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3.091SC Introduction to Solid State Chemistry, Fall 2010  
Transcript – Session 9

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PROFESSOR: This Wednesday will be the first celebration of learning. Test 1 on Wednesday, October 7, you will write during the normal class time. So you'll have 50 minutes. And we want to have a little bit of comfort here, so you won't be sitting cheek to jowl. So before long I'll have the room assignment. So some of you will write in here. We'll have fewer people than seats so that there'll be vacancies next to each person. And then some will write in a few of the other locations, probably 26-100 and the gym above the Walker Memorial. And we'll get that out to you. And next week on the 6th we will have no weekly quiz, because enough celebrating. No point in testing you on the 6th and then on the 7th. There will be, of course, the mini-celebration tomorrow, quiz 3. And I'll be available for office hours later today. Oh, and the coverage, just to remove the mystery, will be right up to the 7th of October. I've been doing this for over 30 years and I've learned that in order to inspire interest on the part of the student it really pays to have the coverage of the celebration extend up to the lecture before the celebration. Now obviously I'm not going to drill deep on something I taught you on October 5, but it would be a good idea to stay awake during all of the lectures between now and then.

So last day we talked about ionic bonding. And ionic bonding occurs with electrostatic attraction between ions that have formed through electron transfer. And we saw the energy of the ion pair given by this formula, where we have Coulomb's law with the Born exponent. And then this is plotted. This is  $E$  at  $r$  equals  $r_0$ , and we learned that there were two terms. The attractive term, which is the Coulombic force here shown. And then there's a repulsive term, which results from electron-electron interaction when the two lines get very, very close together. And this is taken from your text. And I think they did a very nice job here of illustrating as you go to high values of  $r$  they're depicting that you have the ions separated by considerable distance. And there's a certain amount of stored energy, but not a lot.

And then if you go much, much closer than the hard sphere sum of the ionic radii, I think they're depicting here that there's some squashing of the electron clouds. And you can see that the energy has gone way, way up. So this is an unfavorable situation, meaning that the energy here is greater than 0. And there's a sweet spot here at 236 picometers, which represents the ideal location. And that is the sum of the radius of the sodium ion and the radius of the chloride ion. And so you can see how energy tracks. And if you go far, far, far away to the point where they're at infinite separation, there's no energy stored. So everything makes sense.

And then we said, well what happens if we keep packing these things? We rationalized that they would continue to do so and ultimately form a 3-dimensional crystal. And so you can see there's a lot of similarity between what's above and

what's down here. This has been written for a 1-1 system. In other words, a cation plus 1 and an anion minus 1. But it could be mediated by the valences.

And what we have here is the structure factor. This Madelung constant tells us how much we get decrease in the energy of the system by going to a 3-dimensional array. So depending on the atomic arrangement we'll have a different value of Madelung constant. We saw that for sodium chloride the value is 1.7476. And different crystals have different things. And what determines the crystal structure? It's a combination of the size of the two ions and their valence. So what we saw for sodium chloride, this is a structure type. So obviously sodium chloride is sodium chloride crystal structure, but there is an entire suite of compounds that have radius ratios and charges that end up with a sodium chloride type crystal structure.

And then towards the end we started looking at the Born-Haber Cycle. And the purpose of the Born-Haber Cycle was to give us a sense of scale of the various constituents in the formation of a crystal. And what we noted, the takeaway message from the Born-Haber Cycle, is that this enthalpy of crystallization, which is basically this term here, is huge. It's huge. It was the big component of the energy required to form the crystal. It's large and it is negative.

So what I want to do today is start by talking about shortcomings of the business of ionic bonding. See, how did we get to ionic bonding? We started with this idea of octet stability. Octet stability was the driving idea behind all of this. Octet stability, and in the case of ionic bonding this was via electron transfer. And so that got us a long way, but it has its limitations. So let's put up some new data.

So suppose I look at compounds like H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>. Do these things form ionic bonds? How does octet stability play here?

And so let's start by looking at hydrogen. So if we took hydrogen and started with atomic hydrogen and added an electron to it, then we would form an anion known as H minus. And H minus looks pretty good because it's isoelectronic with helium. So maybe this isn't going to be so bad a day. But if we're going to have a bond then we need to form an H plus. So let's do that. So that would be, then, H goes to H plus, plus an electron. And that's really nothing more than a proton. So that doesn't look too appealing. That's probably a high energy state. And besides, in the same location at the same time-- in other words, same temperature, same conditions-- half of the hydrogens have to acquire electrons and half of the hydrogens have to lose electrons. And that's not going to happen. They're either going to have a propensity for electron gain or a propensity for electron loss. So it looks like ionic bonding is not going to help us explain the formation of molecules such as H<sub>2</sub>, N<sub>2</sub>, and so on.

So who came to the rescue in this case to get us out of the conundrum? G.N. Lewis. G.N. Lewis was actually born in Weymouth, Massachusetts and he finished his PhD at Harvard in 1899. And then, like so many Americans of the day, went off to Europe and he postdoc'd in Europe for a while. And then he came back and got a job at MIT. And he taught at MIT from 1905 to 1912. And then in 1912 he was lured to the West Coast where they were starting to establish the chemistry department, the University of California at Berkeley, and he went out to Berkeley and that's where he spent the rest of his career. And we can speculate why he went. Maybe he was fed up with the weather here. Actually, today is one of those few days-- write it down, because one of the few lovely days in Massachusetts.

So G.N. Lewis, what did he say? He said, well I've got an idea here. He said, what if hydrogen achieved shell filling not by electron transfer but by electron sharing. So he posited the idea of shell filling by electron sharing. This is in contrast to electron transfer. So let's see. Oh. There's an image of G.N. Lewis. He died, actually, on the job. He came back to his lab one day after lunch and hit the floor. So he worked right to the very end.

Here's some data taken from a lab notebook and memo, actually. 1902. And what do you see here? Well, he developed a notation for us, and we still use this notation to this day: Lewis notation. So here's lithium and he's got one electron. But we know lithium has three electrons but only one valence electron. And then there's beryllium and magnesium-- two electrons. Aluminum with three. Here's fluorine chlorine, and when they ionize he puts the eighth electron right here. And look at this one for silicon. He's got probably some kernel inside the atom, thus. So he's even starting to think about concentric shells. This is 1902. Remember the Bohr model isn't until 1913. So you can see people struggling. And notice that we have eight electrons in a shell-- that's where we're getting the octet stability-- and he's using cubes. Now we know that the cube isn't the shape of the shell, but it's a pretty good device to help you keep track of electron number-- because there's eight corners on a cube. So it's another example of how that's not what it is but it's a really good model and it keeps you out of trouble and allows you to go forward. So this is going back-- way, way back-- for G.N. Lewis. Now let's use this idea and account for the formation of H<sub>2</sub>. So here's hydrogen, and using the Lewis notation we'll put a dot here for its one electron. And we'll bring in a second hydrogen and we'll use a cross, or an x, to indicate the electron from the second hydrogen. And now we're going to double count-- in other words, double attribute. These are shared electrons so they count for both atoms. Double count the shared electrons. And when you do so what do you come up with? Well, the element on the left has two electrons and, therefore, is isoelectronic with helium. OK? Maybe it was a California thing. They were sharing. And then there was sort of another California concept, like. So it was like helium. And then on this side this is also sharing. And it's kind of like helium. So now we've achieved the stability of the filled shell by sharing the electrons.

OK. And I think I even have another slide of how-- this is the more modern version of it. Electron dot. So the nucleus and the inner-electrons are contained inside the chemical symbol. And, actually, this goes all the way to modern quantum mechanics. Density functional theory does the same thing: lumps all of the inner-shell electrons plus the nucleus into one piece, and then the valence electrons are outside. And so starting in 1902 with some little dots and crosses we go all the way to DFT today.

All right. So let's do another one. How about nitrogen? Let's try nitrogen. So when we going to nitrogen we know the valence electron's 2s<sup>2</sup> 2p<sup>3</sup>. So put nitrogen here. One, two, three, four, five. Now these three electrons here are according to the Hund rule. So it's p<sub>x</sub>, p<sub>y</sub>, p<sub>z</sub>, and this is the 2s<sup>2</sup> sitting over here. And I'll bring in a second nitrogen, and there's its 2s<sup>2</sup>. 2p<sub>x</sub>, 2p<sub>y</sub>, 2p<sub>z</sub>. And now what do I have? Look at the nitrogen on the left. Two, four, six, eight. So the nitrogen on the left feels as though it has access to eight electrons. The nitrogen on the right-- two, four, six, eight-- it feels as though it has access to eight electrons. So both nitrogens are isoelectronic with neon if we push on this concept of electron sharing.

Now there's a second thing I want to do. It's to draw attention to two types of orbitals. So these three orbitals in the center consist of electrons that are shared. So these are going to be called bonding orbitals. And "bonding" and "blue" both begin

with a "b", so I'm going to denote the bonding orbitals, or bonding domains, as distinct from the nonbonding domains in red. Red are nonbonding domains. Always two electrons per orbital. They like to live in pairs. That's the way it works. OK? And so each one of these pairs is a bond. So I can then write nitrogen with three lines through it indicating I have a triple bond. Three pairs of electrons, three bonding domains, triple bond. This is all in formation according to the concept of electron sharing. And Lewis coined a name for the type of bond that is formed in this way. He said we get bond formation involves cooperative use-- sharing, cooperative-- of valence electrons. So now we can take the "co" symbol here and the "valence" here and come up with the term "covalent bond." Covalent bond, thanks to G.N. Lewis.

So, again, to make sure we're very clear, ionic bond results from electron transfer, covalent bond results from electron sharing. Now we can do this-- so let's go to heteronuclear molecules. These are homonuclear. So let's go to heteronuclear molecules.

And so let's see. I've got some rules up here, I think. Yeah. Drawing Lewis structures. So let's go to a heteronuclear molecule. And I'm going to choose as an example sulfur dioxide. And I don't expect you to be able to name these things on site. I will always give you the name. I'll say sulfur dioxide, parenthesis,  $\text{SO}_2$ , blah, blah, blah. OK?

So sulfur dioxide. I want to put up the Lewis structure of sulfur dioxide. So center the element with the lowest average valence electron energy. So it turns out that the average valence electron energy stack like this. Sulfur is the lowest, then chlorine, and then oxygen. This is this ranking of average valence electron energies. And you'd be given those data. So it says put sulfur in the center. So I'll put sulfur in the center. And then what does it say? We're going to count all the valence electrons. So sulfur over here is  $3s^2 3p^4$ . So that gives me six valence electrons. And there's two oxygens. And oxygen lies above sulfur, so that's  $2s^2 2p^4$ . So that's 2 times 6. So that's 12. All right? Let's put the 6 over here. And then there's chlorines in this compound, so that's  $3s^2 3p^5$ . So that's 5 plus 2 is 7, 2 times 7 is 14. And we add this whole thing up, we get there's 32 valence electrons.

And draw a single bond from each surrounding atom to the central atom. All right. Again, this is a model. I'm not saying that this is the shape of the molecule, but it's a way to count. All I'm doing is trying to keep track of bonds and paired electrons. So I can put chlorine on either side. And I'll put an oxygen below and an oxygen above. All right.

So that's already two, four, six, eight. So I'm losing eight. So 32 minus 8 is 24. And so with the 24 that means I've got 12 pairs of electrons to place.

So let's start putting the Lewis structures up. So chlorine consists of one, two, three, four, five, six, seven. And I'll do the same thing on the other side. Two, four, six, seven. And oxygen has six, so that's two, four, six. And then the lower one, same thing. Two, four, six. And sulfur has six. I'm going to use x's for sulfur. So I'll put one x with the chlorine, another x with the chlorine. Two with the oxygen, two with the oxygen. And so now we're in pretty good shape, right? We can identify bonding and nonbonding domains. Here's the bonding. One, two, three, four. And then the nonbonding. Looks like there's 12. And sure enough, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12. The 12 nonbonding domains. 4 bonds. And we have the Lewis structure for this particular compound.

And one last little piece worth pointing out. Notice that in the bonds to the chlorine you have two electrons, as you need. One electron comes from the chlorine and one electron comes from sulfur. But in the bonds between the sulfur and the oxygen the sulfur's so desperate to form a bond that it actually donates both electrons to the bond. And oxygen's happy because it's isoelectronic with neon, and sulfur's happy because it's going to be isoelectronic with argon. But, you know, it has to go to some lengths. So this is called a dative bond, when both electrons come from the one element.

OK. Well, this is great. I'm going to do one more. How about methane? CH<sub>4</sub>. So I'm going to start with carbon. Carbon's going to go with this on there. And a carbon is 2s<sup>2</sup> 2p<sup>2</sup>. And so I'm going to use the box notation now. See, this is the Lewis structure, this is chemical equation, now we're going to a box structure. We can move fluidly from one model to another. We had cubes up there. It's all good.

So this is 2s. And now this is 2p<sub>x</sub>, 2p<sub>y</sub>, and 2p<sub>z</sub>. Now according to this, 2s<sup>2</sup>, that gives me an electron pair. And now I've got 2p<sup>2</sup>, which according to the Hund rule goes in like this. Well I've got a problem here. How many unpaired electrons? Two. Now what's my maximum number of bonds I can form by electron sharing? It's two according to this. So the best I can do, best possible here, is CH<sub>2</sub>. And that's no good. We know from mass measurements it's CH<sub>4</sub>. The stoichiometry's CH<sub>4</sub>. And besides, what are these orbitals going to look like? These are the p orbitals, so they're dumbbell-shaped and they're orthogonal, right? They're 90 degrees, which means if I formed this thing-- which is called methylene-- if I form methylene I'd end up with CH<sub>2</sub> looking like this, which has a dipole moment. And we know from spectral measurements and electrical properties measurements that this thing is symmetric. So this thing-- electron sharing isn't working. It's not working.

So we need another patch here, and that patch comes from none other than Linus Pauling. Another American. You see, it's American science today and it's in the 20s. That's why we have Gershwin playing at the beginning. Celebration of American science. So Pauling was born in Portland, Oregon. He was the son of a pharmacist. And he went to Caltech, got his PhD in 1925. So the Rhapsody in Blue came out in 1924 when he was just hunkering down to his thesis. Probably listened to it, got some pleasure out of it, as most people did. So then he finishes, 1925, at Caltech in Pasadena and he goes to Europe. Now he chose wisely. He chose four postdoctoral positions. These are people he postdoc'd with. First with Sommerfeld, then with Bohr, then with Schrodinger, and then finally with Bragg. You'll learn about Bragg. Bragg got the Nobel Prize for X-ray diffraction. So that's not a bad preparatory start.

So he comes back and teaches at Caltech. In fact, I have a picture of Linus Pauling. There he is. That's a middle-aged Linus Pauling, probably around the time he got the first of two Nobel Prizes. So what did Pauling do? Pauling said, why don't we mix the orbitals? They're all in the shell  $n$  equals 2, and what we're trying to do is to fill the  $n$  equals 2 shell. So how about mix? Let's mix 2s and 2p states in order to maximize the number of bonds. Remember, when you form a bond you decrease the energy of the system. Four bonds is a greater decrease in energy than two bonds. So the system, if it could-- and they're all within the same shell. You notice he didn't say, gee, if mixing 2s with 2p is good let's go get some 1s. Well 1s is down in  $n$  equals 1, and there's no way you can mix. They had to be in the same shell. Mix states in order to maximize number of bonds that can form. It's all about maximize the number of bonds that can be formed. And this, of course, is by electron sharing.

We're talking about covalent bonds here. OK? And he termed these mixed orbitals "hybrids." Termed the mixed orbitals as "hybrid orbitals." They're cross-breed-- part s, part p.

So now let's look at the energy level diagram-- or the box notation. Forgive me. So I'm going to mix s and p. So I've got a single s and I've got three p's, so this is called  $sp^3$ . Each one of these is a mixed  $sp^3$  hybrid orbital. And I've got four of them. And how many electrons do I have? Four. So now I use the Hund rule and in go the electrons. One, two, three, four. And now I have the ability to form four bonds.

But it gets better. Here's the next thing. These are degenerate. They're all in the same state. That's why we're using the Hund rule. And so degeneracy in energy implies degeneracy in spatial orientation. So what does that mean? It means that if these are four bonds equivalent, then the way those bonds will arrange themselves in space is to be equivalent. So if I've got a central carbon here and I'm going to put four sticks from the central carbon so as to make the four sticks symmetrically disposed in space, that dictates the architecture of the molecule. And how do I put four sticks off of a central point symmetrically disposed in space? One, two, three, and four. This is meant to be the corners of a tetrahedron. Each one of these is 109 degrees apart. And this describes a tetrahedron. So now I've got carbon in the center, and now I've got the hydrogens at the four corners of a tetrahedron. There is the structure of methane. And each of the hydrogens has a shared electron with the carbon, making it isoelectronic with helium. And the carbon has four of its own electrons, four shared with the four hydrogens to make it isoelectronic with neon. So everybody's happy. Shell filling, and it's all good. So now it's symmetric and it has no net dipole moment. Everything squares with the data.

Well, good for Pauling. But he went further. He went much further. What Pauling wanted to do was to make it quantitative. And so he wanted to have something analogous in covalent bonding to what we have in ionic bonding. So what Leslie is now rubbing off the board there is-- no, keep going. It's good. It's OK. This is a rule of academics: You always erase that which you will refer back to. We need more boards in here. How many boards do I fill in a period? 9, 18? Maybe what? We need about 24 boards. That's a good lecture.

All right. So here's what Pauling was thinking about. He was thinking about the analogy, for example, if I want to get the energy of magnesium oxide I can use the formula that Leslie has just erased, and it looks like this. So if all I need to know is the radius of the anion, the radius of the cation, its charge, and the Madelung constant and then I just plug in, I get the crystallization energy.

But then suppose instead of magnesium oxide I want to go to magnesium chloride. I can use the same formula only I need the Madelung constant. This is the Madelung constant for magnesium oxide. If I have the Madelung constant-- forgive me, script M-- for magnesium chloride, and I know the ionic radius of magnesium cation and chloride anion, away I go again. I need this. I need, of course, the Born exponent. This Born exponent and away we go. The same formula applies. So I can build with a library of basic physical data.

So what did Pauling do? Pauling said, what if we can do the same thing for covalent bonds? Is there some kind of an analogy? So he said, let's take a look at an arbitrary heteronuclear compound. So I'm going to do this with HF, hydrogen fluoride. So, first

of all, let's build a hydrogen fluoride molecule. H with its one electron, and fluorine with its seven. So now hydrogen sharing an electron with fluorine is isoelectronic with helium. It's happy. And fluorine sharing the electron hydrogen is isoelectronic with neon. It's happy. So again we see shell filling by electron sharing.

So what Pauling wanted to ask is, can I get a measure of the HF bond energy knowing only the bond energies of H-H and F-F? So then if I knew all the homonuclear bond energies and then I mixed these to make heteronuclear bonds, is there a path from homonuclear bond energy to heteronuclear bond energy?

So let's look and see what the numbers are. So hydrogen. The hydrogen bond's fairly strong. It's 435 kilojoules per mole. That's mole of bonds. 435. Fluorine-fluorine is 160. And so what do you think the value of the H-F bond should be? Well when I first look at this I say, well it's part H and it's part F, so it's somewhere between 435 and 160. I don't know if it's the arithmetic mean-- you know, add these two and divide by two-- or maybe it's the geometric mean-- multiply them together and take the square root-- but it's got to be somewhere in between. What do the data show? The number's 569, which is greater than 435. So I take a bond of 435 and a bond of 160, I put them together I get 569. That's very, very strange.

But Pauling was smart. Pauling said, I have an explanation. He says, suppose when these electrons are shared in between the two atoms, suppose they're not shared equally. Suppose there is a displacement of the electrons. So instead of putting them dead center, as I've been doing up until now, suppose the electrons are actually drawn closer to the fluorine. So we still have octet stability, or in this case duet stability, but the sharing of the electrons is not equal. So this is charge displacement.

And what does charge displacement constitute? Well, charge displacement means stored energy. And Pauling quantified that stored energy. And so what he did is he said that you increase the bond strength by thinking of it as a two-step reaction. So in the heteronuclear bond that is a bond between two different atoms. So in a heteronuclear bond we form by what-- and this is my coinage, you don't see this anywhere in the book-- two-step, share and then pull. So share is, as the name implies, we share electrons to achieve octet stability. But then because we have unequal atoms we pull towards one of the atoms. And which one do we pull towards? Well, we pull towards the one that's got a greater appetite for electrons. And we've already gone through this concept. Which atoms on the periodic table have the highest appetite for electrons? The nonmetals. The weakest appetite is the metals. The metals are good donors, the nonmetals are good acceptors. And fluorine's up in the top right corner, so fluorine has a very, very high appetite for electrons. And, indeed, in this bond the electrons are pulled to the right.

And why Pauling got the Nobel Prize and Lewis didn't-- it's my theory-- is that Pauling was quantitative. So he came up with a quantitative measure. He devised a quantitative measure for the degree of unequal sharing, thereby allowing us to make these calculations with some accuracy. And he called that quantity electronegativity, and it's denoted by the Greek symbol  $\chi$ . OK? And he devised a whole scale. How did he get the scale? He looked at bond energies for all sorts of pairs of elements across the periodic table and went through an exercise with pencil and paper that today we would call multivariable regression analysis. And came with a set of--

[SLIDE APPEARING]

PROFESSOR: Oh, I'll come back to this. This is the structure of methane. This is the s and p. Oh, let's take a break. You can stack. All right. So this is what methane looks like. There's the s, there's the p. And the sp hybrid looks like this. It's sort of an asymmetric dumbbell. And these four things stick out. And then you bond the hydrogens and there's the methane.

OK. So here's what the electronegativity scale looks like. It looks a lot like the scale for average valence electron energies. The nonmetals have the highest appetite for electrons period, which means in a bond they're going to hog the electrons. And the nonmetals have the weakest appetite, and so they're going to end up having the electrons in a covalent bond pulled away from them. So nonmetals have high electronegativity, metals have low electronegativity.

And now here's taken from the text. And you see that the electronegativity is periodic. If you go across a period the metal has the lowest value and the nonmetal has the highest. And there's fluorine, number nine, at a value of about 4. It's got the most intense appetite for electrons. And then you jump down here to sodium, et cetera, et cetera. Here we are going across the lanthanides and whatnot. And this is taken from your text. There's fluorine, 3.984. That's the thing. And down here we have very low values of electronegativity.

So with electronegativity we are now able to make calculations. And this is the Pauling formula for calculating the bond energy in a heteronuclear bond starting from homonuclear bond energy. So let's continue with the HF. So if I want to get the bond energy of HF I'm going to take-- and this is the Pauling formula-- the geometric mean. So I take the bond energy of hydrogen-hydrogen times the bond energy of fluorine-fluorine, and square root. So that's the geometric mean of the two. And then comes the Pauling piece that gets him the Nobel Prize. You take the difference in the electronegativity between the two elements squared, and then the factor 96.3 gives us the unit consistency with kilojoules per mole. So the greater the difference in electronegativity the greater the contribution here in terms of the deviation from just the geometric mean of the two homonuclear bond energies. Or put another way, if you have a homonuclear atom such as H<sub>2</sub>, if it's  $\chi_H - \chi_H$  is 0, so this second term goes to 0. And obviously when fluorine is one of the members you're going to get a very, very high number, because this has the most-- and it doesn't matter which order you put them in because you're taking the square, so it's always going to come out positive.

And I want you to appreciate the sense of scale here, so if we go in here we'll multiply. This is going to be 435 times 160. And I'm going to take the square root of this. And then this is 96.3. And you look on your periodic table this is 2.2 for hydrogen. Fluorine is 3.98. And I know there are different tables of electronegativity. I don't care. Just whatever you've got on your periodic table. The one in the book is a little bit different but it all comes out in the wash.

So you multiply all this out, and we find that the first term is 264 kilojoules per mole and the second term is 344. So this second term is even greater than the first term. So the amount of energy in that electron displacement is substantial. And if you sum the two of these you get 608. Now you might say, well wait a minute. The real number is 569. But 608 takes you in the right direction and accounts for the contribution of electron displacement. 264 is just plain wrong. So this was an important start for Pauling.



And he has labels on these two contributions. This first term, which is just the combination of the homonuclear bond energies, is called purely covalent. It's the purely covalent contribution. And it's what I've been referring to as the sharing. This is what you get from sharing. OK? And then this second term here with the difference in electronegativity is what you get from what I've been calling the pull on the electron pair. And Pauling called this the partial ionic character. He's not saying that there's electron transfer, but it's a move in that direction. Partial electronic character.

So what I've done here is I've decided I'll make a sort of a panorama of what we've seen up until now. And so I'm going to make something called the electron sharing meter. All right. So if I look at a homonuclear system like hydrogen. So my meter reads neutral. So the arrow's at 12 o'clock. The electrons are shared equally. And then if I go to HF what do I have? Well, I know that the fluorine is pulling the electrons. And so we can designate that by writing delta minus, delta plus. delta the physicists use. The lowercase Greek delta means little bit of. All right? So delta minus means it's a little bit negative. And we've got charge neutrality, so if the fluorine end is a little bit negative then the hydrogen end has to be a little bit positive, which means this thing has a net dipole moment. It's a dipole. And the arrow points to the negative end. One way to think about it is I put a little slash there and that starts to look a little bit like a plus sign. You can come up with your own way to remember it. So it's got a little bit of a dipole moment. And people depict dipoles usually as ovals, and they'll put a minus end and a plus end. So it's net neutral but the charge is not uniformly distributed. OK? So our sharing meter in this case is going to show something to the right. We've got electrons that are unequally shared, and that moves over to the right.

And, you know, the dipoles have interesting properties. Oh, there's a plot of electronegativity  $\chi$  in the bar plot. And actually this is an interesting one. Just parenthetically, you see hydrogen here? Hydrogen's weird. They put it in the periodic table above lithium but it's not an alkaline metal. And you can see it just doesn't belong there. And there's a lot of conversation about putting it maybe somewhere centered above the p block elements, because it certainly doesn't belong next to helium. But it probably doesn't belong above lithium either. Anyway, I thought that was very interesting. I can tell from the response of the class, why does he care?

[LAUGHTER]

PROFESSOR: All right. Now this is really-- I'm going to use an adverb here-- this is really important. All right? So here's HCl, is a cousin of HF, and you see in the upper frame it's just a bunch of HCl molecules just bopping around any which way. So there's the delta plus and the delta minus. Now if you take these dipoles and you put them in an electric field they will align themselves, and the positive ends will face the negative plate and the negative ends will face the positive plate. And there's energy stored when the random orientation goes into an ordered orientation. This is the principle behind a capacitor. A capacitor is nothing more than a whole bunch of aligned dipoles. So if you want to invent a supercapacitor that we can use on a car to extend the range of the automobile so we can reduce our dependence on imported petroleum, you're going to look for molecules that have a honking big dipole moment. That way you get more energy per unit electric field. So, again, a simple idea that tells me how to go and invent. I can go back to my office and go and invent something right now just based on this lecture 9.

[LAUGHTER]

PROFESSOR: See, you go and invent. You start the company, you make the billion. Remember good old Professor Sadoway at MIT, and established the fellowship for students, and so. All right. But you have to know what a dipole moment is. Got to know what a dipole moment is.

OK. So there's the dipole moment. And then lastly I'm going to put sodium chloride. So what's sodium chloride look like? Well it's Na plus and Cl minus. So the electron has transferred completely. So this isn't even sharing at all. So this is really bury the needle. This is not sharing. In this instance the sodium doesn't even get visitation rights to the electron. The electron's gone. Whereas here hydrogen gets to see the electron on Saturdays kind of thing. Depends what kind of lawyer fluorine had. That's what it all boils down to.

All right. This is the same thing that I just showed you. But you see, the textbook gives you, as the name implies, dense text. I gave you the sharing meter. The sharing meter is far more expositive.

All right. And then, finally, the percent ionic character is given by this formula here. So this is 1 minus the exponential. So the exp term, this exponential of-- what is it-- minus 1/4 times the difference in electronegativities squared. This notation means e base natural logarithms, minus 1/4, blah, blah, blah. That's what this thing is. So if you plug in, multiply by 100% you get something that goes from 0 to 100. So obviously when delta chi is 0 you get 0%. e to the 0 is 1, 1 minus 1 is 0, and so you have no ionic character. And so if you plug in the numbers for HF-- so you're going to take this difference here, square it-- it ends up giving you 1.8, which gives you a value of about 56% ionic character. So it's as though the electron is sort of half transferred.

But you might also look at it from this perspective. If you take 344-- because this is the partial ionic character, which is the energy of electron displacement over the total energy in the calculation-- that turns out to be 57%. So this stuff makes sense. There's a sensible metric here at work. And so this is what Linus Pauling got his Nobel Prize for, and it's the description of polar covalency. And polar covalency is operative when you have heteronuclear bonds, because the two different elements don't share the electron equally. And the Pauling formula allows you to calculate that. And his formative book was written in 1937, called *The Nature of the Chemical Bond*.

OK. So turning to the last five minutes, I want to bring to your attention some covalent molecules. Today we're going to talk about Freon. Freon was an invention, it was a designer chemical, invented by Thomas Midgley. This is me. I named him "sp3." That's his nickname. Thomas sp3, for the hybridized orbital. So he was working at the Dayton engineering laboratories in Dayton, which was owned by General Motors, and he was working in the 20s at a time when there were no refrigerators in American kitchens. The only refrigerants that were used were either toxic or flammable, things like ammonia, methyl chloride, sulfur dioxide. And you read about horrible accidents. People making ice cream at some plant and the compressor blows up and two or three people are killed. So it was deemed unsafe in the American kitchen.

In the 20s Midgley discovered this molecule, which looks just like methane only we've replace the hydrogens with two chlorines and two fluorines. So this is called dichlorodifluoromethane and it's a chlorofluorocarbon, a CFC. And this was fantastic stuff. It it was colorless, odorless, tasteless, non-toxic. It was not just used as a refrigerant, it was used in propellant. When I was your age all of the sprays-- whether it was hair spray, shaving cream, any aerosol-- was propelled by Freon-12. It was fantastic stuff.

Well, it turns out that in the upper atmosphere-- you know, you go pss pss pss. You got people all over the world doing this, eventually this stuff starts floating away. And what turns out in the upper atmosphere where we don't have shielding from ultraviolet-- you know how to do this calculation, because you can look up the energy. And, in fact, it's part of your homework, where you look at the energy differences and the electronegativity differences, you can compute the wavelength of light that's capable of breaking the carbon-chlorine bond. And it turns out to be in the ultraviolet. Once the chlorine is broken you have a chlorine radical, and that chlorine radical goes over here and attacks ozone.

[CELL PHONE RINGING]

PROFESSOR: Cell phone-- out. Just get up and leave out of courtesy.

[CELL PHONE STILL RINGING]

[LAUGHTER]

PROFESSOR: Hello?

The first year I was teaching 3.091 there was a Nobel Prize awarded to Mario Molina, who was a faculty member here in Earth and Planetary Sciences who had worked years earlier at University of California, Irvine, and had speculated on the mechanism by which ozone depletion occurs and linked it to rising levels of CFCs. Initially-- that's why it says a vindication-- people pooh poohed it, said it was crazy. There wasn't enough of this pss pss to cause any trouble. But then later with the NASA program they started taking a lot of images and they could track ozone levels in the atmosphere and start seeing that not only was ozone changing but there were actually pockets where ozone was being depleted at an accelerating rate-- because obviously the atmosphere isn't constant composition and constant temperature. Duh. So anyways, yeah. There he is. And this was the paper that was published in 1974 in Nature. And this was done before computers. The PC wasn't invented and commercialized until the early 80s. So this was typeset, and the person who typeset it obviously didn't take 3.091 because instead of "atom" hyphen "catalysed" we have "atomc-atalsed." But even ignoring the spelling error in a Nobel Prize winning paper--

[LAUGHTER]

PROFESSOR: --the Nobel committee overlooked this. Yeah. So there it is. And then they went to HFCs and so on. There's a lot of activity in this. And what happened is when we changed from CFCs to HFCs we had to change the design of the compressors. And what happened was everything got much, much more efficient. So this was an example of necessity for a change that was driven by concern for the

environment. Instead of putting people out of work and killing an industry, gave us much more efficient refrigeration.

And the last thing I'll show you is this to draw your attention. This was in your textbook. This is the cap at the top of the Washington Monument. The Washington Monument was built to celebrate the American centennial, 1876. They finished it in 1884. And this is 100 ounces of aluminum, because aluminum was a precious metal. It was priced higher than silver. 1884. Two years later Charles Martin Hall and Paul Heroult invent an electrochemical process that drives the price of aluminum down to the point that we make beer cans-- I mean soda cans-- out of it today.

[LAUGHTER]

PROFESSOR: And a good example of how chemical innovation can lead to superior products. I'll see you on Wednesday.

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