**PROFESSOR:**    All right, let's resume our discussion. And we'll finish it for sure by the end of today. And as you say, you can tuck this away for study on your own or for future reference or whatever you want to do. So if we could assign sizes to atoms and ions, we could do a lot towards predicting what sort of structures they might form if we knew the composition.

The composition-- again, assuming there is only one type of anion and one type of cation, the composition is determined by the valence. The composition fixes the ratio of coordination numbers. And the structure will have lowest energy when we have the maximum number of anions around cation and vice-versa.

So we're in great shape. And this is simple, idealized, but very powerful stuff if we knew the sizes that were assumed by ions. And that, really, is an absurd notion, to talk about an atom as though it behaved like a sphere with finite dimensions. If we plotted the density of the electrons as a function of distance R from an atom, it does something like this. At very small distances, that defines a shell of a rather small volume, so there are not many electrons. Rises up to a maximum, and then tails off gradually.

So what is the radius? The maximum in the distribution of density. So the notion of radius is absolutely nonsense in terms of the actual distribution of electrons on the atom.

However, one can get from your fraction measurements a determination of the lattice constant. And even with routine methods, you can get the dimension of the lattice to extraordinary precision. The typical lattice constant is about 10 Angstroms. You can get this through routine methods to plus or minus 1 in the fourth decimal point. So this is a precision of 1 part in 10 to the 5th.

You can get atomic positions when they are not fixed by symmetry to get a coordinate to plus or minus 0.yyyy plus or minus 1 in good cases. So that is 1 part in 10 to the 5th. Missing a factor or 10 somewhere. This is plus or minus 1. That's 1 in

10 to the 4th. So you can get this information very accurately.

One thing I always like to point out here is that a thermal expansion coefficient for most inorganic materials is something that never gets much lower than about 1 or 2 times 10 to the minus 6. So if you're going to push the measurement of a lattice constant to the ultimate accuracy, you'd better have a thermometer on the top of the X-ray generator, or your measurement is meaningless. The thermal expansion can be more than the uncertainty in your measurement. So you should report, for very precise measurements, the temperature at which you made your measurement.

OK, you can get interionic distances with very high precisions. And if you look at a series of compounds-- and these are the ones that are discussed in the notes, which have the rock salt structure type. So here is the cation, here is the anion. The anion-cation distance is simply equal to 1/2 of A for the rock salt structure.

So that's easy. You don't even have to know the atomic positions. Just measure the lattice constants. And then you would find, for example, that R, NA plus R, CL is equal to 1/2 of A for NaCl. Very precisely know the sum.

How do we split this up? Well, let's look at another compound. Let's look at R, NA plus R for bromine. And that would be 1/2 of the lattice constant of NaBr. Hm. More data, but we haven't solved anything. We have three radii, only two measurements. And you can see, if you try to push this further, you can never get enough information to split up the interionic distances into sums of individual radii in any sort of unique fashion.

So you have to start somewhere. And there are different sets of ionic radii that were proposed early in the game. And they are discussed in the notes. I give you an example of some of the sums of radii for the oxides and sulfides and selenides of the transition metals. You can see that as the anion atomic number increases, the size of the lattice constant goes up. So you could get, for example, the difference in size between a sulfur and an oxygen and the difference in radius between a selenium and a sulfur. But you could never get the absolute values.

There are four early sets of radii. And they are tabulated for you part way through the notes. And there's a cautionary lesson here. One the early series of radii-- see, even the old workers in this field appreciated the role of ionic sizes in determining structure. So they wanted to set up self-consistent schemes of radii. And the earliest one is by, really, the founder of crystal chemistry, a man named Goldschmidt. Linus Pauling got into the act very early on.

If you look at this table that I copied from these separate publications, four different people-- Goldschmidt, Pauling, Zacharias and Ahrens. Some people left out the radii of certain species. Other people left out different radii depending on the compounds that they looked at. If people looked at the same ion, they very often got very, very different values, depending on their starting point.

Look at the size of barium, for example. Zacharias said 1.29. Ahrens said 1.34. Pauling said 1.35. Goldschmidt said 1.43. Depends on the starting point that they used for the initial radius. And once you've determined that, everything falls into place.

Another basis for determining radii, Bragg determined a number of the structure of important silicates. Why silicates? Because as you walk along the ground, you're walking on silicates. These are part of the minerals that form the Earth's crust, so there was a lot of interest in those. Bragg, from his early work way back in the late 1920s, found that the size and shape of the Si04 tetrahedron forms tetrahedral coordination because silicon is so small compared to oxygen.

The interionic distances were always about the same. The tetrahedron was always regular. So what Bragg said was, a-ha, this is a tough little nut in silicate structures. Doesn't deform. The size is always the same. It's always regular. The reason must be that the oxygens are just in contact. So he used the dimensions of an Si04 tetrahedron, took the radius of oxygen as half the edge.

Pauling used a different starting point that has been followed. There's still another way of determining radii. Is there any physical property of a material which might

also be shown to be proportional to the size of the ion? And the answer to that, which I'll pass over quickly, is yes. Quantity called the ionic electrical polarizability, which is the relation between an applied electric field and the dipole moment that is induced on the atom when you separate the electron cloud and the nucleus.

And a simple model shows-- and this is carried out for you-- that you can relate the ionic electronic polarizability to the volume of the atom, and it turns out to be beautifully simple, that the polarizability is simply 4 pi epsilon 0 times the radius of the ion cubed. So therefore, you can split up ionic radii in proportion to the cube root of the polarizability of the ions.

Well, that trades one problem for another. How do you get polarizabilities? It turns out that the index of refraction of materials is given by the sum of the number of each species per unit volume times the ionic polarizability of that species. And there is a famous equation called the Lorentz-Lorenz equation. I can never resist calling it not the Lorenz-Lorentz equation but the Lorenz-Lorentz equation equation because it sounds like you're saying everything twice.

If you note that the dielectric constant of a material is related to the square of the index of refraction, instead of n squared, you can replace the n squared by epsilon, the dielectric constant, and then the equations become known as the Clausius-Mossotti equations. And I always take that as a nice illustration of the fact that a very simple change of variables can be all it takes to become famous and immortal. [INAUDIBLE] what happened to Clausius and Mossotti.

Where do you get polarizabilities from? This was looked at by a number of people. One of the most complete were three people, Tessman, Kahn, and Wild Bill Shockley of transistor fame. So you can find these numbers, and you can get a self-consistent set of radii.

But note in the table that I give you here that the individual numbers are very different. And two caveats that I have to issue is you can't mix ionic radii in different people's tables because they have different starting assumptions for the standard radius. If you do that, you're mixing apples and oranges. And I wish I had a cookie

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for every half-baked book on chemistry that said, hey, Ahrens has got something for americium and Pauling doesn't.

Let me put the value for americium in there. Totally wrong that they are established on different bases. So you can't mix apples and oranges. You have to use a self-consistent set of radii. The ones that were followed until very recently are Pauling's radii. And Pauling's radii are based on a standard radius for oxygen, which is 1.40 Angstroms for the radius of oxygen.

The other thing that I have to issue as a caveat, which I hope you won't forget, is that radius ratios do a pretty good job of predicting the expected coordination number. But if you are very, very close to a limiting critical radius ratio, all bets are off. Because then you're really asking the question, if I have this polyhedron of ions, if I squish them a little bit so that I increase the coordination number, does that give me a lower energy in return for the price that I have to pay to deform the ions that I'm packing together?

And that is not possible to answer on the basis of a rigid sphere model. So when you're very close to a critical radius ratio, you really can't say for sure whether the structure will go to the lower coordination number or the higher coordination number. So you have to be careful of that.

Finally, people have continued on. And stuck in the margin of these older radii is a reference to a paper by two people, Bob Shannon, who was a crystallographer at DuPont,  and Charlie Prewitt. I'm very proud that he became so notable, because he was my office mate in graduate school. So I like to promote his radii whenever I can. And in *Acta Crystallographica* in 1969, they published a set of radii, which is in the nice typeset version that's Xeroxed directly from their paper in *Acta Crystallographica*.

And the headings need explanation. There's the ion and its valence, then the electron configuration. And what's interesting is that some of the transition metals, for example iron, can be in a high-spin or a low-spin configuration depending on whether the moments on the electrons are all parallel or anti-parallel. High-spin and

low-spin configurations give ions with very, very distinct radii.

So the second column, EC, stands for Electron Configuration. Then comes coordination number. And here is another feature that we really should not overlook, that as even rigid spheres-- here's an A, and here's a B-- acquire progressively higher coordination numbers-- let's look at just coordination number three and coordination number four, because they're easy to draw.

In addition to the attractive force between anion and cation, there is also a repulsive force between the anions. So here's the repulsive force between this B and its neighboring B and this B and its neighboring B. And the resultant is a force that tends to push apart the A and the B ion.

For four-coordination, remember first of all, the Bs are closer, so the repulsive force is stronger. But there are four of them, as well. So this turns out to be a larger repulsive force. So the conclusion is that the radius of A would be expected to go up slightly as the coordination number increased, simply because there is a repulsive interaction between the coordinating Bs. And that will tend to push them apart more strongly as the coordination goes up.

So the third column in the Shannon and Prewitt tables is coordination number. And if you look at several ions, they're-- for example, barium has 6-coordination, 7-coordination. 8, 9, 10, and even 12. And as you go down that list of radii, it gets larger as the coordination goes up. And it's a relatively small effect that's on the order of 5 or so percent. But still, when trying to calculate an interionic distance, you should use the radius that is appropriate for the coordination numbers.

The fourth column is spin. And the spin stands for high spin or low spin. And you will find that for the transition metal atoms-- for example, $CO_2$ plus low spin or high spin, and note the rather different radii for these two configurations of the electron moments. Yeah.

**AUDIENCE:** Under coordination number, what's the difference between 4SQ and just Q?

**PROFESSOR:** You would guess that the lowest energy configuration for four-coordination would be

tetrahedral, because that keeps the anions most widely separated. There are cases where the coordination is plainer. So the "SQ" stands for square, and that's unusual. And you'll notice that that appears for things like silver, which has a considerable covalent character to it. For gold, 3-plus. That's one of the noble metals, again, that has a considerable covalent character to it.

So you'll notice that as the coordination number goes up, you get a different radius. Now, there are then a set of numbers, and these are numbers that are based on different starting points. The furthest column to the right, quote "IR" quote, this is based on Pauling's starting point.

And Pauling's starting point, if you go way down the list onto the second page, is that for 02 minus for oxygen in six-coordination, the standard radius from which everything else hinges is 1.40. The Pauling radii had been so commonly used that Shannon and Prewitt decided to use 1.40, Pauling's radii. So all of their numbers are compatible with the early Pauling radii, except they're based on thousands more crystal structure determinations.

There is another column, second from the right, called CR. And that stands for Crystal Radii. And there were two people that proposed that Pauling's radii really didn't give a feel for the proper sizes of the ions. And they went on at great length to explain what "proper sizes" is. And the only difference for the sizes that are based on, quote, "crystal radii" is that if you go all the way down to oxygen, the size of the oxygen ion in six-coordination is given by 1.26.

So all of the anions in the crystal radius column are smaller by 1.40 minus 1.26. I can do that in my head. That's 0.14 Angstroms. Run down the list. They're 1.4 Angstroms smaller for the anions. And the cations are 0.14 Angstroms larger. So there are two alternative sets of radii, one based on the traditional Pauling radii, 1.40 for oxygen in six-coordination, and the Fumi-Tosi radii, 1.26, which maybe give a better picture of what the sphere sizes actually, quote, "look like," unquote.

But note the tendencies. There is a progressive change-- whoever's starting point you use, there's a progressive change in size with coordination number. And let me

give you, if I may, at this point, give you-- again, a little knowledge is a dangerous thing. One of the structures which I worked on many years ago was a puzzle, and this was the prototype fast ion conductor silver iodide.

And nobody had been able to determine the structure for several reasons. Nobody had ever made a single crystal of it, and all the diffraction data you had available for the structure were five or six intensities. And there were about seven parameters necessary to fully describe the structure, so you were out of luck.

We learned how to make single crystals. But before that-- no, he will go nameless. He said, OK, let's see what's going on here. Oh, we'll get the radius of silver. We know that in silver iodide, the iodines are in body-centered cubic packing. And we know what the lattice constant is, because we got that from powder diffraction data. Huh, the silver ion is too big to fit in either the tetrahedral interstitial site or the octahedral interstitial site in silver iodide.

So he said, therefore, the structure has to distort, and it's really tetragonal. But there are going to be domains. a tetragonal domain in one orientation here, a tetragonal domain in another orientation here. So he gets himself a random number generator and takes numbers one, two, and three and puts it on a cubic lattice to determine what the distortion will be. Said, hey, I got a bunch of ones here and a bunch of threes here. This crystal is built of domains.

And the reason the silver ions migrate rapidly is that a domain can pop from one mode of distortion to another, and that's essentially going to transport the silver ion from one end of the domain to another. This guy got two papers out of it. What he had done was he looked up the radius of silver in Pauling's tables. And he didn't realize that all of Pauling's original radii were normalized to octahedral six-hole coordination, which makes the radius larger. And that's why the silvers didn't fit in any of the interstices.

If you take the tetrahedral radius for silver, which is where it actually sits in the structure, it fits as snugly and nicely as you please in the tetrahedral interstitial site in the body-centered cubic arrangement. So this guy made an idiot of himself

because he didn't realize the basis on which these tables had been established. But he's nameless, so I can call him names. So anyway, again, a little knowledge can be a dangerous thing.

Moving on, in the few minutes that we have left to devote to crystal chemistry. Pauling's radii, and even better still now, the Shannon-Prewitt radii, let you predict nearest-neighbor configurations-- coordination numbers with fair degree of confidence. Pauling-- and this was one of the things that he received the Nobel Prize for-- proposed a set of five rules that are called Pauling's Rules for ionic structure. The first thing he said was something that we've already stated, a coordination polyhedra of anions is formed about each cation, and the cation-anion distance is determined by the sum of the radii, and the coordination number is determined by radius ratio.

So there are three principles in here. The two most important ones is that expressing faith in a set of radii to determine interionic distances and the fact that if there are radii that can be assigned to the atoms, you can predict a coordination number. So that's Pauling's first rule. Actually, Pauling's first rule was first stated by Goldschmidt. But to have a complete listing of guiding principles, he included that there and didn't claim it was his own.

But then he does something that is rather interesting. This is the only one of the rules that is quantitative. If you had an ionic structure, and you could determine its unit cell, the structure should be electrically neutral if it's composed of ions that are charged. So therefore, you would not make a structure in which all the cations were up in one corner of the cell, and all the anions were down in the opposite end of the cell. That would be something that might be electrically neutral, but it would be a high-energy configuration.

So Pauling's second rule is a very cute way of expressing the fact that a structure should be atomistically electrically neutral, as well as microscopically. And he did that in the following way. He said, let us look at the coordination number the cation, A, and look at the coordination polyhedron. And let's define as the bond strength, S,

as the ratio of the cation charge plus Q divided by the coordination number of A.

And then he said that in a stable structure, if we look at the anion, the sum of all the bonds donated to-- he visualize the charge being donated to the anion. The sum of all of the bonds from the same cations or from different cations, if that's the nature of the structure, should be equal to the charge of the anion. So let me say "cation" here.

So it's a cute way of expressing local electroneutrality. Actually, that's been superseded by an extension of this general principle. And I may not have time to discuss it today, but I'll give you a handout next time. It's not in the notes, either. This is a relatively recent tool that most people are not familiar with, so I'll return to it briefly next time.

The next rule says, OK, we know how to determine the coordination numbers. To describe the structure, we should be able to say how these coordination polyhedra fit together. So looking at the coordination numbers-- well, let me do a three-dimensional case, because that's the realistic situation. Let's suppose we have coordination number eight, which we often do. And besides, that's easy to draw.

So he says that in a stable structure, the coordination polyhedra tend to share corners. And I might say also that they tend to have the line between cation, anion, cation to be a straight line, as opposed to sharing edges. So for eight-coordination, this might be a pair of cubic coordination polyhedra sharing edges. And especially corner sharing is more favorable than sharing faces.

It's a very specific statement on how the coordination groups whose geometry is determined by size should fit together in a structure. And it has a very simple basis, an almost trivial basis. As the polyhedra of the given size share corners and then edges and then faces, the cations inside of these polyhedra are progressively getting closer and closer together.

And clearly, that increases the repulsive energy. So the cations are most widely separated if not faces, not edges, but corners tend to be shared. Puckered a little

bit. Maybe this is not exactly a 180-degree bond angle. But corner sharing is still favorable.

And rule D is essentially an appendix to that, and it says, and how, if the charge of the cation is high and the coordination number is low, the higher the charge of the cations, the stronger that repulsive interaction. The smaller the coordination number of the cation, the closer together they become in, let's say, face sharing for tubes as opposed to face sharing for tetrahedra. The lower the coordination number, the closer together the cations come, regardless of the precise shape of the coordination polyhedra. So rule D says, and how for high charge and low coordination number.

The last rule, sometimes called the "rule of parsimony," the "rule of stinginess," says that the number of different kinds of atoms in a structure tends to be small. You can read in two different interpretations of the term "different kinds of cations," and both of them are right. You could mean different in terms of different chemical species. In other words, if you take a pot and dump half of the elements in the periodic table into the pot, melt it up, and then cool it down to crystallize the phase, you're not going to incorporate all of those ions into one crystal structure. They have different sizes. They have different coordination polyhedra. The different coordination polyhedra have different sizes.

So to try to fit all of those things together in one structure is just going to cost you a lot of energy. It's going to be much more efficient to form two or more phases, which have much lower energy, and then pay the price of an interface between them. So have a chemically complex melt or solution, you're going to get different phases. You want to incorporate everything into one structure.

The other interpretation of different is in terms of their coordination number and their coordination polyhedra. If the size is such that a particular cation wants to have tetrahedral coordination, you would expect them all to have tetrahedral coordination and not have a mixture of cubes and tetrahedra and octahedra. If it works for one coordination through the chemical species, it'll work for them all. That rule tends to

have some, but not terribly many, exceptions. But there are cases where you find two different coordination numbers. But very often, that's because of a covalent character.

So there's some discussion and elaboration of each of those rules. I'm just about out of time, and therefore out of crystal chemistry. Another entirely different approach to structure is to say that the anions are the big things. And if the energy of the structure is lowered by taking ions of like charge and getting them as close as possible to the larger ions, say the anions of opposite charge, there is a strategy for making the arrangement.

And I think it's the same strategy that I use when I'm packing a suitcase for a trip. Take the big things-- the books, the shoes-- and arrange them in the suitcase as densely as possible. Then I take the little things-- the toothbrush, the socks, and so on-- and I stick them into the interstices that are left.

And this other view of examining structures and interpreting says the same thing. Take the big things-- not the shoes but the anions-- and arrange them as densely as possible. And this gets into the question of close packing of spheres. Then take the little guys, the tiny little cations, and stuff them into the holes that are left in the close-packed arrays.

So another way of interpreting structures and predicting structures is to look at the sort of interstices that exist in a close-packed array. Regardless of the stacking sequence of spheres, there are always two kinds of interstitial sites, one tetrahedral, one octahedral. And there are two common, but not exclusive, types of packing arrangements, which you probably know. There is the cubic close packed array. There's a little diagram of close-packed sheets here.

And there are two sorts of interstices shown in the figure on the first page of the notes on packing considerations. There's one set of triangles that points in one orientation that forms a hollow in which you can drop down a second layer of spheres, another triangle that is the closest triangle to the first one that points in the opposite direction. Each represents a potential location for the next close-packed

sheet, but those two different locations are too close together to both be used. So you have to pick one or another.

And if you label those three different locations A, B, and C, any arrangement of spheres that does not place two letters in succession will give you a close-packed arrangement with exactly the same density. So ABC AC, AC, ABC, AC, AC is a packing of close-packed spheres that is exactly the same density as AB, AB, which is hexagonal close packed, or ABC, ABC, ABC, which could be shown to be the face-centered cubic structure.

So that is another way of looking at structures. And specifying the space filling in simple ionic structures is another way of looking at structures. And at that point, I'll quit. There are some examples of close-packed structures and derivatives thereof that form the last pictures. And I'm going to stop and suck in air and mention as one last thought that only five of Pauling's rules are stated here. There was a sixth Pauling's rule, and that's not commonly listed. And I'll tell you what it is. The sixth rule says, massive doses of vitamin C can cure the common cold.

Actually, that was something that Pauling pushed. And interestingly, about three years before he passed away, Pauling came to MIT and gave a lecture in 6120. And as you might expect of MIT undergraduates, after he finished his lecture, there were a few questions. But there were about a dozen students who came up with bottles of vitamin C and asked Pauling to autograph them for them. And he did so with good humor and thought he had perhaps won a few converts in the process. So that's it. Getting silly, so it's time for all of us to go home.