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PROFESSOR: So we will have weekly quiz tomorrow. There's been a lot of coverage, and so to focus you a bit, I'm going to confine the weekly quiz to glasses and chemical kinetics. So you don't have to worry about diffusion. We'll catch up on that, but I know there's so much material there. Let's keep it confined to glasses and chemical kinetics. And I'll be available today 4:30 to 5:30. If you can't be at that time, send me a note, and I'm sure we can figure out a time to get together.

So what I want to do today is to start a new unit. We're going to start talking today about solutions, and do some solution chemistry, OK? Today we talk about solutions. And you might initially say, why are we talking about solutions? This is solid-state chemistry.

I think up until now, you've seen that it's pretty rare that we use solids in their pure form. We usually have mixtures. So for example, when we studied glasses, we modified the glasses with an alkaline earth oxide. Well we, in fact, were making a solution of more than one component. So it's to get certain properties that we study solutions.

Secondly, coming out of liquid phase is a way to make solids. So in terms of processing, we need to understand something about solutions.

And then lastly, we're going to be studying, towards the end of the semester, a big unit on biochemistry. And biochemistry, why, you say, biochemistry? Why is he doing biochemistry? I thought this was solid-state chemistry. We are solid-state devices, but we're made of soft matter. At least the exoskeleton is soft matter. The endoskeleton is ceramic, right? Our bone structure is ceramic. Hydroxyapatite, calcium hydroxyapatite, and the outside is a polymer. So look at this. Conformational changes in polymer. But the chemistry, the biochemistry, so much of it takes place in aqueous solution. So hence, we better know something about aqueous solution.

So to this, we go almost right back to the first day. You remember, was the second lecture, and we showed this figure, and all the different categories of matter. And we started over here with elements, and we moved into some pure substance compounds, et cetera, et cetera. Now we're going to move over to here. So homogeneous mixture containing uniform composition and properties, as opposed to a heterogeneous mix. So we're now over here. We're working our way through the diagram.

All right. So let's get a couple of basic definitions up. So the solution is really a mix of at least two constituents.

One, the majority constituent is called the solvent, and then we can have one or more solutes. So the solvent, this is the majority constituent, and then the solutes are the minority constituents. And in some instances, it's pretty hard to tell which is which.

And as far as types of solutions, I want to broaden this. You know, when I say solution, you're probably thinking about aqueous solution. But I want to take a minute and work through this chart. And this is all posted, so you don't have to write it all down. Just follow with me.

So most of the general chemistry subjects will just stop at the end of the first line. They'll treat solutions as aqueous solutions. But in material science, we think of things broadly. So a good example of a simple aqueous solution is sodium chloride and water. Sodium chloride is the solute and water is the solvent. But you can have a liquid solute. So wine-- in case you've ever encountered this beverage, it's primarily water, but it can contain up to about 14% ethyl alcohol, and there are other constituents that give the color and the flavor and so on. And you can have a gas in a liquid, and that would be seltzer, where CO<sub>2</sub> is dissolved. It's actually dissolved. If you take a look at a bottle of bubbly water on the shelf, you don't see the bubbles. The carbon dioxide is actually dissolved. You can have a gas as a solvent, and air would be an example of that, where the solvent is nitrogen. And then we have as solutes oxygen, argon, carbon dioxide, if you live next to a power plant, it's sulfur dioxide, if you live next to an aluminum smelter, it's tetrafluoromethane, and so on. So we have all kinds of solutes in the air.

And then we can have solid solutions. And OK, as soon as you see the word solid, you know, that means you're 3.091. So what do we see for solids? Metal alloys. We saw carbon dissolved in iron. Well, that's a solution. It's homogeneous, single phase, just as the definition on that chart 1.11 said. Semiconductor, boron doping into silicon, the boron sits on a silicon lattice site. So this is a true solution. The boron is the solute, and silicon is the solvent.

We can have the ceramic. We talked about the oxygen sensor. The oxygen sensor is zirconia, which has been stabilized with the addition of calcium oxide. As one example. In contemporary work, they might use another oxide. But what's the purpose of the calcium oxide? Well, I told you that it's to increase the vacancy population, give you a rapid response on your oxygen sensor. And as we're going to learn later, that's true, and there's a second value in putting in the calcium oxide. And it stabilizes, that's why they use the term stabilize, it stabilizes the cubic form of zirconia.

Zirconia has a different crystallographic modifications. The cubic one is the one that gives us the best ability to transfer oxygen, and the addition of calcium oxide as a solute, the calcium ions actually sit on the zirconium lattice, that's a true solid solution. It also makes the cubic zirconia stable, and with Christmas coming, you know, it's the poor man's diamond, and that's the same material there. And to modify a glass, as I mentioned earlier, adding a

alkaline earth oxide breaks the silicate network. That's a solution.

Now here's an inverse one, where the solid is the solvent, and the liquid is the solute. So this was dentist's office practice going back to the time when I was your age. If you had a feeling, the dentist had silver and mercury in the dentist's office, and would add liquid mercury to silver and make up this amalgam, and then jam that into the tooth.

Actually, that was the B part of the operation. There was this dentist here in the United States, and if I could find him, I would like to have a word with him. But he had this theory. You see, the amalgam is a metallic alloy. And so obviously, it has metallic bonding. And the tooth is-- it's a ceramic. So what kind of bonds are going to form between a metal and a ceramic? They're not very good.

So this dentist had the theory that the way to increase the bonding capability of the amalgam to the tooth was to maximize contact areas. So when you went in with a tiny, tiny little cavity, the dentist would drill the tooth out, removing about 75% of the volume of the tooth, and then they would make this amalgam and shove that in.

And you'd wear that for about 20 years, until one day you bite into a muffin that's got a little piece of walnut shell in it, and the amalgam flexes, and your thin-walled tooth goes bang! Like that. And now you get to go back to the dentist's office for yet some more medieval treatment.

Actually, things have improved somewhat. Thanks to material science. But they're not using this amalgam anymore. But there are a number of us who are still walking around with silver and mercury in our mouths, and-- yeah. Enough about my dental problems.

Now let's go on to intercalation. You can put a gas into a solid. And I told you about this one, where if you want to store hydrogen, and this is a big problem, if we're going to talk about hydrogen-powered vehicles. A problem as big as, how to get the fuel cell cheap enough, is where are you going to store the hydrogen on the car, and one of the materials that's been proposed is this alloy of lanthanum and nickel that can intercalate huge amounts of hydrogen. So that forms a solid solution.

So those are examples of solutions, and we're going to go back and make sure that we cover the basic Gen Chem at the top here. But I want you know that solution chemistry is very broad.

Now when you dissolve something, you actually have things down at the atomic level. So for example, in brine, you actually have below two nanometers as particle size. You actually have sodium ions and chloride ions dissolved completely, which means that the solution is clear, colorless, and transparent to visible light. Water is clear, colorless, transparent to visible light. If you had sodium chloride, it remains clear, colorless, transparent to visible light.

You can't filter, and you can't wait for the sodium chloride to settle out, because it's bonded within the structure of the liquid water. And this has implications. There's so much water on the planet, but there's not so much fresh water on the planet. And desalination can't be accomplished by filtration. A filter that had a pore size small enough to trap sodium ions, the pore size would be so small, water molecules couldn't go through. So this is the concept.

At the other end, you can get something called a suspension, where the particle size is greater than about 1,000 nanometers, and blood is a good example of that, where it's opaque. Visible light doesn't go through, but you can filter out some of the matter in blood. And if you let it sit for a while, it'll settle in its gravitational field.

And in between, you have this whole zone of colloids. And so between colloids and suspensions, the only difference is particle size. And this whole thing we would just call a dispersion of another phase, either another solid phase, or another liquid phase.

And it's kind of an interesting physical chemistry about the dispersion, what makes it work. For example, in milk, milk is a good example of a dispersion. You have a fatty phase, and you have an aqueous phase. The aqueous phase, where all the minerals are. Why? Because the minerals are-- what kind of compound? They're not metallic, they're not covalent. They're ionic. The ionic compounds dissolve in the aqueous phase, and then in the fatty phase, that's where you have the protein and so on.

But the fatty phase is clear and colorless, and the aqueous phase is clear and colorless. And yet milk is white. It's, as the term implies, it's milky. Why? What's going on? You have a second phase here. This could be the fatty phase, and this is the aqueous phase. They're both clear and colorless, but they have different indices of refraction. And since this has  $n$  fatty phase, and this has  $n$  aqueous phase, this interface scatters the light.

So if you want to start a business, if you want to try to tailor the index so that the index of the aqueous phase matches the index of refraction of the fatty phase, you'd have the two dissolve, one and the other, and it would be transparent, divisible light. So you would have milk that isn't milky. I mean, the public would be very confused. But anyways. So that's what you do.

So why does this thing not settle? Because they do have a density difference, and again, going back to the days when I was not a college student but a youngster, there was still this form of milk called pasteurized milk. Well, all milk is pasteurized, but this milk was not homogenized. And what would happen is, there was this person that would deliver milk. This was a borosilicate glass bottle. And here would be the cream. The cream would rise to the top. We have all these expressions in our language. And then this would be the milk here, and you could skim this off for coffee or sugar, and then this would be a low-fat milk.

But people wanted this all mixed, so then they went to homogenized milk. So what is homogenized milk? This is your red cap, now. All the milk is homogenized. This was a big thing. This was simply called pasteurized.

I'm going to get to the physical chemistry here. It's very interesting. Because this is lower density, and yet in homogenized milk it doesn't rise. So let's take a look at what goes on in the physical chemistry of homogenized milk, because it's all about these various systems. So I'm going to take this particle here, and its sum insoluble cluster. And I'm not specifying the cluster size. It's probably greater than about two nanometers.

So there are two forces acting on this. There's a settling force and there's a buoyancy force. Obviously, otherwise it wouldn't float. So there's some kind of a buoyancy force. Settling force and a buoyancy force.

Well, the settling force, this is just the gravity. Right? This is the force of gravity. And we know the force of gravity. That goes with the mass.

Come on, get that cell phone out of here.

This force of gravity goes as the mass, and the mass, we know, goes as the volume. And the volume goes as the cube of the radius. I'm assuming this is a spherical particle, all right?

Now, the buoyancy force. The buoyancy force is the interfacial force between the two. There's some binding across here. Maybe weak van der Waals, or if this fatty phase has molecules in it that are polar, then there could be dipole-dipole interaction. But in any case, there's some kind of an interfacial force here. And this is all chemical bonding between solute and solvent.

But you see, the force is a weak force. If it were a really strong force, it would dissolve this thing. It won't quite dissolve it, but there is some kind of dipole-dipole weak force. And this one here is operating across the surface area. That's the contact. So this force goes as the area, and area goes as the square of the radius, whereas mass goes as the cube of the radius.

So you know, from your math, that  $r^3$  dominates  $r^2$ , but only at large  $r$ . It's not always the case, is it? Maybe before you got here, you thought that. But now that you've been at MIT a few months, you know that  $r^2$  can dominate  $r^3$  at small  $r$ . Interfacial forces dominate. And that's exactly what happens in these dispersions, and that's why they don't settle out.

Now, homogenized milk is simply milk that has been agitated in such a way as to reduce the fat globule size below a critical value so that these interfacial forces hold the fat globules in suspension. If you waited long enough, they would agglomerate and settle, but that time is probably longer than the shelf life of the milk. So the milk probably spoils before stuff settles out.

So this is all very important to understand. The range that exists between insolubility and this sort of clustering, and suspension, and so on.

By the way, a lot of pharmaceuticals are like this. A lot of pharmaceuticals. So when it says, shake well before using, they're not kidding. Because the active ingredient will settle. And you're drinking just the solvent, just the vehicle. And all of the potency is on the bottom of the bottle. Shake that thing up! I can't say what it does to the taste, but that's another problem.

Actually, I threw in this slide here. We're not going to spend any time on it, but you can look at it at some point. This is a whole taxonomy of colloids. Solid-liquid emulsions, aerosols, they're all part of this magic zone between solubility and just brick, all right? There's this whole fine, pardon the pun, the whole fine structure.

OK, So let's get to the chemistry. Obviously there's something to do with bonding here, right? So here's a simple experiment, and this is taken right from the reading. So I've just taken this episode that is written up in the reading. So we've got two beakers here, and in each beaker, we have a bilayer. We've poured in some carbon tetrachloride, liquid, and we've poured in some water. And these two are immiscible, because carbon tetrachloride is obviously a non-polar liquid, and water is a polar liquid with hydrogen bonding capability.

And in one beaker, we introduce crystals of iodine. In the other beaker, we introduce crystals of potassium permanganate. And then we shake them up, and we wait. And eventually we see that on the left, the iodine dissolves in the carbon tetrachloride. And we're using the purple color as an indicator. And this is kind of cute, because both potassium permanganate and iodine will render things purple. So you're comparing purple to purple. They could have chosen something else, but this is kind of cute.

All right. So here you end up with a solution of iodine and carbon tetrachloride, whereas on the right side, you end up with a solution of potassium permanganate and water, and nothing in the carbon tetrachloride.

So what can we infer from this? Well, let's take a look at the possible interactions. So first of all let's categorize H<sub>2</sub>O. This is polar, it's a polar liquid, with hydrogen bonding capability.

Carbon tetrachloride is non-polar. It's very toxic. When I was a child, we had this in the medicine cabinet. It's a non-polar solvent. It's fantastic for getting grease stains off. Every man had this. With a little handkerchief, you'd take a little grease stain off your tie. You can't buy this stuff. You can't even buy it for research anymore. It's too bad. It's great stuff. Highly toxic, though. But you know, there's a time and a place.

All right. So then here's iodine. Iodine, we know, is non-polar. It's a homonuclear molecule, it has to be non-polar. And so what holds iodine together in the crystal? There's only one bond, and that's van der Waals, right? It's a

van der Waals solid, whereas potassium permanganate is an ionic solid. Potassium permanganate is ionic, and it consists of potassium cations and permanganate anions.

And what we find is that the non-polar solute dissolves in the non-polar solvent, and the ionic solute dissolves in the polar solvent with hydrogen bonding capability. So from this, we can infer the general rule, which is encapsulated in the language used in chemistry textbooks. Like dissolves like. And what they're really saying here, is that like solutes dissolve in like solvents. Solute-solvent is like dissolves like.

OK. It's a good place to start, but it's an incomplete picture. So I want to show you that there's some sophistication here. This is taken from one of the other books. And it shows just the rules for ionic compounds in water. And I just showed you, from this example, that the ionic compound dissolved in water. And what you see here is that some ionic compounds dissolve in water, but there's a whole set of insoluble ionic compounds. So it's not straightforward.

But we know from 3.091, we know that we can make sense of this on the basis of competition. Competition between what holds the compound in the solid state versus what will pull it into the liquid state. So for example, we can compare sodium chloride, which we know dissolves in water. So sodium chloride, as a crystalline solid, will dissolve to form sodium chloride aqueous solution.

Whereas if you look at magnesium oxide, which is also an ionic crystal, it does not, to any standard imaginable, dissolve to form an aqueous solution of magnesium oxide. And what's the difference here? The difference here is, compare solvation energy, in other words, the energy that you got by pulling this into solution, and forming bonds between sodium and chlorine in water, with the crystallization energy.

And what's that all about? Well, that's the Madelung constant, remember? Madelung constant.  $q_1 q_2$  over  $4 \pi \epsilon_0 r$ , where this is the cation anion. And you can see here that sodium chloride has sodium cations and chloride anions, and there's a certain binding energy in the crystal. Magnesium has 2 plus. Oxide is 2 minus. The binding energy between magnesium and oxygen is so great that there's no driving force to dissolve.

Now, I don't expect you to be able to look at this and tell me whether something's going to dissolve or not. But if I were to say to you, explain why sodium chloride forms solutions with water, and magnesium oxide doesn't, that you could go through this rationalization.

And here's a cartoon from the textbook that tries to illustrate this solvation. Here you can see a crystal of sodium chloride, in the inimitable fashion, as drawn by chemistry books, where the chloride ion is green, and the sodium ion is blue. And that's OK. I can live with the color-coding, as long as we agree amongst ourselves, these ions are clear and colorless, because they have octet stability in their electronic shell.

And here's water, with the hydrogen shown in white, and the oxygen shown in red. And you can see that the oxide end, the oxygen end, the delta negative end of the water, is trying to wrest sodium cation out of the lattice, and ultimately surround it by a cage. And the same thing here. You see the hydrogen ends of the water trying to pull chloride out, and ultimately surround it with a water-like cage.

So this is the competition I was talking about. In the case of sodium chloride, water wins. In the case of magnesium oxide, water loses. The binding energy between magnesium and oxygen and the crystal dominate. So you don't see that solvation.

OK. Let's talk about metrics now. Let's look at some metrics of solubility. It's quantifiable. So we can express a measure of solubility in terms of a quantity known as molarity. So we can express moles of solute per liter of solvent. And this is called molarity, and the symbol is capital M. So we can say, for example, a 1 molar solution of sodium chloride in water, we'll write 1 molar NaCl, and then we'll write subscript aq, meaning aqueous. So it's an aqueous solution at a concentration of 1 mole of NaCl per liter. And the liter is named after a person, so that's capital L, per liter of solution. And remember, the solution is the sum of the water plus solute.

For dilute solutions, there's very little difference between the total amount of water and the total amount of solution. But in certain instances, the presence of the solute actually has a volumetric change on here. So strictly speaking, it's per liter of solution

And as I've shown you, there are degrees of solubility. So people represent the threshold of solubility as  $c$  of the solute. When  $c$  of the solute is less than about a million molar, 0.001 molar, we call this insoluble. So something is vanishingly soluble, we say that's the value. So we'll call this the threshold.

And then, something that's quite soluble, we'd say that the concentration of the solute starts to exceed at about 0.1 molar. And then we would say, that qualifies as soluble.

So now let's look at two extremes in solubility, operating off of this. So in the one case, we can have complete solubility. So examples of that, where things are completely miscible in one another. Complete solubility. By the way, some people will use the term miscibility. When something is miscible it means it's soluble. Same idea. If something is insoluble, some people might say it's immiscible. Same thing. OK?

So complete solubility is ethyl alcohol and water. You can mix them in all proportions. Continuously variable. On the solid alloy is silver and gold. Silver and gold, you can make alloys of any composition between 100% gold and 100% silver.

Now, that's the exception. Most cases are situations of limited solubility. So they go up to a maximum, which we



can denote C-star or C saturation. This is the maximum solubility.

So an example of something that's sparingly soluble in water is silver chloride. Let's look at silver chloride. So silver chloride, I'm going to start here, silver chloride as a crystal, and I'm going to dissolve that in water. So that gives me  $\text{AgCl aq}$ . So that's just simply the formation of an aqueous solution of silver chloride. And when the reaction moves from left to right, we call that dissolution.

The silver chloride is dissolving, and when the system moves from right to left, we call that-- now here I'm going to nitpick with the book. The book calls the left reaction crystallization. And that's correct. It is crystallization in this case, because silver chloride is a crystal. But it is possible, in other systems, to have the solute come out of solution, and make a solid that is noncrystalline. And you know that all crystals are solids, but not all solids are crystals. You can have an amorphous solid. So what would happen if you were to bring out of solution an amorphous solid? It would be silly to call it crystallization. So I prefer to use the term precipitation.

And there's another term that you can use, and I learned this one from reading the literature of geochemistry. What the geochemists call the reaction going from solution to make a solid, they say the system exsolves. This is dissolve, this is exsolve. So this is called exsolution. It's amazing what you can do when you know a little bit of Latin. So this exsolves. So that's the exsolution, or the crystallization reaction.

Now I'm going to show you what won Arrhenius his Nobel prize. Arrhenius did not get the Nobel prize for his brilliant work on activation energy. He got his Nobel prize on the theory of electrolytic dissociation, which was, people knew that you could dissolve salts and water, but they didn't know how. And it was Arrhenius who said that the salts go into solution by dissociating and forming ions. So goes in as  $\text{Ag} + \text{Cl}^- \rightleftharpoons \text{Ag}^+ + \text{Cl}^- \text{aq}$  plus chloride ion-- thank you.

And that, ladies and gentleman, was a Nobel prize for Arrhenius. And you can see that there's a relationship between the amount of silver chloride and the amount of ions. So there's a mass balance there, that the concentration of silver chloride dissolved, in fact, equals, in this case, by stoichiometry, the concentration of  $\text{Ag}^+$  plus, because of the nature of the dissociation reaction on a mass balance basis. And that also equals the concentration of the chloride ion, OK? So that's the way we can look at the system.

And how do we know that this thing has limited solubility? Well, there's various ways of measuring it, and one of them involves conductivity. Here's the conductivity of pure water. And you know that water has very, very poor conductivity, and in fact, what's happening here, when we add silver chloride is, we're adding charge carriers, because the audience are charged species. So they can carry charge. And you can see that this is a measure of conductivity as a function of silver chloride concentration. And as you add silver chloride to higher and higher values, the conductivity goes up. And look at even the tiniest amount of silver chloride has a conductivity that's

about, what, half an order of magnitude higher than the conductivity of pure water itself. So I would say that this is akin to doping, isn't it?

So up here, when you've got  $10^{-6}$  Siemens per centimeter conductivity, that aqueous solution is demonstrating the extrinsic behavior. This is very similar to doping. And at some point, we get to this value here, around  $10^{-5}$  moles of silver chloride per liter, and then adding more silver chloride has no impact on conductivity. Which tells you that you've hit saturation. This is akin to adding more and more sugar to the cup of tea, until finally the sugar just falls to the bottom. You can stir all you want, but you won't get it to dissolve, because you've hit saturation. So that indicates the presence of a saturated solution.

And so we can talk about that value, and we can say that for silver chloride, the concentration at saturation is equal to  $1.3 \times 10^{-5}$  moles per liter. Moles of silver chloride per liter. And obviously, that's equal to, according to that, it's equal to the silver ion concentration. I'm going to use square brackets to indicate moles of silver, ion per liter of solution, which is also equal to-- pardon me-- it's also equal to the chloride ion concentration at saturation.

Now I'm going to ask you a simple question. Suppose I've got a beaker here, and I know the maximum I can get here, the maximum is  $1.3 \times 10^{-5}$ . Now this is a really simple question. Suppose I am about to add silver chloride-- let's say this is 1 liter already. All right? I've got one liter. And you'd tell me, well, you can put in  $1.3 \times 10^{-5}$  moles to get the saturation. Suppose instead of 1 liter of pure water, I had 1 liter of water already containing, say,  $1 \times 10^{-5}$  molar silver chloride.

Well, that's kind of obvious, isn't it? I'm only going to be able to put 0.3 moles in, because  $0.3 \times 10^{-5}$ , because I've already got silver chloride in there. That's easy.

Now let's make the question a little more interesting. Suppose instead of a certain amount of silver chloride in there, I have no silver chloride in there. But I've got, say, 0.1 molar sodium chloride. It's a salt. It's a difference salt. So the question is, does the presence of a different salt have an impact on how much silver chloride I can put into this solution? And the answer is, yes. The answer is yes.

So what we find is that the presence of the other salt, in this case, has an impact, because sodium chloride goes in as sodium plus, and chloride minus. So there's already a boatload of chloride ion in there, and that has an impact on this relationship.

So how do we answer the question, what is the solubility of silver chloride in the presence of other chloride ions? And for that, we define something called the solubility product. And you need it in order to answer the question, how do you determine the solubility of a solute when there are other solutes present already?

And it's denoted capital K, lowercase sp, subscript. Solubility product. And it's equal to simply the ion products of the constituents.

So the solubility product of silver chloride is the product of the silver ion concentration, and the chloride ion concentration. And you know that in a solution of silver chloride alone, if nothing else, that the concentration of silver ion equals the concentration of chloride ion. That's the whole business of dissolving by itself.

And so I can then just say that  $K_{sp}$  will then equal the concentration of silver ion squared, which we also know is equal to the concentration of silver chloride aqueous. See, all of these are the same. So this solubility is the same. I can just put that in, which is just concentration of silver chloride. Square that. So if I square  $1.3 \times 10^{-5}$ , I end up with a solubility product of  $1.8 \times 10^{-10}$ .

So now I can use this in order to determine how much solubility I get in the presence of another salt. So in this case, I'm going to put 0.1 molar sodium chloride. And these are strong salts, so we're going to get complete dissociation. Gives me 0.1 molar sodium ion, and 0.1 molar chloride ion, when it dissociates.

Now you see the difference. Because the silver chloride, by itself, gives me  $10^{-5}$  molar chloride ions. When I add sodium chloride, I get 4 as a magnitude more chloride. So let's go back to the  $K_{sp}$ . So  $K_{sp}$ , this is for silver chloride.  $K_{sp}$  for silver chloride is going to be equal to the silver concentration and the chloride concentration. And in this case, the silver concentration is just equal to whatever that solubility is. Because there's only source of silver ion, and it's silver chloride. So I can write that as concentration of silver chloride. That's good.

And now this one here is what? I've got two sources. I've got silver chloride, I've got sodium chloride. So it's going to equal this thing here.  $0.1$  plus whatever I get from silver chloride. And it's vanishingly small, isn't it? The concentration of silver chloride, whatever it is. This is nothing, so I'm just going to neglect it. It's dominated now. The chlorine is flooded by the silver chloride.

And this product is a constant. That's still equal to  $10^{-10}$ . So I can turn this around and solve for the concentration of silver chloride, which is equal to the concentration of silver ion. And that's equal to, what is it,  $10^{-10}$  divided by  $0.1$ , which then gives me-- what's the number here? Plug that in. And I end up with  $10^{-9}$  molar. Right?

So look. Look at what's happened by having the chloride present from sodium chloride in such a large amount. It's repressed. It has repressed the dissolution. The presence of chloride then has a negative impact on solubility, and instead of having  $10^{-5}$  molar, it's down to  $10^{-9}$  molar.

And this effect of repressing solubility by adding a second solute is called the common ion effect, OK? Solubility

repression by second solute is known as the common ion effect.

And this is used in processing. If I want to trigger the precipitation-- see, if I started with a solution containing 10 to the minus 5 molar of silver chloride, and I throw in some sodium chloride, it'll start precipitating out silver chloride. So if I wanted to make a fine precipitate of silver chloride, I make a pregnant solution. And I could drop the temperature, because you can imagine that solubility is a function of temperature, or I could keep it isothermal, throw in some sodium chloride, and out comes silver chloride. So since the common ion effect on it and its value in processing. OK. Good.

Well, I think I'm going to hold it there. I'll show you just one more thing.

If you've got stoichiometry like this-- this is a difluoride of magnesium. If it goes into solution, you get magnesium cation plus 2 fluoride anions. And so if I wrote the  $K_{sp}$  for this reaction, it would be the product of the magnesium concentration and the fluoride ion concentration. Because there's the two here, this is squared. So this, too, will transfer up there, and then throw in some sodium fluoride, and cause the other thing to exsolve, and away we go.

All right. I've got a couple of things to show you. We're talking a lot about Arrhenius. This is a book I have. It's an English translation of a book written by Arrhenius in the late 1800s, and it was printed in English around 1908. And Arrhenius was a genius. He wrote on all sorts of topics here. Biology, physics, you name it. And one of the things and he was interested in was the origins of the earth. So this chapter is called, Celestial Bodies as Abodes of Organisms. Already speculating on whether you could have life as we know it exist elsewhere in the universe.

And one of the things he talks about is global warming. So this is Arrhenius on global warming. I'll read you the last paragraph of this chapter. There had been some major volcanic eruptions that had caused cooling when Krakatoa in 1883 and Martinique in 1902. Major plumes of soot that caused dramatic decreases in temperature. So now here comes the last paragraph.

We often hear lamentations that the coal stored up in the earth is wasted by the present generation-- remember, this is written 100 years ago-- without any thought of the future. And we are terrified by the awful destruction of life and property which is followed the volcanic eruptions of our day. We may find a kind of consolation in the consideration that adheres in every other case. There is good mixed with the evil. By the influence of the increasing percentage of carbonic acid in the atmosphere-- that's  $CO_2$ -- we may hope to enjoy ages with more equitable and better climates.-- Remember, he's a Swede; it's cold-- especially as regards the colder regions of the earth, ages when the earth will bring forth much more abundant crops than at present for the benefit of rapidly propagating mankind.

So it's interesting to see the world-- it's a great book to read. And you can see people in the 1830s were already

calculating heat transfer coefficients to how much the earth was changing.

We're going to post these to the website. This was, last year, in the *New York Times*. Every Tuesday they have a science section. And this was about glass. And very, actually, with your 3.091 knowledge, you'll read this like a newspaper, and it'll be very easy. And they go through the structure. Here's the structure of a window glass. You can see the network, former network modifier, and so on. And they talk about how difficult it is from a first principle's standpoint to model the structure of glass. These oxide glasses are complex and not easy to model. So when you're trying to engineer the glasses, instead of trial and error, it's hard to do so by theory. And it talks about some efforts at theory, and so on.

And the last thing I want to talk about is bulk metallic glasses. You recall that I showed you metallic glass that was made by melting gold silicon, and dripping it onto a water-cooled copper wheel that was zooming around to give us a cooling rate of about a million degrees a second.

And those strips had to be very, very thin, the metal strips. Because you've got liquid dripping down, and we're pulling the solid away, and there's a finite thickness here. Let's use a Greek letter,  $\xi$ . There's a finite thickness  $\xi$ . Because what's happening is that this is the water-cooled copper wheel, and you're extracting heat here. But eventually, the thermal conductivity of the metal is the limiter. In other words, I don't care how cold. You can put this in liquid helium if you want. You can't get the heat through the metal fast enough. And what happens is, when you look down here, the lower part is amorphous and the upper part is crystalline. So you don't end up with metallic glass. You end up with some metallic glass, and the upper part is crystalline.

So what happens when you end up with the limitation being the thermal conductivity of the metal? At that point, you're finished. And this was typically on the order of microns. And then they got up to, sort of, submillimeter. And that was it. So the glass that I showed you was foil.

Now what happened was, with more research-- so here we are. This is Pol Duwez at Caltech, gold silicon. And this is the thickness in centimeters. So you were down here at some tens of microns, all right?

Now, in the '60s, research at Harvard uncovered a set of palladium alloys that had better thermal conductivity and, remember the first day, about the analogy to the musical chairs? These things have slightly more complicated crystal structures. So for a given cooling rate, the metal has more difficulty finding the proper lattice site. And they were able to make metallic glasses that were on the order of 0.1 centimeters. That's still fairly thin.

And then back to Caltech in the late '80s, early '90s, and a man by name of Bill Johnson was able to develop a set of alloys that can be made in bulk form. Totally amorphous metal. And these are known as bulk metallic glasses. And look at the complexity of the alloy designation.

So now you see, well, why are they doing this? Because look, this is strength versus elastic limit. So you can either have things like polymers, that you can stretch very, very far, but they don't have much strength. Or you can have things like certain steels, that are very, very strong, but you can't bend them very far. And bulk metallic glass has put you right up here. You have strong alloys that have very, very high elastic limits. So they make great golf clubs and tennis rackets and so on, because they can flex way back, store enormous energy, and then spring. So here are some bulk metallic glasses, and here's a classic one. This is zirconium, titanium, copper, nickel, beryllium. All right, now how do we get that? Well, zirconium and titanium are body-centered cubic, we've got copper and nickel are face-centered cubic, and beryllium is hexagonal close-packed.

So the idea here is the principle of confusion. So the alloy is fighting with itself. You know, am I face-centered cubic, am I body-centered cubic, am I hexagonal? And this confusion about what the crystal structure is to be leads to quenching and the disorder of a liquid state, and preventing the formation of grain boundaries, dislocations and so on.

So I want to show you one example besides golf clubs. Dave, could we cut to the document camera here? Get this thing down.

So this is a-- I'm not endorsing the product at all, but you know, this is one of the companies that makes, this is SanDisk, I think. And they make these flash memories. This just looks like another piece of metal, and in fact, it's very disarming, because they call this model the Titanium. Well, it has about 13% titanium. The interesting thing here, what's so cool about this, this is bulk metallic glass. And what's attractive about the fact that it's bulk metallic glass is, that it can be shaped by casting, from the liquid state to very, very fine precision.

So you see all of these slots and everything, and on the side, all of this kind of stuff, and on the end. All of this is done by casting from the liquid state, in one operation. And this is a clam shell. There's two pieces here. I don't know if you can see, but there's two pieces that have been sandwiched together. You can see on the edge there. And the impact that has on manufacturing costs is phenomenal, because normally you make the basic shells, then you have to drill, and you've got to auger out, and so on. This thing, one step operation, including the labeling. There's no subsequent processing.

And this is done by a company out in Michigan called Liquid Metal. And they've licensed the technology and so on. And again, I'm not trying to make a commercial thing, but I'm just trying to show you that these ideas of changing properties for engineered materials, you know, are around us everywhere. And this is relatively recent. Bulk metallic glass. Fantastic example of structure property relations. OK.