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3.091SC Introduction to Solid State Chemistry, Fall 2010  
Transcript – Session 26

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PROFESSOR: So a couple of announcements. Weekly quiz Tuesday. And also on Tuesday, I want to draw your attention to the event in the slide. We have a poster here for a lecture that will occur right in this room, at 4:00 on Tuesday. And it's entitled the Wolf Lecture. The Wolf Lecture was established here about 30 years ago in honor of Professor John Wolf. John Wolf was an antecedent of mine. He was the person that invented 3.091. And in 1961, he dared, as a metallurgist, to launch a variant of freshman chemistry. And you're the beneficiaries of John Wolf's initiative.

And he also was a spectacular teacher, quite a showman. And in his honor, they instituted in the Department of Material Science and Engineering, the Wolf Lecture, which, as the poster says, is the entire community is invited to attend, but it's geared towards freshman. So this is a lecture that the rules are. Talk about whatever you want in terms of material science and engineering, but make it entertaining, and make it engaging and accessible to freshmen.

You should go to lectures. If you can't go to this one, then by all means, go to other seminars. If all you do when you come to MIT is go to class, you're missing out on some of the richness here. We have all sorts of people coming through here every day. And you can go to these seminars, you can learn a lot.

You might say, well, I'm just a freshman, I'm not going to understand everything. I go to these things. I don't understand everything. But I learn something, because the first few minutes of the lecture, if the speaker is any good, he or she is going to set up the topic for you. If you follow the first five minutes, you'll have something that, you know, gets you oriented to the topic.

And then the other thing, the other reason to go-- you see this on the poster-- room 10-250, reception immediately following. That means there will be refreshments! Food, for that, you know, pick-me-up in the late afternoon. So you go to the seminar, you know, sometimes they have refreshments before the speaker. I'm not going to tell you have to go into the seminar, having eaten the food and partaken of the refreshments. You didn't hear me say that. But anyways, there's always food around here. Go to this one. I think you'll enjoy it.

And the speaker is Professor Michael Rubner. He's a faculty member in course 3. An excellent teacher. As you see, MacVicar Faculty Fellow, which means he's been acknowledged as a good teacher. I think you'll learn a lot. And he's talking about nature-inspired, so biomimetics, how we see things in nature and then mimic that design in advanced material science.

OK. Enough said. Let's get on with the lesson. Last day we started looking at solutions, and we recognized that bonding is the key to understanding, and it's encapsulated in that catch-all phrase, like dissolves like. And towards the end, we talked about  $K_{sp}$  as a metric that helps us understand common ion effect. Common ion effect, again, if I tell you you have, say, 100 units of sodium chloride that can go into solution, you would say, that's the solubility limit.

But then if I tell you, I've got a solution that already contains 25 units of sodium chloride, that's a no-brainer. You've only got another 75 units to go. Now I say I've got potassium chloride in there. So now you stop and think, wait a minute. It's not sodium chloride, but it is a chloride. How do I think about this? Common ion effect through  $K_{sp}$  helps you reason through it. It's when you have more than one solute, and one of the constituents of the solute is already present.

So today I want to talk about a subset of solutions, and in particular, I want to talk about acids and bases. And this is important, not only in materials processing, but we're going to have to understand this if we're going to go forward later and talk about biochemistry.

So, you know, they're around us everywhere. You know, you probably got up this morning, you washed your hair with a pH-balanced shampoo, maybe had orange juice or grapefruit juice with citric and ascorbic acid. Your radio is powered by zinc alkaline batteries. I started my car, it's got the lead acid battery in it, and electricity for all my appliances came from coal-fired power plants, spewing out  $SO_2$ , turning out acid rain. So we're off to a good start! It's Friday.

So now we want to go back and understand this from the beginning. So we're going to start with a history lesson. And the history lesson starts in ancient times. Acids were known all the way back in early times for processing of food and materials. So who among us hasn't eaten something that has been pickled? Pickle means to have been processed in acid solution. In fact, the word acid comes from the word *acidus* in Latin, and *acidus* means either sour or tart.

But the modern chemistry of acids and bases starts with Lavoisier in France in 1779. And I'm going to be naming many scientists from different countries today, so I'm going to use the international symbol. You know, these ovals that you put on the back of the car, so now if you see a car with this on it, you know it's a French registry. So he's probably got a Peugeot, and he's driving around with his Peugeot.

And what Lavoisier said, in trying to understand acids and bases, is-- it's a really interesting story. He said that oxygen is present in all acids. And why? Because he spent most of his career studying combustion, so he was very concerned about oxygen.

And the interesting thing is that oxygen, the name of the gas, oxygen, actually comes from the greek *oxy*, which means sharp, and, you know, the particle *gen*, as in to generate or to be born. OK? So it's interesting that this gas is named incorrectly. It's named for an attribute that is ascribed to acid, and it's wrong. And it's in other languages, too. The word oxygen translates into other languages as meaning something sharp, and it has nothing to do with it.

But while we're on the topic of Lavoisier, Lavoisier did study oxygen. And there was an intense rivalry between Lavoisier in France, Joseph Priestley in Britain, and

Scheele in Sweden. And all three of them were working simultaneously to study combustion and understand oxygen.

And here I've got a very nice image. This is a portrait of Lavoisier with his wife. And it's hard to see. If the lights were a little bit dimmer, you'd see-- notice here, you see all of this chemical apparatus. There is bell jars, and various glass apparatus. His wife was his partner in the laboratory. She was unique among French women in that she read English. And in his rivalry with Priestley, he relied on his wife in order to read Priestley's writings. So they worked together. She even helped him in the laboratory. They married at the time he was 27 and she was 13, and they were-- what are you so shocked about? It's France, and it's 1779! Get over it! Anyways, she helped him a lot, and we'll say a little bit more about that later.

OK. So now let's go on to the next part of the history lesson. So so far, we've got one explanation, and it's wrong. So let's go to the next one, and we'll go to Britain. Sir Humphry Davy in London in 1810. So we'll put GB here, and he's driving around in his little Jaguar, I suspect. And he said something that was correct. He said that it's hydrogen present in all acids. And that was pretty much it. He was a great scientist, did some very good work, but really didn't do anything quantitative here.

So for the quantitative stuff, we have to wait for almost the end of the century. And we go up to Sweden again, to Arrhenius. And Arrhenius, in 1887-- so I'll give him a Volvo.

And he said that the acid is a substance that disassociates to produce protons. So the acid is defined as a solution that dissociates to give protons. I'm going to say H plus, meaning the hydrogen ion, or P plus, and we're going to keep using the term proton. I'm not going to say hydrogen ion, I'm going to say proton. So proton in solution. So this is what he defines. And he further defines the base. He defines the base as the complement to the acid. And he says that the base is something that dissociates to give us hydroxyl. The base dissociates to give OH minus the hydroxyl.

And so now we've got this whole concept of electrolytic disassociation, which is what wins him the Nobel prize in 1903 for this thing. And then we saw last day how the addition of ions to water gives charge carriers. And so the presence of protons and hydroxyl is, in fact, the way we have any charge carried through water.

So up until now, when I said electrical conductivity, we were pretty much referring to electronic conductivity. But there's a second kind of conductivity, and we can have ionic conductivity. Ionic conductivity, as the name implies, is not by electrons, but by ions. And this is typically ions in solution. Ionic conductivity in solution, and a solution that is an ionic conductor is called an electrolyte. So we have electrolyte in our bodies, saline, about 5% chloride. We have electrolyte in batteries that are ionically conductive. And the term simply means, we have conduction by ions. And so it was the theory of electrolytic dissociation that won the Nobel prize.

So how does this work? So we can start with something like HCl gas. I'm going to dissolve it in water, and this will give me proton, H plus. And I'm going to write aq, meaning that it's dissolved in water, and the chloride ion, also dissolved in water.

And so this gives me an acid. This is a proton donor. And now let's look at something like sodium hydroxide. Sodium hydroxide at room temperature is an ionic compound,

so it is a solid, but it is soluble in a polar, hydrogen-bonded liquid, so H<sub>2</sub>O, to give hydroxyl aqueous plus sodium ion aqueous. So again, we see the dissociation.

And then we can have, from here, a neutralization reaction. And the neutralization reaction is simply reconstitution of the solvent. So neutralization, another way to think about it, because we're not going to be confined to water by the end of the lecture, neutralization is simply a reaction that results in reconstitution of the solvents.

So the solvent, in this case, is water. So how would we reconstitute water? We combine proton with hydroxyl. So let's do that and see the result of that reaction. So if I take, and run it in the vertical direction, proton plus hydroxyl, we'll give water again-- let's give H<sub>2</sub>O liquid-- and now you can see Na plus Cl will give me NaCl, aqueous dissolved.

So this is what you probably learned in your high school chemistry, that acid plus base can give you salt plus water. So you see all of this resulting from just the simple Arrhenius definition.

So this is good. We've got off to a decent start here with Arrhenius. But then the theory has its limitations, as they all do. And how do we discover the limitations? With some new data. So let's look at some data.

So it had been known for a long time that ammonia, when it's dissolved in water, can act as a solution capable of neutralizing an acid. So if ammonia dissolved in water neutralizes an acid, then this must be a base. But look, there's no hydroxyl here. So the Arrhenius definition of base is inadequate to account for this.

So let's just get that down. Ammonia, which you know is a gas at room temperature, will neutralize acids. But no hydroxyl present. So something's going on here that we can't account for by the simple Arrhenius definition.

So to get us out of this conundrum, we had to wait until 1923. And two scientists simultaneously enunciated the same ideas. So I'm going to put them both down. 1923. Bronsted, who was in Denmark, and Lowry, who was working in the UK. Also 1923. And I'll give him a Jaguar as well.

And so the two of them proposed a broader definition to account for what's going on here. And what did they say? They said that acid-- they'll keep the same definition as Arrhenius. So an acid is going to be a proton donor. So that's good. Let's even put here, same as Arrhenius.

But now here's the difference. The base is no longer confined to hydroxyl chemistry. They call it a proton acceptor. And that's different. So hydroxyl-free.

Now, let's be careful here. If I propose this new definition, I can't throw out hydroxyl. So you've got to watch to make sure that by broadening the definition, we don't exclude hydroxyl. So the theory has to encompass what we already know, and then continue to encompass things that tend to contradict what we already know.

So let's take a look at what this gives us. So I'm going to write a broader equation here. I'm going to write this as the acid. So what do I have? I have every acid has to

have a proton in it, plus some residual. So I can rewrite the acid in this form. I'm going to react it with a base.

So according to this definition, this has to be a proton donor. And this, you're going to watch me on this one. This is going to be a proton acceptor. And we'll put some identities here. Eventually we're going to write this with ammonia in it, but let's just do the broad definition.

So what happens is, if this is a proton acceptor, on this side of the equation, it takes the proton from here. This is the proton donor. It gives it away, and we end up with a BH plus. So this proton acceptor has accepted the proton, leaving behind the deprotonated A minus. That's a nice little reaction.

But now, if you'd nodded off for the last 90 seconds, and then opened your eyes and said, well, he said acid is a proton donor, this thing can give up a proton. So OK, I'm going to call this thing a proton donor. And this is most certainly a proton acceptor. Look, it has accepted the proton. So this is going to be a proton acceptor.

So now I've got in this equation two proton donors and two proton acceptors. And they're linked. This proton donor, BH plus, is linked to B. So I'm going to put a little yolk over this one. And this HA, the original acid, is linked to this base, A minus. So I'm going to put a yoke over that. And the Latin word for yoke, to yoke, is jugere, from which we get the word conjugate. So I'm going to call these things conjugate acid-base pairs. And every equation has two. Because you've got a proton donor proton acceptor.

So now this is, follow the bouncing ball. If you want to understand acid-base chemistry, just follow the proton. Here's proton here, goes over here. Here's something deprotonated, now it's protonated. That's the rhythm here. So the whole thing is, acid-base reactions can be defined as a proton transfer reactions.

Remember we talked about ionicity and electron transfer in order to achieve octet stability? So we saw the whole life and times of electron transfer reactions. Now life and times of proton transfer reactions.

OK. And last thing I want to do, is to just make sure that we see the definitions. You know, all queens are female, but not all females are queens. So this one here, what's this? This is definitely, it's a proton donor. So it's an acid. So it's definitely an Arrhenius acid, because it's got a proton, and it's also a Bronsted-Lowry acid.

Now, what about this one? This is a base. It may not have hydroxyl in it. May or may not. So this is definitely a Bronsted-Lowry base, but I can't say for sure that it's an Arrhenius base, because Arrhenius has to be O minus.

This one here, what about this? Unless it's OH minus, this one here is, what? It's Bronsted-Lowry base. And this one here, this can be both Bronsted-Lowry acid and it can be an Arrhenius acid. So this is how we can differentiate them. OK, good.

Now let's go to the ammonia, see if we've got ourselves out of the conundrum so we can write now  $\text{NH}_3$ . And I'm going to say that this is ammonia that's already dissolved. So ammonia is already in aqueous solution, and it reacts with water,  $\text{H}_2\text{O}$  liquid, to do what? This is supposed to be a-- if this is a base, remember, this is the thing that we're trying to demonstrate. If it's a base, according to this, it's a proton

acceptor. So I'm going to stick a proton on this, and I'm going to get  $\text{NH}_4$  plus the ammonium ion. And how did I get the ammonium ion? I took a proton from water, leaving behind  $\text{OH}$ .

So can you see that how this thing works? By gobbling up protons, by becoming a proton vacuum cleaner, it takes protons out of water, leaving an excess of hydroxyl. And in effect, now we've got something that's tantamount to an Arrhenius base. But it all started off with this.

So now we can link these two. I'm going to yoke ammonium and ammonia as conjugate acid-base, and there is water and hydroxyl as acid-base pairs. So again, let's get the colors going. Here we've got Bronsted-Lowry-- the bases are always going to be in blue. Blue and base both begin with the letter B. So this is definitely Bronsted-Lowry base, but it's not an Arrhenius base. This is a Bronsted-Lowry base, and it's also an Arrhenius base. This one here, we can call this one-- in this case, it's a proton donor, so it's both an Arrhenius acid and a Bronsted-Lowry acid.

But look at this. You'd say, OK, I know what he's doing. Arrhenius, Bronsted-Lowry, Arrhenius, Bronsted-Lowry. This is Bronsted-Lowry only, this must be Bronsted-Lowry only. But look! This is a proton donor. It dissociates to give protons. So this is both Bronsted-Lowry and Arrhenius. Most people will miss that. We'll get to see, maybe, on a subsequent celebration, how many of you miss that. OK. So.

So now, let's go into the chemistry here. Because I said up here at the beginning of the lecture-- what is it-- bonding is the key to understanding. So what is it about bonding here that defines the Bronsted-Lowry base?

So I'm going to write this reaction in this way, now. I'm going to put-- here's the proton, which is coming from water. And I'm going to write that with  $\text{NH}_3$ . I'm going to use the Lewis structure. So, you know, Lewis structure looks like this, Nitrate has got five valence electrons, three of them are bound, and now I've got this long pair.

So what do we know about the electronic structure of proton? What does it look like? What's the Lewis structure of proton? How many electrons on proton? None. This is nothing. This is very needy. It's like the neediest friend you have. You know, the one that's always taking stuff from you, taking your emotional energy, giving back nothing? That's proton. That's the human equivalent of proton. So if proton wants to make a bond to form  $\text{NH}_4$ , proton is going to come over here and exploit both electrons.

So if this is going to be a proton acceptor, the only way it can be a proton acceptor is to have two unused electrons available. This is going to be a dative bond, agreed? Dative, because both electrons from the bond come from the nitrogen. The proton doesn't contribute anything.

So that's the hallmark. The proton acceptor axiomatically must have an available non-bonding pair. So wherever you see non-bonding pairs, wherever you see a compound that has this capability, it could serve as a Bronsted-Lowry base. We know that water, because it has hydroxyl in it, has to satisfy this.

So let's take a look.  $\text{H}_2\text{O}$  we can do similarly. Oxygen. It's got 6 electrons, 2 are in the bonds and we have 2 non-bonding pairs. So then when we attach proton here, we make something called hydronium. We make hydronium ion.

So it's a little fancier than just saying, I've got this naked proton with no electrons swimming around in water. In fact, it's more coordinated like this.  $\text{H}_3\text{O}^+$ , and while we're in the neighborhood, we might as well show. This is  $\text{sp}^3$  hybridized. We've got one, two, three, four orbitals. Hydrogen's on three. It's got a net charge of plus 1, and lone pair on the fourth side. So there's the structure of hydronium. And we can now write the equation. We can say  $\text{H}_2\text{O}$  liquid plus  $\text{H}_2\text{O}$  liquid gives me  $\text{H}_3\text{O}^+$  plus, plus  $\text{OH}^-$ .

So this is now the self-ionization or self-dissociation reaction. So now I can pair these as well. I can yoke these. I have acid-base pair. So this is acid here, and the conjugate base is water,  $\text{H}_2\text{O}$ . Hydroxyl, we know, has to be a base, and its conjugate acid is water.

So you see, in the same equation, same place, same time, water is acting as both acid and base relative to these two species. And so we call such a such a compound that acts as both acid and base, we call it amphipathic. Has two moods. You know, amphi, like in amphitheater. Have you ever seen a Roman theater? It looks like this from the top down. It's got all this, you know, like this, and all the people are here, and there's the stage up here. But if I make a theater in the round, that is amphitheater. Or as it's commonly mispronounced, ampitheater. 3.091ers do not say ampitheater, they say amphitheater.

So this reaction here is self-dissociation. Right? This reaction is self-dissociation of water. Or because we're forming ions, it's also called self-ionization. Self-dissociation or self-ionization of water.

Now, turns out that the chemical's power of  $\text{H}_3\text{O}^+$  plus and  $\text{OH}^-$  is very high. So this reaction doesn't go very far to the right. The amount of the dissociation is tiny, and to be specific, at 25 degrees C, the amount of, if you take deionized, deaerated water, absolutely pure and pristine. The amount of native  $\text{H}_3\text{O}^+$  plus and  $\text{OH}^-$  is on the order of one part in 10 million. So  $\text{H}_3\text{O}^+$  plus concentration would be 10 to the minus 7 molar. And obviously, from the stoichiometry of the equation, you get the identical amount of  $\text{OH}^-$ . Well, that's in the self-dissociation.

And so you have very, very few charge carriers, which is why high-purity water is a very poor conductor of electricity, even as an electrolyte. And that's, I've told you in the past, that could be one indicator of certain toxins. If you measure the conductivity of water and you discover it's abnormally high, and it's putatively supposed to be pure water, that's an indication that it's not pure water. There's some other charge carriers present.

So we can write a  $K_{\text{sp}}$  we analogy. And it's called the water ionization constant, which is the product  $\text{H}_3\text{O}^+$  plus and  $\text{OH}^-$ . And you can do the math. That's 10 to the minus 14 is the product. And you can use the common ion effect here. If I introduce some other acid, look at how this equation helps you the same way that  $K_{\text{sp}}$  did. If I have acid, in other words, protons donated from some other source, that means this number is going to be higher than 10 to the minus 7. If this number is higher than 10 to the minus 7, and the product must be 10 to the minus 14, this must be lower. So when I have,  $\text{H}_3\text{O}^+$  plus goes up, then  $\text{OH}^-$  must go down, and under these circumstances, we have something that is called proton-rich. And we call this acid, simply because the proton concentration exceeds the hydroxyl. And likewise for the other.

And so we can make a plot of this, and that's shown here. And all we've got is OH versus H<sub>3</sub>O<sup>+</sup>. And you can see that it's a right hyperbola. But it goes back to that comment that I made in the past about how you graph data. I don't know what to do with that, because it's curved. I can't tell whether the data are good or bad. So instead of looking at something like this, y versus x, I want to transform so that can get a straight line. Because then I can make a judgment about goodness of fit and so on.

So I need some f of x versus g of y to, quote unquote, straighten this out. And we have that, thanks to another Dane, by the name of Sorensen. Sorensen was the one that gave us another way to think about it. Sorensen, who in 1901, and he's got the DK on his-- he's probably got a Volvo, too. Or maybe he's driving a Saab.

So he was a biochemist at the Carlsberg brewery. Yes, they had biochemists, because they wanted understand the chemistry of beer production. What a concept. Having people that understand the technology of the business. So he was working at the Carlsberg brewery, and he decided to take this acid-base business and turn it into something that's much more readily recognizable.

And so he defined a concept called the chemical potential, which, if you like, is the reactivity, the chemical potential of hydronium. And he gave it the symbol. Lowercase p for potential, and uppercase H as, obviously, for the hydrogen ion. And he said, I'm going to make this a logarithm. So it's logarithm, and in those days, everybody was using slide rules, so it's log base 10 of the concentration of hydronium. And being a good engineer, he recognized since this starts off at 10 to the minus 7, the log of a number less than one is going to be negative. And who wants to deal with negative numbers? So you put a minus sign here. That way, pH normally is a positive number.

And now you can see the results of Sorensen's straightening things out for us. So now you go over a wider range, and you can see, you have nice straight line relationship, and then you can get data on there, and so on. And this is taken from your book, and it shows the pH values of some common substances. If you start here at neutral pH 7, you have milk, you have human blood, normal things that you would expect, fluids and so on, are hovering around 7. If you take some coffee, you're going to go into the acidic region. You see tomatoes down here at about 4. Wine, you'll see in the reviews of wines, they'll say it has balanced acidity and so on. Yeah, it's down around pH 3. And carbonated soft drinks, some of them get down to 2. Vinegar is wine that has spoiled. Vin aigre, which means eager. The Middle French eager meant impetuous, or tart, or something. So this is spoiled wine. And the pH changes. So by measuring the pH of wine, you can tell if it's changing or not. There's lemon juice.

Gastric juices in the stomach can get down to 1, pH of 1. But you want that happening only at one point in the digestive cycle. If you run around for long periods of time at pH 1, you will ulcerate, in other words, you'll puncture the walls. And if that's about to happen, you need to neutralize. So how do you neutralize? You go up with something that has a high pH.

So you can start with something like Alka-Seltzer, sodium bicarbonate at about 8.4, or milk of magnesia, 10.5. Why is it milk of magnesia? From last day, because it's not a solution, it is a suspension. The magnesia is in suspension. The magnesium



hydroxide. And that's one of those mandatory shake well before using, because all the magnesia is on the bottom, and you've got this almost clear, colorless liquid on the top. So you're just drinking water. Not going to help you if you've got stomach pain, but gastric juice is down here. If you're really desperate, don't reach for ammonia. You have to be patient. They have to work with milk of magnesia. OK. So that's the range.

So what else do we have here? Let's take a look.

So far we've been assuming that when we add acid to the system, we get 1 to 1 dissociation. So the next message that I want to give you here, is that not all acids are of equal strength. See, I could look up here and say, well, maybe the reason that the lemon juice is down it at 2 and the gastric juices are at 1 is simply a concentration effect. How much acid was introduced.

No, there's another explanation for it. And that is that certain acids don't fully disassociate. So for example, if we look at 1 molar HCl, hydrochloric acid, you look at 1 molar hydrochloric acid, that goes 100% into solution and gives us 1 molar H<sup>3</sup>O plus. So 1 to 1 correspondence between how much hydrochloric acid we introduce, and how much hydroxyl that we generate. So this is total dissociation of the HCl. And as a result, we call this a strong acid.

In contrast, let me show you a weak acid. So a weak acid is going to dissolve, but it doesn't dissociate. So there's really two steps here. First you've got to get the stuff in solution, and then once you get it in solution, it has to break apart. It's possible to go into solution and not break apart. In which case, you don't have the protons, but you've got the solution. That's not an acid.

So a weak acid would be, let's, in contrast, look at a weak acid. A weak acid would be something like acetic acid, which is CH<sub>3</sub>COOH. And this is for historical reasons. Normally, the proton that's going to dissociate is at the front of the formula, but this was written long ago, before people understood this theory. And that's the way you'll see acetic acid written. So really, this is the proton, and the CH<sub>3</sub>COO is really the acetate anion, Ac, acetate anion.

So we're going to put that into solution, like this. I'm going to put it into water, H<sub>2</sub>O liquid. So this is the salt out of solution, and all we're going to do is make it into the aqueous solution of same COOH, and I'm just going to write aq.

Now, if this were strong acid with impunity, I would write whatever the concentration of acetic acid is, I break it apart, and I get the full amount of the proton. What happens is that this, now plus H<sub>2</sub>O, gives me H<sub>3</sub>O plus plus the remaining acetate, which is CH<sub>3</sub>COO minus.

And now, here's where the weakness is manifested. The degree to which the acetic acid grabs protons from here, and then ends up being protonated, is very, very small. It turns out that in the case of 1 molar-- I'm going to write acetic acid this way, now. HAc. So this thing here is the CH<sub>3</sub>COO minus, all right? It turns out that in 1 molar acetic acid, we get only 0.4% reaction. 0.4% reacts and dissociates. So to give protons, it hangs onto most of its protons. So we can then represent this in the form of an acid dissociation constant. And that it looks like this. K<sub>a</sub> for acid. So on the right side, what we're going to do is make a mass balance here. We're going to take the product of the proton, the acetate divided by the undissociated acetic

acid. So we'll put  $H_3O^+$  plus concentration times the acetate concentration divided by the undissociated  $HAc$  aqueous.

So I'm trying to represent what the ratio is here. And instead of being one to one, it's 10 to the minus 5. Very, very weak. You get a little bit, but not much. Now, you could say, well, 10 to the minus 5, this is, just for reference, it's 100 times 10 to the minus 7, which is the  $K_w$ . So the point here is, if you put in acetic acid, you'll end up with 100 times the proton population that you would have had by just self-dissociation. So it isn't acid. It is donating protons. But it's not doing it a lot. So this is called a weak acid, because it's a poor proton donor.

And so we can then look at a comparison to, say, over here,  $HCl$ . Let's go back here, and we can write the acid dissociation constant for  $HCl$ , for the strong acid. And in that case,  $K_a$  over here, which is going to be the  $H_3O^+$  plus  $Cl^-$  minus,  $H_3O^+$  plus. In the case of  $HCl$ , we're going to get proton and chloride over undissociated  $HCl$  dissolved in water.

And that's 10 to the plus 6, which for all intents and purposes is infinity. You put in 1 molar  $HCl$ , you get 1 molar  $H^+$ . And look at the ratio. 10 to the sixth, 10 to the minus 5. There's a 10 to the eleventh relationship between the weak acid and the strong acid. And here's the cartoon that shows this strong acid, put in this amount, 100% dissociation, weak acid gives you small amounts of proton, and a very weak acid is imperceptible amount of dissociation.

And here's a table that quantifies it. So the strong acids up here with the  $K_a$ . This value of  $K_a$  has to be greater than 1, because it's saying that we're getting a lot of dissociation, the reactions moving to the right. And you have these numbers here. 10 to the ninth, 10 to the eighth, 10 to the sixth. Those are differences without distinction. If I say the ratio is a million to one, or a billion to one, for all intents and purposes, you have dissociation.

And then here are the weak acids. Look. 10 to the minus 3. There's phosphoric, hydrofluoric, and so on, all the way down. There's carbonic acid, 10 to the minus 7. So there's the list.

And just another cute demonstration of the relationship between bonding and acidity, the acid strength increases from left to right, and the bond strength increases from right to left. You know,  $HF$  is very strong. It's a hydrogen-bonded. Very tight  $HF$  bond. But what determines if it's going to be a strong acid or not? It's how willing  $HF$  is to give up its  $H$ . But its  $H$  is tightly bound. So oddly enough, in  $HF$ , you don't give up much of the  $H$ .  $HF$  is over here. It's less than one. It's a weak acid.  $HCl$  is a pretty strong acid. If you want to go heavy-duty,  $HBr$  and  $HI$  are even stronger acids, because they have a weaker hold on the hydrogen within them, so they are much, much more generous proton donors. So you can see that from there. OK.

So what's the takeaway message here? The takeaway message is that equal acid concentration does not mean equal acid strength. You have to be mediated by the  $K_a$ . Equal acid concentration, which means, how much did you dissolve? Does not equal acid strength.

And what's the reason? Because equal acid concentration, this is a function of solubility, whereas this is a function of dissociation. So many dissolve, few

dissociate. How about that? There's a nice tagline you can use. Use that at a party this weekend. Many dissolve, but few dissociate.

All right. Now I want to go very, very high. Big concept, all right? Last definition of acid-base comes from the United States. G. N. Lewis. Same G. N. Lewis who gave us the Lewis cross and dot structures, covalent bonding, didn't stop inventing. So we're going to put U.S.A., with a Chevrolet out in California.

And what did G. N. Lewis tell us? He said, I want to extend the Bronsted-Lowry concept. But you know, let me give you an analogy. Have you ever stood on a bridge and watched the traffic go? You see it starts from a stop sign or a traffic light. Light turns green, the first car pulls away, the second car pulls away, the third car pulls away.

The other way you can look at it is, when the first car pulls away, there's a car vacancy. And instead of watching the cars go from right to left, watch the car vacancy move from left to right. And the two are linked. And point of fact, if you're the fourth car from the traffic light, light turns green and you hit the horn, why? You can't drive. You have to drive only into a car vacancy, and it takes time for the car vacancy to get to you. When the rate of vacancy flux is not matched by the rate of car flux, then we have a collision, and then we exchange papers. So it's a mass transport problem.

So now what G. N. Lewis said was, instead of looking at this reaction as a proton transfer reaction, and looking at proton attachment, or proton acquisition, he said, why don't we look at this from the other side of the relationship?

And so he said, let's look at something like, for example, we've got  $\text{NH}_3$  here. So let's put the N with the 2 electrons. And we've been talking about this from the perspective of the bond being formed here through the acquisition of the proton. Lewis said, I can view this from the other perspective, and say, I'm going to view it from the perspective of the nitrogen. From the perspective of the nitrogen, this reaction represents the donation of the electron pair. A very high concept.

So this base is not about proton attachment. It's about donating an electronic pair. So let's get that down, because that's really good. So I'm going to say something that's a base looks like this. This is what a base is. It's a lone pair. This is electron pair, very high level base. And what's the proton give us? What we're doing, is we're talking about electrons and donation.

So what's this other thing in that same category? An electron pair can match up with an empty orbital. That's the only place electron pairs can go. They go to the empty orbitals. So electron pair is a base, and this is just a circle around nothing. OK? This is nothing. But it's a special kind of nothing. This is called a vacant orbital. And I'm going to call a vacant orbital an acid, in the most general sense.

So now I'm going to take an electron pair plus vacant orbital, and what did they react to give me? Covalent bond. You'd expect that from G. N. Lewis, because G. N. Lewis enunciated covalency. That's why you'd expect it from G. N. Lewis. So this is, vacant orbital plus electron pair gives covalent bond. Very high level. Very high level.

So what is a base? A base is now not just a proton acceptor. It's an electron pair donor, and the acid is an electron pair acceptor.

So now there's no chemistry here. No chemical identities. Which means, I can even go from-- I don't even have to be in solution. I don't have to be in a liquid. This could be a gas and a solid. Could be a gas plus a gas. So this is, like, Darwinian. You know, we've come out of the primordial ooze, and now we can fly, because we can talk about any chemical reaction we want. Any state of matter. It's fantastic. Absolutely fantastic.

So here, let me do one last color drawing. We want to do this one here. This is Lewis and the biggest concept. So we're going to go like this. Base like this. Base with its lone pair hanging out plus acid gives us-- three colors. This is great. We've got all this colored chalk, it's Friday, what could be better. All right. So now we're going to end up with A, B, there it is.

This is the Lewis concept. Lewis acid-base concept. In the broadest thing. Now I'm going to show you an example of how you can use this. I'm not going to stop here. OK, let's go.

All right. So we're going to talk about acid rain from burning of coal. You know, about half of the electric power in this country comes from burning coal, and coal contains about 1% sulfur. You can purify it of sulfur, but it takes money to do so. A ton of coal will give you about 25 million British thermal units, and that's the number in SI units and joules. So 3 tons of coal will give you 1 megawatt per day.

By the way, it takes about one gram of uranium to do the same thing. So someday, when you're sitting there as a policymaker, you've got a choice of 3 tons of coal or one gram of uranium, keep this fact in mind.

A 10 megawatt plant burns 30 tons of coal per day, containing a third of a ton of sulphur, which makes 2/3 of a ton of SO<sub>2</sub>. And SO<sub>2</sub> is a precursor to acid rain. Now we can reduce that SO<sub>2</sub> emissions by reacting SO<sub>2</sub> with a lime, CaO, according to this reaction, to make calcium sulfite.

And now I'm going to bring in this. Lewis. Oh, here's from your textbook, there's the scrubbers with the calcium oxide, and water missed, and so on, and eventually they trap the SO<sub>2</sub>. They do nothing to the CO<sub>2</sub>. So all the CO<sub>2</sub> is going up. So here's calcium oxide, which is a solid. It's lime. You know, stuff you sprinkle on football fields. And this is SO<sub>2</sub>, and it's got this structure with the resident bond double single. The oxygen here acts the way it did in the glasses, as a modifier. It goes in and breaks this double bond, and now we have three single bonds.

So we can look at this from Lewis acid-base. You know, calcium oxides, electron pair donor. If it's an electron pair donor, it's a base. So it's a base. And you know SO<sub>2</sub> better be an acid, or your theory is nuts, because SO<sub>2</sub> is a precursor to acid rain. So it has to be an acid. It's an electronic pair acceptor, which is what we said. It's an electron pair acceptor. So this is a Lewis acid-base reaction that is a gas-solid reaction. So we started with aqueous solutions, and we end up generalizing all of these types of reactions. So that's pretty good.

Here's a plot of acid concentration up in the sky, here. You're Here. Yeah.

Last thing I'll do, I talked a lot about Lavoisier and Scheele and Priestley. This is a play, if you've got the little bit of time this weekend. You might try reading it. This is

Carl Djerassi and Roald Hoffman, both Nobel Prize winners in Chemistry. Not the same year. They won independent Nobel Prizes, and actually speak to each other, and they collaborated on this play.

Here's the setup, the premise. The premise of the play is that the Nobel committee decides to give Nobel Prizes retrograde. Before 1901. You see, you can't get a Nobel Prize posthumously. You've got to do something great, and you've got to keep on living until you get the prize. So they decided they're going to go backwards, you know, maybe give prizes to people like, I don't know, Maxwell or Faraday or whatever.

And they decide, it should be simple in the old days. Because we didn't have all this dog-eat-dog competition in science, and big grants, and corporate interests. Should be simple. Until they hit the Nobel Prize for the discovery of oxygen. And then they hit the wall with these three different competitors. And so the story goes that the three competitors and their wives end up in Stockholm, and the interactions the take place.

And it's really fascinating, because you have Lavoisier, who was the political conservative but the chemical radical, Priestley, who was the chemical radical but the political conservative-- by the way, Lavoisier. You know how he died? He was guillotined during the French revolution. And people think it's because he was a tax collector. Not true. He was a tax collector. The real reason is Marat, who was one of the chief justices of the Jacobin terror, was also a scientist. And around 1740, Marat had submitted an article for publication, and it was rejected. And Lavoisier was on the editorial board.

And so sometimes when I get an article to review, and I have to give it a negative review, I think about this story. And sometimes, I will just say, you know, I'm really busy teaching 3.091 and I won't get to this on a timely basis.

OK, people. Have a nice weekend.

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