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PROFESSOR: So collective knowledge got us a bunch more points. So the rules for significant figures are on the back page of the handout from Friday. And so we want to think about how many are after the decimal point here. So there are three after the decimal point, which gives you three here in your answer. Log significant figure rules-- yes.

So in base, and some in chemical equilibrium, which are all kind of the same thing, you can have subtraction and addition, then multiplication and division, and then end your answer with logs-- three significant figure rolls in one problem. Yes, it's coming. So you want to get those get those rolls down.

OK, so today we're going to talk about solubility. And this is really a direct kind of growth out of thermodynamics and chemical equilibrium. You're going to be seeing a lot of the same ideas in solubility. And then at the end of the class we're going to start acid-bases.

So far, we have been discussing mostly pure substances, and that is all changing right now. Because most substances are actually mixtures. So most of the time, you have two things mixed together. So mixtures-- you have a homogeneous mixture of something, something's dissolved in something else, and a solution is a homogeneous mixture.

And so in your solution you have a solvent, which is the thing that is dissolving the other thing, and the other thing is the solute. So the solute is any dissolved substance in a solution, and the solvent is the substance that does the dissolving. And water is a great solvent. One of the most common solvents is water. So when you have your solute in your solvent and it's nicely dissolved, then you have a solution.

So let's look at examples of things that dissolve in other things, and first we're going to talk about NaCl, common table salt, dissolving in water. So any NaCl is held together by an ionic bond and it forms crystals where you have these beautiful arrangement of our sodium plus and our Cl minus. And a polar solvent, like water, will, what's called, hydrate the ions and pry them away from the surface.

So if we look at this picture, and we have our sodium and our chloride surrounded in our salt crystal, we have water, which is red with those two little white dots, which are the hydrogens on the water. And so we have our bent geometry for our polar water molecule. And the water is coming in, and it's hydrating the ions.

And so here, you see the edge of the salt crystal, and now the water is kind of pulling one of the ions apart. And here you see the ions are coming out of the salt crystal and dissolving in your solution. So a polar solvent like water can just pry that crystal apart.

So stirring can speed up this process. It doesn't often change the properties. It doesn't make things more soluble. But it will speed it up, because if you stir it, you're going to get more of that water having access to the edges of the salt crystals, and helping to pry apart and hydrate those ions so that they solubilize.

We have an equilibrium expression for solubility, so we're just following right along with chemical equilibrium. And so we have our solid NaCl going to our hydrated ions, our Na plus, that was pulled out by water, and our Cl minus. And this in here, it says aqueous, abbreviation for aqueous, so we have our dissolved ions. That's how we would interpret that. And S here as for solid.

So we've also not paid much attention to phase of things at this point-- a little bit when we were talking about increasing entropy. We were talking about gases going to liquids and solids, and vice versa, and predicting the change in entropy for those processes. But now we're going to spend a lot of time paying attention to the phase. And so solubility, something solid, going to its aqueous ions.

So we can write an equilibrium expression for this. And it has a special name-- KSP, SP stands for Solubility Product. And so KSP would be equal to the concentration of sodium ions and the concentration times the concentration of chloride ions. And equilibrium constants are products over reactants. We don't have our reactant in this equation because it is a solid. So it doesn't appear in the equilibrium expression. So our equilibrium expression, which here has the special name of KSP, is just those ions in solution, the concentration of each ion times each other.

All right, so let's have a little practice with writing KSPs. And so we have a clicker question on that. All right, 10 more seconds.

Great. Yup, so again, we don't want to have the solid in the expression, and we need to remember the stoichiometry, always need to remember the stoichiometry. OK, so they're solubility product.

OK, so now let's think about something that is not ionic. Let's think about glucose. We've talked a lot about glucose. Let's think about glucose dissolving in water.

And here I have a picture of two beakers, a beaker where it's clear, and a beaker where there's a lot of glucose sitting on the bottom. And so we can think about the solubility here. So how can this dissolve? It can't form ions. It's not made up of ions like sodium chloride. So how does it dissolve?

Well, it can dissolve, again, water molecules-- water's amazing-- water molecules form hydrogen bonds with the glucose and pull one of the glucose molecules that is at the edge of the solid piece of glucose, pulls it out into solution by hydrogen bonding to it. So again, it's solubilizing the glucose that's in this solid form by interacting at the surface and prying layers of glucose molecules off by hydrogen bonding to them.

Luckily, you know all about hydrogen bonds, so just to do a little clicker practice, why don't you tell me what kind of hydrogen bonds glucose is capable of forming if it is, in fact, capable of forming. But I kind of gave away one of the answers here. 10 more seconds.

All right, good. Zero put four. That's awesome. You were listening to what I was saying. Yes, so that is correct. And if we look back at the molecule for a minute-- so it's a hydrogen bond donor because of these OH groups all along here. And so OH, there's an electron negativity difference of greater than 0.4, so it's capable of being a hydrogen bond donor.

But this double bonded O here, it's not a complete Lewis structure. It's missing its lone pairs. But it has lone pairs on that oxygen, and that could be a hydrogen bond acceptor. So we have hydrogen bond donors and hydrogen bond acceptors in this molecule, and water can also be a hydrogen bond donor and acceptor. It has two hydrogens that can form hydrogen bond. It also has two lone pairs, which gives it its bent shape. So it can be a donor and acceptor. So it's capable of interacting with glucose and pulling that solid glucose into solution.

So if we look at these two pictures, this could be glucose [INAUDIBLE] in solution. You can't see any glucose, but here you see a level of glucose at the bottom. And a solution is considered saturated when all of the solvent has dissolved as much as it can, but a little bit of

undissolved solute remains. So this over saturated. Often it's just saturated when you have just a little bit more than can be dissolved. You've gone past that point. You can't get any more dissolved in that volume of water. This has a pretty large excess.

So sometimes when you get your solution, you get your solution clear, your glucose has dissolved or whatever it is you're working on has dissolved, and then you maybe add a little bit too much, and it all crashes out of solution again, you have the precipitant just coming out. So undissolved solute, another name for that, the name that's used more often, is precipitate. So it precipitates out of solution if it has too much in it. So if you are not part of the solution, you are part of the precipitate.

That's my t-shirt. OK, so dissolved and undissolved solute-- they're not doing nothing. They're in dynamic equilibrium. Just like all other kind of chemical equilibrium, there is no net change, but the process is still going forward and back. In fact, the rate going forward is equal to the rate going back. The same is true here. The dissolved and undissolved solute are in dynamic equilibrium with each other.

So how much can you get in there? How much solute can you get into your solvent? And that depends on the particular substance and its molar solubility. And molar solubility is defined as S . Either little s or a big S . I've seen it both ways in textbooks. So the molar solubility, S , is the molar concentration in that saturated solution, where you've put just a little more in than can be completely dissolved. And so that represents the limit of the ability of that solvent to dissolve that solute, that particular compound. And its units are, perhaps unsurprisingly given its name, is molar, moles per liter.

So molar solubility is related to our friend K_{sp} , but it's not the same thing, or at least most of the time. I think none of the time exactly the same. So when you're talking about the molar solubility of either ion, you're talking about that concentration of sodium plus or chlorine minus. So you're talking about the moles per liter that can be dissolved in that particular amount of solvent or kind of solvent. And so those concentrations are the molar solubility.

And again, our K_{sp} is going to be equal to the concentration of the sodium in solution and the concentration of that chloride that's dissolved. So in this case, the relationship is that K_{sp} would equal the molar solubility squared, the molar solubility of this times the molar solubility of that. So if you know one, you can derive the other, and you can do that on a problem set, in particular. So those are the definitions of those terms.

So molar solubility, how much of something dissolves in another, whether it dissolves it all will depend on, again, the nature of the material and the nature of the solvent. Are they miscible? Is there a way, like water, getting in there and forming hydrogen bonds, for example.

And this leads to a rule that a lot of people tend to know, which is like dissolves like rule. So if it's a non-ionic substance, then you need to pull it out of the solid by hydrogen bonding, if that material has nothing to hydrogen bond to, if it's completely non-polar, water is not going to be able to solubilize it. So polar things, polar liquids like water, are generally the best solvents for things that are ionic, like salts, or polar compounds.

So it doesn't have to be a salt. It can be a compound made of carbon, but it needs to be a polar compound so that the water can get in there and form those hydrogen bonds. So you can see that knowing what is capable of forming hydrogen bonds can be really useful to think about what's going to be dissolved in what other type of material.

So non-polar liquids, like hexane, for example, are better for non-polar. So non-polar like dissolves likes. And so that's why people go to dry cleaners, because you don't want to use water to wash certain things. You want to be dry. You want to get your non-polar stains out.

So this is very important. There's a number of applications of these principles. This is important in the pharmaceutical industry. So we talked about some of the molecules that are used as pharmaceutical, in terms of being polar and non-polar, and vitamins the same way.

So when you're designing a molecule that you want to get into the body and react with a target, if you design something that is really non-polar, the human body-- there's a lot of water parts. And it's not going to necessarily get to where you want it to go. But if it's too polar, it might just get washed out. So you want the right amount of polar non-polar to stay in the body long enough, but also to get to where it needs to go.

So a lot of people who are designing molecules to treat disease are very concerned about, can we make this molecule more polar? Can we make it more soluble? It hits our target beautifully. It really destroys that enzyme. It would be a fantastic chemotherapeutic agent. But we need to figure out how to make it get into the cell that it needs to target.

And of course, so if you're going to go into drug designer medicine, you care about this. If you're going to become a parent, you care a lot about cleaning. And it's a daily event. How am I going to get this stain out of my child's clothes? Every day this is a question. So this is

important.

All right. And one other example in the long of cleaning-- I just want to share with you a short story about a chemist, Robert H. Black, and a life altering event that happened to him. So one day, Mrs. Black said to Mr. Black, clean the bath tub. This was an unprecedented event in the Black household.

So Robert Black went in to clean his bath tub, and it was really hard. And he scrubbed, and he scrubbed, and he scrubbed, and he scrubbed. And he was a chemist, so he knew what kind of chemicals you would need to clean a bath tub. You want to have things to dissolve your likes, so you want to have your polar and non-polar. You want to have a chelating agent to pull the heavy metals out of the tub scum, a surfactant, to make them bead up so you can wash them away, alcohols, to remove sort of the more greasy kind of stains. So he knew all of this.

But he realized that if you didn't apply cleaner on a regular basis, the tub scum got so thick and so nasty, that the cleaner couldn't penetrate the scum, and you need surface area. These things work by dissolving out. They touch the surface. So you need to have a surface.

So he had this idea that instead of having this tub scum build up so much that it was a real problem to clean it, that you could take all of these things that chemists knew would be useful and package them in something that was a daily cleaner. So he advertised these things that, every time you take a shower, you just spray the shower or the tub, and then you never have to scrub your tub again. Because you do a little bit every day, where there's not a lot of surface, so it gets it right off, right away.

And Mr. Black and his wife never had to clean their tub again, because this resulted in sales of about \$70 million per year. And it's important to point out that he wasn't using anything new. He was just packaging his chemicals for daily use, rather than, say, for a weekly or monthly use.

So I think there's a couple important lessons from this. One, it's always important to clean your bathroom. Two, you never know where chemistry knowledge is going to come, what life altering event will cause you to realize that you have in your mind chemistry knowledge that can make you \$70 million a year. And when that life altering event occurs, remember that I take cash and checks and stock options.

I added the last one. I thought, cash and checks-- I should be more flexible. So I'm also going

to take stock options. And this is why I teach you all the fundamentals of chemistry, cover everything that's really important for you to know, because then if you use any of it, you've learned it from me. So just keep that in mind. One never knows what life event is ahead of you.

So what about gas solubility? We talked about solids. Now let's talk about gases. So whether a gas is going to be soluble is going to depend on Henry's Law, or we can find out about it solubility. So a solubility of a gas-- we're going to call that little s , that's our solubility-- is directly proportional to the partial pressure of the gas and a constant called Henry's Constant. And that depends on the nature of the gas and the solvent and the temperature.

So let's think about this rule in this plot in a clicker question. All right, just take 10 more seconds. Awesome. That is correct.

So let's just take a look at that. So one of the clicker questions, which is kind of getting you to read the graph, and so it was asking, say at 0.5 atmospheres, it said oxygen is more soluble than helium. This is molar solubility versus partial pressure. At point 0.5, sure enough, oxygen is more soluble. So that was just reading the plot.

The other one was just interpreting Henry's Law again, that solubility would increase as partial pressure increases. You can see that from the equation. But you can also think about why that's true, and why it's true is the answer to the three, that the solubility of a gas is proportional to its partial pressure.

An increase in pressure corresponds to an increase in rate at which the gas molecules strike the surface. And that makes them more soluble. So again, solubility really has to do with getting at that surface. If you get at the surface, then you can dissolve your material.

All right, so why should you care about the solubility of gases? And I'm going to give you an example. This is another in your own words, so we'll watch the video. And I think tonight there's some kind of big climate change thing. I've seen fliers around. I haven't paid enough attention to what's going on.

But climate change is certainly a very hot topic, if you'll excuse that right now. I didn't really mean it. It just kind of came out. But CO₂ is a greenhouse gas. It's a big problem.

And so a number of researchers here at MIT are thinking about ways that you can capture and store it somewhere, get it out of our atmosphere. Other people are thinking about ways

that you can change industrial processes to make less CO₂. There's a lot of research going on.

So today you'll hear from Hector Hernandez, who had a Ph.D. in chemistry from the chemistry department here at MIT, did his post-doc here at MIT in chemical engineering, and is now a professor of chemical engineering at Masdar Institute in the United Arab Emirates. So this is one of the MIT satellite universities that are popping up all over the world.

So Hector was born, I think, in Honduras, and then lived in Florida, ended up in MIT, and now he's at the United Arab Emirates. So that's just another example of, one never knows what's going to happen to you. All right, so you can hear from Hector in his own words.

So Hector's personal video's online. I think it's a fun one to watch. There's a couple things that are really interesting about his personal story, including the fact that as he mentioned in past life he did some construction, he started undergrad at age 30, I think, where he was basically building houses and fixing cars and he realized that his back might not survive this being his permanent career.

So he decided to use his brain instead of his back. And so started undergraduate, now he's a professor. So it just shows there's a lot of different paths to success.

All right so CO₂-- big problem. We were trying to use, in that case, he was interested in turning it into biofuels, they were interested in ways to store it. You care about solubility of gases and you care about Le Chatelier's principle of driving things the direction that you want to make the products you want.

OK, so let's think more about these factors that affect solubility. And one thing that's very important, for sure, is temperature. So temperature-- most substances dissolve more quickly at higher temperature, which is often what you want. But it doesn't always mean if you increase the temperature that you're going to make it more soluble. You may just make it dissolve faster, but not actually change the end product.

Some things are more sensitive to temperature than others. So most gases, for example, are less soluble in warm water than in cold water, but with solids, it's much harder to predict what effect temperature might have on their solubility, even though for many things it will make it faster.

So let's think now about how to drive a reaction, and what factors are involved, and what's favorable and what's not favorable. And when we're talking about those things, we're going to be back to our thermodynamics, back to enthalpy, entropy, and Gibb's free energy.

So all these have little special sub names. So when we're talking about delta H and we're talking about solutions, things dissolving, we're talking about delta H sub sol, for solution, or if you could think of it as solubility. And one point that I'll make-- a lot of times when people are learning a new field, they're like, oh, there's so much to learn. But you get to some point, everything is just kind of like a subtle difference in something you've already learned.

So if you already learned about delta H, this is just a slight modification of what you learned. You don't have to learn a whole new thing. So that's one of the good things about the course. You start recognizing, I already pretty much know this. I just need to add a little sol to the end.

So delta H of solution can be measured. You can measure it from heat released when something dissolves, or measure it by the heat absorbed and at constant pressure. And so the sign of delta H sol will tell you about whether heat is released or heat is required when something dissolves. So a negative enthalpy of solution tells us that heat is released when something dissolves.

And many of you may have just experienced this. If you're mixing something together and you're holding the container, and all of a sudden it heats up, then you know delta H sol is a negative value. And of course a positive value tells you that that energy is absorbed, and sometimes things can get very cold when they're dissolving.

So you already kind of knew that that negative delta H tells you that heat is released, and positive delta H tells you that heat is absorbed. So this is basically the same thing that you already learned. It just applies to things dissolving just the same as it does to any reaction.

All right. Now, suppose we want to know whether the reaction is going to be spontaneous at constant pressure or temperature. If we want to know whether it will dissolve spontaneously, what am I asking about? What term do I want to know? I want to know about delta G. I sure do.

Delta G tells us whether things are spontaneous or not. It does with thermodynamics, it does with solubility. Delta G is to predictor of whether something is going to be spontaneous or non-spontaneous by the sign of delta G.

So entropy-- don't want to leave out entropy. Never leave out entropy. My t-shirt's still unaccounted for, after they got back to Massachusetts, they left for New Jersey and Cincinnati again. Last time I checked, they were still in Ohio. Entropy.

So since disorder typically increases when a solvent dissolves, typically, entropy should increase. And there's a little star, and we'll get back to the star, because it doesn't always increase. But typically, it should increase.

So if we're looking at these pictures here, over here you have your nice molecules all lined up in your solid, and it's going to then dissolve. And you can see that when it's dissolved, that's a lot more entropy over there. There are a lot more freedom moving around. This is more constrained. So typically, entropy increases when things dissolve.

So if ΔH is negative, and ΔS increases when a solute dissolves, then what do we expect about the dissolving process? And that's a clicker question. Yeah. So most people have, so we'll take 10 more seconds.

So let's look at both of them, because we're going to do this one in a few minutes. So let's just continue with our notes, and we're going to come back to that one. I don't know. Can we just leave that one up, maybe for a minute? I don't know how long it was going to take to me to get there.

All right, so when we're talking about this-- we'll just keep things in the notes and we'll come back to that one. So if this is negative and ΔS is increasing-- so if this is negative and this is positive, then you're going to have a spontaneous process here. So if you can put in your notes that this should be spontaneous under these circumstances.

Now let's continue on and think about getting around to the next one. So in some cases-- I don't know, hopefully people can see this-- in some cases, entropy of the system is actually lowered when something dissolves. And this is because of what's known as this cage effect. If you have water molecules, when something dissolves, sometimes order around the thing.

And so the water entropy is determining the process. And have this new order because of the water structure. So this can change. So it's not always the case that entropy of the overall system is going to increase.

So here, even if this is a negative value, ΔH solution is negative, ΔG might be positive.

It might not be a spontaneous system. And so the cage effect is why some things that are hydrophobic, just you're having a hard time dissolving them, even if they have a negative enthalpy, even if you would just look at the negative enthalpy and predict that it should be spontaneous. Because even if this is negative, if ΔS is also negative because you have more order due to the water molecules, then the overall term can be positive. It would depend on the magnitude of these and on the temperature.

This is actually more slides than I remember. Before we get to the next-- oh, this is the last one. OK, so when gases are dissolved in a liquid, there is much less freedom. Gases not dissolved can be anywhere. But when they're in a liquid, then there's much less freedom. And so the entropy then is going to be negative, and the solubility will decrease as the temperature rises.

And so that brings us then to our question about ΔH of solution being positive. And now we can look at the answer to that. Now I guess we can go maybe to the other slide. So that was the question that you had here, and I've just put up the answers.

So here, ΔH is positive. And so we have positive minus $T \Delta S$ again. We weren't told anything about ΔS in this particular. Just ask what if it's positive. And so for the first one, it said dissolving is never spontaneous. And that isn't necessarily true, because you don't know what ΔS is.

Dissolving is only spontaneous if $T \Delta S$ is positive and larger than ΔH solution. And that was the correct answer. If this is a big term here, it's larger than that term, and this is a positive value, then you would get a negative ΔG , and it would be a spontaneous process. If we look at number three here, dissolving is only spontaneous if this is negative-- that does not help us at all. And the rate will be slower.

ΔH is not going to tell us anything about rates. Rates are determined by kinetics. Temperature can affect the rates, for sure, stirring can affect the rates for sure, but ΔH being positive is not telling us about the rates.

So you'll see in this particular unit, when you're thinking about solubility, you're thinking about equilibrium expressions, especially equilibrium expression K_{sp}, you're thinking about partial pressures again, you're thinking about effects on the solubility that have to do with temperatures, you're thinking about ΔH , ΔS , and ΔG . So it's really an outgrowth of thermodynamics and chemical equilibrium, but you're just applying, really, what you've already

learned to thinking about a solute dissolving in a solvent. So that's one of the things that sets really great about the course and the next couple units, is that everything's very connected.

So we can just briefly introduce you to the next unit, and we're going to be talking about acids and bases now for several lectures. And I have to say that this is one of the units when we get to kind of acid-base titrations that MIT students seem to struggle with. So we're going to slow this down and really go over it, and have you be awesome at acids and bases.

And I'll mention that one of the reasons why I spent time on solubility and acids, bases, because these are topics that are really important for medical school, and I know a lot of you are not pre-med, but I want everybody in this class to have that background that they could go to med school if they wanted to, or they could just advocate for their own health with a doctor who doesn't know about acids and bases. And I'll tell you a story about that a little later.

Anyway, OK, so acids and bases-- we're just going to some definitions. So the simplest definition of this is that an acid is a substance that when dissolved in water, increases the concentration of hydrogen ions, H plus. Whereas a base is a substance that increases the hydroxide concentration, OH minus. So there are acids and bases that definitely fit this description, but this is a very narrow description of acids and bases.

The next one, the Bronsted-Lowry, is a bit broader. So an acid is something that donates a hydrogen ion, H plus, and a Bronsted-Lowry base is something that accepts a hydrogen ion. And this is really the definition we'll be spending the most time with in the class.

So let's look at some examples of this. So here, we have an acid. And if it's an acid, it's going to be donating a hydrogen ion, and it's going to donate it here to the water. The water acts as a base in that it accepts the hydrogen ion. When it accepts the hydrogen ion, it has one extra hydrogen ion, so it's H₃O plus. And when the acid loses its hydrogen ion, it becomes this base over here, the same molecule minus the hydrogen ion, so now it has a negative charge.

And so you'll will see hydronium ions quite a bit, which is H₃O plus. That's really the more accurate form, rather than just writing H plus somewhere. So that's the kind of true nature of things.

So let me just show you a little animation of this happening. I think it's kind of cute. So here we have our water molecules and we have our acid. It donated a hydrogen ion to these, and then another water came and stole it away. And so there's our H₃O plus.

And so in solution, you have this exchange of hydrogen atoms. The acid is donating, the base is accepting. And as they donate and accept, they become different molecules.

So it gives rise to this idea of conjugate acid-base pairs. So here you see that this acid is paired with this base over here. They're the same, except that one has the hydrogen ion and one does not. And then the other pair is here. It's another acid-base pair. We have water and hydronium ion that also differ by H plus.

So every time an acid donates a hydrogen ion or proton, it becomes its conjugate base. Every time a base accepts a hydrogen ion or proton, it becomes its conjugate acid. So the conjugate base of any acid is the base that is formed when the acid has donated a hydrogen ion or proton. The conjugate acid of a base is the acid that forms when the base accepts a hydrogen ion or proton.

So let's take a look at one more example. If this over here-- is this acting as an acid or base, this molecule here? What do you think? You can just yell it out. It's acting as an acid, right? This is acting, then, as the base.

When this base accepts the hydrogen ion, it forms its conjugate acid. And this then forms its conjugate base, which differs by H plus. So why don't you try one of these, then, on your own? 10 more seconds.

OK, so we can go back to that over there. So you most people got this right, and so you're looking at what's acting as the base and what's acting as the acid. Again, the base is going to be accepting a hydrogen ion. So this is acting as the acid. This forms its conjugate it and this. And quickly, with the idea of something that's amphoteric, which is molecule that can act as an acid or a base. You just saw some nice examples of that.

And finally, just one last definition for acid-bases. And we'll just put this up and that's kind of the end. So the final definition, the Lewis Base, donates a lone pair, whereas a Lewis Acid accepts such electrons.