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5.111 Principles of Chemical Science, Fall 2008
Transcript – Lecture 21

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PROFESSOR: OK, so today we're going to start talking about acids and bases, and this is acid-base equilibrium, so you can't forget anything that you've learned from the last two lectures about equilibrium. And then we're going to talk about, after this, oxidation reduction equilibrium, and so there's a lot of equilibrium going on. So today we're going to give you some definitions. We're going to talk about autoionization of water. We're going to talk about the pH function, which most people are familiar with. We may think about what the pH's are of some commonly found ingredients around campus. And talk about the strengths of those acids and bases. And then if we have time, we'll start thinking about how to work a problem associated with a weak acid.

So actually, I guess, do we want to do that other clicker question, maybe, before we get started? At some point, we're going to ask you a question about when you want forums. So, I'm not sure if we're going to have that for you today or not, but we need to -- we want to have these pizza forums where you can come, and the time isn't always working, so we thought we could use the clickers to figure out what the best time is for people. So we may have that for you later.

So this is the narrowest definition of an acid and a base. So the narrowest definition of an acid and a base is that an acid is a substance when you dissolve it in water, it increases the concentration of hydrogen ions, or H^+ . Whereas a base is a substance that when dissolved in water, increases the concentration of hydroxide ions, or OH^- . So that's pretty narrow. We can be broader. We can talk about Bronsted-Lowry, and here, an acid is described as a substance that can donate a hydrogen ion. And a base is described as a substance that can accept a hydrogen ion. So let's look at some examples using that definition.

So let's look at an example, so CH_3COOH plus water, and I guess I should put that in aqueous, going to hydronium ion plus CH_3COO^- aqueous. All right, so what is going on here? So if we look at the things on one side of the equation and the other, you can see that this is an acid that has lost its hydrogen ion, so the hydrogen is gone, whereas the water molecule has gained a hydrogen ion, and so now it's H_3O^+ . So we have an acid here, it's acting as an acid, and acid acts as a substance that gives up a hydrogen ion, and the water is acting as a base, it's accepting that hydrogen ion. And when it accepts the hydrogen ion, it becomes an acid in the reverse direction, whereas when the acid gives off the hydrogen ion, it becomes a base in the reverse direction.

So in the reverse direction, hydronium ions is giving off a hydrogen ion to this base, reforming the acid, and after a hydronium ion gives off its hydrogen ion, it forms

water again. So that would be an example of Bronsted-Lowry talking about substances as acids and bases whether they accept or donate a hydrogen ion. And this is the definition we're going to be using mostly throughout this unit.

So, let's look at a little movie of this going on. So, in this movie, we have our water molecules with red and the white dots here are their hydrogen atoms, and now we're going to come in and have an acid come in, there's the acid, it has the hydrogen ion on it in white. It meets up with a water molecule, and now you formed hydronium ion. And that forms another water molecule and it passes it along, so there's a different molecule of hydronium ion. So that's what's going on in this definition.

All right. So this brings us to another term, which is conjugate acid base pairs, so you can talk about something being a conjugate base of a particular acid, and so a conjugate base of an acid is a base that's formed after the acid has donated its hydrogen ion. A conjugate acid of a base is the acids that its formed when the base accepts the hydrogen ion. So you can look at those examples here. So we have a pair that we've drawn here with this red line, an acid base pair, and the other pair is the water and the hydronium ion.

All right, let's look at a couple more examples to get the sense of this and figure out what are the acid base pairs. So, one more example. So now let's look at HCO_3^- in an aqueous solution and water, going to, again, hydronium ion, and CO_3^{2-} , also an aqueous solution. So, what is HCO_3^- acting as here? As an acid. And so what does that make water? A base. And so the conjugate acid of that base, again, is the hydronium ion concentration. And the conjugate base of the acid is CO_3^{2-} , over here. And so in the reverse direction, this base will be accepting a hydrogen ion from the acid, forming the conjugates on the other side. OK, now you can do an example. Let's have a clicker question. So identify what the acid and the base pairs are here. All right, let's take 10 seconds.

That's quite good actually. So, that's correct and you can write it in your notes that here we see that there's a little bit of change, water's doing something different. So instead of the conjugate of water being the hydronium ion, we see it's a hydroxide. So here, the water is acting as an acid giving off a hydrogen ion to this HCO_3^- . And so now we have a second hydrogen ion over here, we have the H_2O species, and that the conjugate of water is OH^- . So this is acting as a base, it's accepting a hydrogen ion, this is donating it, it's an acid, this is the conjugate acid of that base, and this is the conjugate base of that acid. So in the reverse direction, this is an acid giving off a hydrogen ion to the hydroxide forming water.

So one thing that you'll notice about these examples that we've written up is that when you see water in the equation, you don't really know what it's going to be doing until you actually look at what the products are and then you can figure it out. So water can act as either an acid or a base in these equations. And if we go to the lecture notes, the term is amphoteric, which is a molecule that can act as either an acid or a base, depending on the reaction conditions. So depending on if it's mixed with something that's a stronger acid or a stronger base than it is. And an example, one of the most common examples is water.

So now let's consider a broader example of acids and bases, and these are Lewis acids and bases, and we're going to actually come back to this around Thanksgiving time when we talk about transition metals. And so here it's really broad -- we're not actually even going to talk about a hydrogen ion at all. So in this case, we're talking

about a Lewis base as a species that donates lone pair electrons, and a Lewis acid is a species that accepts such electrons.

So here would be an example. So we can think about forming a complex, and which thing is going to act as an acid or a base. One will be donating its lone pair electrons and the other will be accepting. So this is a very broad, a much broader definition, and so when you talk about acid base here, so always say as a Lewis acid or Lewis base to make it clear what's going on. So again we have our base donating its lone pair electrons and the acid accepting. All right, so those are our definitions of acids and bases.

So now let's come back to this issue of water and how water can act as an acid or a base. So if it can act as an acid or a base, it seems like it can react with itself to do some chemistry, and it can. So up here, you could have one water molecule acting as an acid, giving up its hydrogen ion to another water acting as a base, forming hydronium ion and also forming hydroxide ion. So then you can ask the question, well, how much H_2O is in a typical glass of water. How much, so you don't like the idea that I'm drinking hydroxide ions, how much hydronium ion and how much hydroxide ion are in this glass of water, how much H_2O is in a glass of water?

So that's the question. So here's the equation again, and we can think about how to calculate it. What do we really want to know in this question? What are we really asking? How much, at an equilibrium situation, how much are products and how much reactants do you have? What can you tell me about ratios of products and reactants at equilibrium? K . And how are some ways you can calculate K 's? Different terms, but, right, it's what about -- what is K ? So we have the equilibrium constant, and there a couple different ways one might calculate K -- you might be given concentrations at equilibrium, or you might be given information about ΔG .

So you can calculate K 's from ΔG° , and this is an equation that you'll use pretty often -- $\Delta G^\circ = -RT \ln K$. So if we want to know K , we need to find out what ΔG° is. What are ways to calculate ΔG° ? So you've seen some of those -- oh, you're probably recognizing these already, temperature and our gas constant. So we can solve for K in terms of ΔG° . And how do we calculate that ΔG° . Well, there are a couple of ways. So you can think about the ΔG° 's of formations, and we can think about one of my personal favorites, which is relationship between ΔH° and $T \Delta S^\circ$. So you can think about your enthalpies and your entropies at a certain temperature, and you can calculate ΔG° , and from that you can get the equilibrium constant.

So this is just a little review showing the relevance of material you've learned before to the material we're covering now.

So we're going to pick one and just calculate the ΔG° . So we can look up these values of formation for our products and our reactants and plug them in, and we get a value for ΔG° of plus 79.89 kilojoules per mole. So we have a positive value here.

So without doing any more math, which we'll do it a minute, do you expect a large or small value for K for the equilibrium constant if ΔG° is positive 79.89 kilojoules per mole.

STUDENT: Small.

PROFESSOR: We would expect it to be small. And you probably already knew that that there's a lot of H_2O in a glass of water. So again, from that perspective, we'd also expect it to be small. So now we can plug those values in, we calculated this ΔG , we know the gas constant, we're at room temperature, and so we get a value of K as 1×10^{-14} at room temperature, and that's a small number. So, the very small value indicates that only a small percentage all your H_2O has ionized, and that mostly, there's H_2O in a glass of water, not so many ions. Not many of the molecules have ionized, because K is a small number, not a lot of products at this equilibrium. So there's a lot of H_2O in a glass of water.

So, this particular K has a special name, and it's K_w , w for water. And this term and this number, if you haven't memorized it in high school, you probably will by the time you're done with problem-sets. This is a very valuable number, you'll be using it a lot in calculating acid base problems, and you will end up memorizing it whether you want to or not.

So, then K_w equals your hydronium ion concentration times your hydroxide ion concentration. Now for a minute, let's consider why that's true. So our reaction, it's products over reactants for an equilibrium constant, but now, all of a sudden, I don't have my reactants going on in here. So the K_w is expressed in terms of the concentration of hydronium ions times the concentration of hydroxide, and it doesn't have this water term at the bottom. And that'll be true for any problem in which the water is a solvent. And so, it's really not going to be changing very much. A solvent is nearly pure, and when you have in a nearly pure solvent or solid, it's not included in the equilibrium expression. So we'll see other examples of this as we go along. So you always want to ask yourself is this the solvent. If so, we're talking about very dilute things going on in solvent, the solvent concentration isn't changing very much, so it drops out of our term.

So, because K_w is an equilibrium constant, the products are always going to be equal to the same thing at the same temperature. So, at room temperature, or 298 kelvin, it's always going to be equal to 1×10^{-14} , and that's why it's such a valuable number. And when we're talking about acid base problems, you're almost always going to be at room temperature, just to not make life more complicated for you. So, you can pretty much assume, it should be in big bold letters if the temperature is not room temperature, so that you can use these values.

All right, so let's look at the pH function now. So what does pH equal? So pH is equal to the minus the log of the hydronium ion concentration, and let's also talk about pOH , and that's equal to minus log of the hydroxide ion concentration. I just told you that K_w is equal to the concentration of hydronium ions times the concentration of hydroxide ions. And now we can express this in another very useful way for you. If we take the log of all sides, actually let's take the minus log of everything, so minus log of K_w equals the minus log of hydronium ion concentration, minus the log of hydroxide ion concentration, and we end up with terms of pK_w being equal to pH , because minus log of the hydronium ion concentration is pH , and minus the log of the hydroxide concentration is pOH . So plus pOH . And we know that this term at room temperature is 1×10^{-14} . So this term at room temperature is 14.0 , again at 25 degrees c or 298 kelvin. So this is also a useful expression. If you know the pH , you can calculate the pOH if you're at room temperature, remembering this number of 14.

So these are things that you will be doing a lot in the problems and you will start remembering all of these numbers really well.

So p h and p o h, what does p h do for you? Well, the p h tells you about the strength of the acid. So the p h of pure water should be neutral, which is 7. And now, tell me what the p h of an acid is and the p h of a base. Let's just do 10 seconds on this, this is pretty straightforward.

So this tests previous knowledge on this topic, and it is very good. People know about what the p h's are. So that's right. So the p h of an acid solution is less than 7, and the p h of a base solution is greater than 7. And the EPA defines corrosive as something where the p h is lower than 3 or greater than 12 . 5. So, if here is our scale of p h, we're neutral at 7, we're acidic below 7, and we're corrosive below 3. We're basic above 7, and corrosive above 12 . 5.

So now what I want to do is ask Dr. Taylor to come up and we're going to measure some p h's of things, so we're going to be interested in knowing how much danger you're in around MIT.

So we're going to have you measure them. We have these little strips on it, and so someone will come around and help you read it, so you can read off the strip of what you have. Should we start with water? This is random MIT water. Let's start there. So, just pick a volunteer.

PROFESSOR: OK, so what we're going to do is have the TA's go in and ask you to read off of a p h strip, what the p h of various things are, and actually Marcus, if you could write on the board what these are. So we'll start with MIT water. So, we know if it's 7 it's neutral, if it's below 7 we're talking about acidic, and above that it's basic. We actually, also for you to be able to visualize as well, what I did is I just boiled up some cabbage last night and brought in the extract with me. And cabbage actually has anthocyanins in it, which is a color indicator, and it changes color based on whether it's in an acidic or a basic solution. So we'll let you see this here. It looks like MIT water, pretty safe to drink, which is good news. We can go ahead and -- so it looks like if we add MIT water to cabbage solution, what do you think's going to happen -- this is neutral right now. Hopefully not much. We either have invalid strips or we'll see nothing happen here.

All right, so you can see we still have the purple color for MIT water. Two confirmations that it's safe to drink right out of the tap when you get home. So, the next thing is vinegar did someone take the, the strip?

STUDENT: We have a 2 and a 1/2.

PROFESSOR: OK, so are we drinking vinegar?

STUDENT: No.

PROFESSOR: Probably not straight. All right, so we've got our cabbage extract here, it's purple. Does anyone have a guess as to what color it's going to turn if we pour in vinegar, very acidic. All right, a couple guesses I hear, blue and pink. They're both good guesses because different color indicators turn different colors.

But, all right, looks like a dramatic difference here. What do we have next out there? Baking soda. Seven for the baking soda. I'm going to guess we did not pour in enough or it is not dissolved here. All right, so let's do our secondary test here and see what happens with the baking soda.

PROFESSOR: [UNINTELLIGIBLE] the water we added it to was also not neutral.

PROFESSOR: All right, so we're actually pretty basic with the baking soda. We won't give it a number because it was just dissolved in water. But we'll remember baking soda, blue here is basic.

So the next thing we're going to test is soda that you drink all the time. I brought Sprite. Coke probably would have been a good pick as well or Diet Coke. So, we'll test what that is. Hopefully it comes out neutral, right? So while we're waiting, we'll start taking a little bit of a look here. All right, we've got a 3. Soda, corrosive. It's not just the sugar that's bad for your teeth. Luckily we see here it is not quite as bad as vinegar in terms of how acidic it is, but we definitely have a color change here.

PROFESSOR: Has anyone used soda for something other than drinking? What did you use it for?

STUDENT: Cleaning pennies.

PROFESSOR: Cleaning pennies, what else?

STUDENT: When you have stuff all over your car battery you can use Coke.

PROFESSOR: And some of those other uses make sense. [UNINTELLIGIBLE] What else?

STUDENT: Taking the galvanization off of a steel wire.

PROFESSOR: OK, so cleaning steel wire. How many of you still drink soda knowing this information?

PROFESSOR: All right, so the next thing we put out there was aspirin dissolved in water, and it's going to depend what concentration we did, but we put aspirin in water and we got a 3 here. So, aspirin sometimes gives you an upset stomach, and that's why Tylenol's an improvement in some ways -- obviously, that has its own drawbacks, too. But you can see what your stomach on aspirin might be feeling like here. So if you're having an upset stomach, something you might do is take Tums or Mylanta or some other kind of a -- yeah, let's measure the p h here. So if you decide to take some Milk of Magnesia after an upset stomach, are you hoping it will be acidic or basic here?

STUDENT: Basic.

PROFESSOR: All right, let's see what we get. All right, so this is kind of thicker. Let's see how this works. I think you can start to see the green at the bottom. So, it's white in here, so this is not just color. So we'll let that slowly mix in. What did we get for a p h, if you can read it on there. This might be another no-go.

STUDENT: It says 7, but--

PROFESSOR: It's probably blue--

PROFESSOR: So, how many people have had lunch yet today? How many are going to have lunch soon? How many are reconsidering what they're going to eat for lunch based on this demo?

PROFESSOR: All right, we'll take a look at one last thing that you might be consuming. Lemon juice, or actually this is lime juice here. All right, we're probably ending with an easy one here. What do you think, acidic or basic for the lime juice. So, really, the question is probably just the shade that we're going to get from going from a purple here.

All right, so what are we reading for the lime juice? A 2, OK.

PROFESSOR: OK, so that's the end of our demo here, providing you with some tips about what is corrosive and what is not corrosive around MIT. And I think the title of this lecture on the syllabus is "is it safe to drink the water at MIT," and the answer is a lot safer than drinking soda.

So let's talk about some acids in water some more, and introduce something you'll use a lot, which is an acid ionization constant. So let's look at an example of an acid in water. So say we have CH_3COOH aqueous, so it's in water, which is our solvent. It's acting as an acid, so it's giving off a hydrogen ion to water forming hydronium ion, and forming its conjugate, which is missing its hydrogen ion.

All right, so here we have an equation, and now we're going to introduce something which is the acid ionization constant, or K_a , and you'll be using K_a a lot in this course, we're also going to have some K_b 's for bases. So the acid ionization constant. And it's an equilibrium constant, so you all know how to write equilibrium constants.

So the equilibrium constant is going to be products, which in this case is hydronium ions times the concentration of the conjugate base of the acid over the conjugate acid. And there is no water in that equation, because here the water is pretty much pure. It's the solvent so its concentration is not going to change very much, so it is left off. And I can tell you that the ionization constant here is 1.76×10^{-5} . Again, that's temperature dependent, so that's at 25 degrees. This is a small number, so that tells us this is not a very strong acid. So it's not ionizing very much in solution. That is a definition of a weak acid, something that doesn't ionize very much. The definition of a strong acid is something that does ionize quite a bit.

So here then, we can write equations generically for acids and bases. You can write an equation generically, H_a being as your acid, plus water, goes to hydronium ions, and your conjugate of the acid, which is A^- . So this is an acid, H_a , in water. We can also write it as H_b plus as an acid in water going to hydronium ion concentrations and the conjugate, which is base, it's lost its hydrogen ion as well. A strong acid is something that has a K_a greater than one. More products than reactant at equilibrium. So that means it ionizes almost completely, so it goes far toward products, ionizes almost completely.

A weak acid is something with a K_a of less than one, which means that when you put this acid in water, it doesn't ionize very much, when you have equilibrium. So

you can tell if something is a strong acid or not by looking at its K_a value, or alternatively you can consider something called pK_a . So the pK_a is minus log of the K_a , and if you have a low value of K_a , you'll have a higher pK_a , and the higher the pK_a then, the weaker the acid. So you can look at K_a or you can think about pK_a in terms of whether something is a strong acid or not.

And so we'll just finish up with this slide. So, up here we have some very strong acids. These K_a 's are much greater than one, and you have extremely low values for pK_a . And if you keep going from strong acids, again, a strong acid has a K_a greater than one, so these are all strong. And so, then weak acids are less than one. And so down here you'd have small numbers for K_a , and so -- up here we have big K_a 's, here we have smaller K_a 's, and the corresponding pK_a 's are going up, and if we keep going, this table is very long, we're going to get some very high pK_a values when you have some very, very small numbers.

OK, we'll stop there for today and continue acid base next time.