one. All right so I'm going to show you polarizability. So here's a series of sp3 hybridized chains. Propane, octane, icosane. They're all the same. They look like this. Ch is sp3 hybridized. And so you just have-- so what is that, C 3 H H. So it's just-- so you have 1, 2, 3 4. so there's hydrogen, hydrogen, hydrogen, and on the fourth one I'm going to make it flat instead of trying to make a tetrahedron. So 1, 2, 3 hydrogens. The fourth one is carbon. 1, 2 hydrogens, carbon carbon. 1, 2 3 hydrogens. So this is C3H8. And compare that to the longer one. Which is octane, which is C8H18. So it's 1, 2, 3, 4, 5, 6, 7, 8. And all you have got to do is, 1, 2, 3, 4, 5, 6, 7, 8. You put four sticks off of every carbon. You can't go wrong. You count them up. You got C8H18. Look at the structures. They are the same.

So how come propane is a gas at room temperature? Whereas octane, which is the principal constituent of gasoline, is a liquid at room temperature? It all comes down to polarizability. This one's got a longer corral. So if you like the delta minus versus the delta plus, it's basically the same here except that separation is bigger. All right, so that's pretty good.

This is the one that gets on my nerves. You see this? It's exactly what I just showed you. So here's methane. And there's the propane. Here's butane and somewhere between butane and pentane we cross the the line at room temperature. So pentane is liquid, butane is gas. And you keep going up, up, up, and finally if you get to C20 you go from liquid to solid because now the van der Waals forces are strong enough that even at room temperature you make a solid. It looks like paraffin. That's why you can melt paraffin, because it's got weak van der Waals forces. So temperature disrupts and it reforms. If you try to break a covalent bond, you pyrolyze the thing and you don't get it back. Secondary bonds allow for ready processing.

Here's what bothers me about this. Instead of talking about polarizability, which is a physical quantity that means something. They say molecular weight. Well it's true that these scales, these are heavier and it's monotonic. But to me what's the relevant physics between the ability to form van der Waals bonds and the mass. It's just a dumb thing. It's not a gravitational effect. So that's why this thing is stupid. And you see it all over in chemistry books. And it's just dumb. And if you put that on my exam you're not going to get points for it. Because that's dumb.

OK let's go to the next one. There's a third type of bonding. There are certain things I feel strongly about and that's one of them. OK so let's look at the third type of secondary bonding. The third type of secondary bonding is called hydrogen bonding. Hydrogen bonding. It's a type of secondary bonding. And it occurs between hydrogen and the most electronegative elements, fluorine, oxygen, nitrogen. Why these? Because they have very, very high average valance electron energy. So the average

valance electron energy I'm quoting in that second column, not megajoules per mole, but in sensible units like electron volts. And so you can see, when you get up around 18, 19 electron volts you cross a threshold. And that's the electronegativity as represented by average valance electron energy.

So you can see that as the electronegativity gets beyond some threshold value, roughly 3, then you can form hydrogen bonds. So this is owing to high average valance electron energy, or if you like electronegativity. Which means very strong polarity in the covalent bond. So you say, well there's polar and there's even more polar. So let's see what happens.

So I'm going to use a prototypical value here. I'm going to look at HF. So if I look at HF let's go through the Lewis structure. There's H with it's 1 electron. And F with the 7. 1, 2, 3, 4, 5, 6, 7. And so we have a covalent bond here. We know fluorine is the most electronegative so we have a dipole moment here. Now the dipole moment is very strong here. This is an accounting procedure to put the two electrons, but it no way represents the physical position of these electrons. They're brought in very close to the fluorine. So it's not some symmetrically disposed between H and the F.

So I can't tell anything about whether HF is a solid, liquid or gas. Why? Because there's only one sitting here. I have got to put at least one more. Because this is a primary bond. And it tells me how H bonds to F. It doesn't tell me how one HF bonds to another HF. So I'm going to put another HF over here. So here's another HF. And it's also dipole. But there's something special about that. Already there's a dipole-dipole interaction. But the hydrogen bond is much stronger. It's much stronger. And why is it stronger? The electron in this hydrogen on the right is pulled towards the fluorine to such an extent that this hydrogen is so denuded of its electrons that it's acting as proton-like. It's proton-like. Now don't tell people that Professor Sadoway said that hydrogen inside an HF is a proton. It's not a proton but it's starting to get more nearly like a proton.

Now what do we know about a proton? Positive charge. Tiny high-charge density. So this hydrogen's looking forlornly over at its electron that's being hogged by the fluorine to a right. And what do we know about these? Oh it's time for colored chalk. It's time for colored chalk! What color are those? They're red because they're non-bonding. And the bonding are the blue in-between. And what do we know about the volume occupied by a non-bonding pair versus a bonding pair? It's larger. Because they're not constrained. So not only do we have a non-bonding pair, they're not just here. They're sort of flopping around. Hanging way out and there's this thing here that's almost denuded of its electrons, so it starts looking over here saying, if I can't get any action over here, what about here?

So that proton starts establishing contact with the non-bonding pair of electrons on the adjacent fluorine And this is the hydrogen bond. The hydrogen bond is here. The hydrogen bond is not here. If you write this I will give you a 0. I'll give you a 0 with a circle around it. It's called the doughnut. That's what you get when you write something so stupid. This is not the hydrogen bond. This is the hydrogen bond. OK? So it works. It works.

Now let's see the effect of it. Let's see the effect. Alright so here's a cartoon showing that in water the hydrogen-oxygen spacing is about 1 angstrom. And the hydrogen-oxygen spacing in adjacent water molecules can be less than 2 angstroms. So

there's certainly a difference. I mean it can't be the same. If it were the same it would be a covalent primary bond. You'd have a network.

Now this is interesting here because this shows the values that are given on your periodic table, which were obtained without the use the average valance electron energies. These trends are correct. But look at this one. They've got chlorine up at 3.16. And all of these have been revised. Now on a test, just use what you've been given on the periodic table. But I want you to understand how this is rationalized with better data coming from photoelectron spectroscopy.

So now I want to show you the implications of hydrogen bonding. The implications. So I've got 4 homologous series. So they're all element plus hydrogen. So let's start with the group 14. That's shown here in purple. And what do we have? All of these, we'll start with methane. CH4, so that's a central atom. 1, 2, 3 4. They're all tetrahedral. Hydrogens at the corners. Non-polar. And no hydrogen bonding capability. So one methane bonds to another methane by weak van der Waals forces. That's how it does it. It doesn't matter if I substitute the carbon with silicon or germanium or tin. I can put SnH4. And how does SnH4 bond to another SnH4? It's just by London Dispersion Forces. That's all that's operative here. And so we have, what makes sense here, is that the heavier, more massive-- no, the ones that have greater polarizability have a higher boiling point. Because their van der Waals forces are stronger. That means you have to go to a higher temperature to achieve disruption. Same temperature, weak van der Waals force: gas. Same temperature, strong van der Waals force: liquid or solid. And you see the boiling point here.

Monotonic from the lightest to the heaviest. Now let's go to the next one. Let's go to the green line, group 15. Well group 15, what's that look like? Let's look at the structure of group 15. Group 15 is-- ammonia is one of them. So we can look at the structure of ammonia. And if we use VSEPR we'll end up with something that looks like this. I'll go through the whole thing. You're going to end up with three bonds like this. It's a tetrahedral skeleton with a lone pair. Ah, colored chalk.

So now, what happens? I can't say anything about this. Why can't I say anything about whether this is a solid, liquid or a gas? It's the only one there. I have got to put another one. So put another one up here. N. H. H. H. Same gambit with the hydrogen fluoride. This hydrogen sees this lone pair and establishes a hydrogen bond. And that adds to what otherwise would have been a dipole-dipole. This has a net dipole along moment, agreed? There's a dipole-dipole moment here. But this bond is even stronger. The hydrogen bond is even stronger than dipole-dipole interactions.

So now let's look at the graph up here. So what about in phosphene, PH3? No phosphorous isn't electronegative enough. So in phosphene, in arsine and in stibine we don't have hydrogen bonding. So you see this series in the group 4 here? It goes monotonic from the heaviest element down to the lightest element. But here, heaviest, less heavy, less heavy, and the lightest element that should be down here is up here. Why is the lightest compound not down here? Because of the addition of hydrogen bond.

So ammonia is off the line. This line shows the trend based on dipole-dipole interactions only. And you can see the difference. See if you have van der Waals forces alone, versus dipole-dipole, dipole-dipole are stronger. So SnH4 has a lower

boiling point than SbH3. I can't predict this but I could ask you, if I gave you this data, I'd say, can you explain this to me?

Let's keep going. Let's go to group 16. So, telluride, selenide, suphide, the oxide, H2O, water. It should have a boiling point of minus 100 centigrade were it not for hydrogen bonding. How does water work? Again, SP3 hybridization. Oxygen, 1, 2, 3, 4. Two lone pairs. 1, 2, H, H. And now what happens? I bring another water molecule over here and hydrogen bonding. And that hydrogen bond raises the temperature, raises the requirement for thermal disruption and moves the boiling point of water up to 100 degrees celsius.

It it weren't for this we wouldn't have this conversation. Because we wouldn't have evolved as a species capable of conducting business at room temperature if water boiled at minus 100 celsius. Hydrogen bonding is critical. It's absolutely critical. So now you know. And this isn't just some little bit of pedantry for a professor. This is very important. Because we're going to learn later that, when it comes to biochemistry, we will appreciate that most biochemicals are made of carbon, oxygen, nitrogen and hydrogen. And that means you can have hydrogen bonds here. And you can have hydrogen bonds here. Hydrogen bonding is critical to life. So this is a very important thing to know about.

OK we have a minute or two. So you can see polarizability increases here but hydrogen bonding operative here. That's explains the mystery. All right we're going to jump over this because we are out of time. And so I will simply show you a few pictures. Pictures! So this is a conference in Copenhagen in June of 1936. And there's Fritz London. But look at who else is at the conference. Niels Bohr, Wolfgang Pauli, Werner Heisenberg, Max Born. Remember the Born Exponent? You better remember it for Wednesday. This is Lise Meitner, you haven't met her yet. We'll get to her. This is Walter Stern. Stern-Gerlach. And this is James Franck. That's just the first two rows! That's quite a conference.

Here's a picture of Fritz London sitting on a bench in Berlin with Erwin Schrodinger. Schrodinger is brooding; he's thinking. Fritz London is smiling. You know why? Because he's figured it out. He's figured out. It's time-fluctuating dipole, but he's not going to tell Schrodinger. He's going to say, you have to read about it. But you have to go to the library. Because if you don't read the primary sources, if you go to Wikipedia, you won't find this. Because this is not going to be in Wikipedia in 1913. OK, last thing-- hold on, hold on, hey wait a minute! Where are you going? We're not done yet. Did the professor say class is dismissed? No.

So here's a biography of Fritz London, which I would recommend if you have a few minutes and you'd like to unwind. Go out, sit in the sun and read something like this. It tells the story of how he came up with these ideas. The rise of fascism in the '30s. He comes to the United States, takes a teaching position at Duke University. All of the people that he met along the way. All these people that we study, all this stuff, it's all there from his perspective. And the perspective of his biographer. Plus the pictures. So anyway, primary sources. Go read the primary sources. All right, class dismissed.

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