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CATHERINE DRENNAN: There are five types of problems. We just did two. And now I'm going to convince you that salt and water problems are in fact the same as weak acid weak base problems. So we're going to move now to today's handout.

So the pH of a salt solution is determined by what made that salt. So a salt is formed when you neutralize an acid with a base or a base with an acid. And so depending on what acid and which base were used and mixed together, the salt might have a different pH.

So an example here if we had HCl and NaOH, that's going to give our friend table salt NaCl and water. The pH of the salt and water is not always neutral. In this case it would be, but it's not always neutral. It depends on the nature of the acid and the nature of the base that were mixed together to form that salt. So there are some rules to help you figure out whether something's going to be acidic or basic.

And if you have a salt that contains a conjugate acid of a weak base, so it has a conjugate acid in it, it will produce an acidic solution. And if you have a salt that has small highly charged metal cations like iron plus 3, that will also be acidic. So we saw last time I had the prescription medicine for my daughter, which was iron sulfate, was highly acidic.

So note that periodic table group 1 and group 2 ions, lithium plus 1, calcium plus 2, sodium plus 1-- these are all going to be neutral and in fact, anything plus 1 neutral. And then salts that can take conjugate bases of weak acids will produce basic solution. So you're going to be asking yourself, does this solution have a conjugate acid of a weak base? Does it have a conjugate base of weak acid? Does it have group 1, group 2-- what's in there? And then you can think about whether it's going to be acidic, neutral or basic.

So let's look at some examples. So we have a salt, NH_4Cl . And we want to figure out is this going to produce an acidic solution, a neutral solution or a basic solution. So we need to think about what went in to making this salt. And we're going to break apart the salt and we're going to think about NH_4^+ and we're going to think about Cl^- . So let's think about NH_4^+ first.

And we're going to ask the question is NH_4^+ a conjugate acid of a weak base and therefore, a weak acid itself? One way to answer this question is to look up the K_a for NH_4^+ , which happens to be 5.6×10^{-10} . You could also ask about the weak base that it came from. The weak base in this case, its conjugate base, is NH_3 and ask if that's a weak base. So if you have something that is an acid here, you can think about what the base would be by removing H^+ . If you remove H^+ from NH_4^+ you get NH_3 . And you can say, is NH_3 a weak base and look up a K_b . In this case, it's 1.8×10^{-5} .

So what do you think? Is this a weak base and this a weak acid with those numbers? What do you think? Is that a weak acid? Is that a strong acid? So it's a weak acid. Is this a weak base? Yeah. So we can look also in this chart down here and so NH_3 is a moderately weak base and NH_4^+ is a very weak base, but it is very weak acid, but it is a weak acid.

So we do have a conjugate acid of a weak base. So it is acidic, not super acidic, but it is acidic. NH_3 is a weak base and so we probably had NH_3 as our base that was being added and it formed the conjugate acid in this. So then this would produce an acidic solution, because we have this conjugate acid that's formed. So from this part, just from the NH_4^+ , it should be acidic and now we can consider Cl^- .

So here we're asking the question is Cl^- , a conjugate base of a weak acid and therefore, itself a weak base. And if you tried to look up the K_b of Cl^- , you would not find it in any table. But you could find in a table its conjugate acid. So if you add H^+ to Cl^- , you get HCl , and so you could look up a K_a for that in the table and it's times 10^7 . So is this a weak acid?

AUDIENCE: No.

CATHERINE DRENNAN: It's a strong acid. So it's not a weak acid, it's a strong acid. So is Cl^- going to be basic? No. So it is not, it is not going to be a basic solution. If we look over here, we see HCl is a strong acid and so its conjugate base is ineffective in its base. It just doesn't work as a base at all.

So with a number of 10^7 , it really goes to completion. It's a strong acid by our definition. And so Cl^- is not going to do anything to the solution. It's not going to be useful as a weak base. So this solution is going to be neutral, or at least the part of the solution due to Cl^- will be neutral. So here we have something that is acidic and something that's neutral. And so overall, the solution is acidic.

So you need to break down the two parts. You had an acid and a base being mixed. Here we had HCl mixed with NH₃ and formed this NH₄ salt. And that's going to be acidic, because HCl was a weak acid and its conjugate is ineffective. Whereas, NH₃ was a weak base. So it has a conjugate acid that's a weak acid, a very weak acid, but still a weak acid.

All right. So that's how you think about these salt problems. So they really break down to weak acid and weak base problems. So why don't you give this one a try?

[AUDIENCE MUMBLING]

CATHERINE All right, let's do 10 more seconds

DRENNAN:

[AUDIENCE MUMBLING]

CATHERINE That is correct. All right, let's look at why that's correct. So it will produce a basic solution. So
DRENNAN: we're going to break it down to Na⁺. That's one of the things in there. And we ask is Na⁺ a conjugate acid of a weak base? Is it going to be neutral, acidic or basic? And what's it going to be? It's going to be neutral. It is not a conjugate acid of a weak base. It's group 1. It'll be neutral. So this is not contributing to the pH.

So let's look at the second part and look at CH₃COO⁻. So we have-- this can be divided into Na⁺ and HC₃OO⁻. And then we ask is this a conjugate base of a weak acid? Or we could ask the other question is this over here a weak acid? And the K_a for that was given. So is that a weak acid or a strong acid? Is it weak or strong? Weak, yes. So the answer is yes. It's weak and so it's conjugate base would also be a weak base. And so therefore, this will be acidic.

So sometimes you'll be given K_a, sometimes you'll be given K_b's. If you're given either one of them you can answer the question. If you want, you can convert your K_a to your K_b. What would you use to convert K_a to K_b? K_w, right. But just with one of these pieces of information, you should be able to answer this question.

So let's just look at the general rule now. You have a compound XY. That can be broken up into X and you'll ask yourself is X a conjugate acid of a weak base? If yes, then the solution will be acidic. If no, it will be neutral. For Y, you have Y⁻. Is Y⁻ a conjugate base of a weak acid? If yes, then it's going to be add some basic nature to this. If no, neutral. And then over all, you

say, if it's acidic plus neutral, that's acidic, basic plus neutral, basic, neutral plus neutral, neutral.

And if I give you a question of something that is acidic and basic, you can answer the question without doing math, because it'll depend on the K_a of one thing and the K_b of the other thing. And you'll have to see which one's a stronger acid and which one's a stronger base. And so you can't just simply answer the question.

Now you may note, that I did mention that problem set 7 is long. It takes a long time to do these problems. And so on the exam, writing a fair exam when the problems take a long time to do is hard. But these are short little things. I could ask you to predict the pH of salt by just thinking about things and looking up some K_b 's and some K_a 's. So these are good short questions on the exam. So I'm probably not going to give you one if it's supposed to be a short question that is an acid and a base mixed together, because then you'd have to do some math. So keep that in mind.

All right, so salts, salt and water problems, are really just weak acid in water or weak base in water problems, which you already know how to do. So we're going to move on now to buffers. Buffers.

So a buffer is a solution that maintains approximately a constant pH, there'll be a little range of pH can change, but the buffer tries to keep the pH constant. You use a buffer to keep pH constant. Why is this important? Well, buffers are very important in biology. We all work at a constant pH. Living things need to be at a constant pH, but a lot of times chemical processes also need to be at a constant pH.

And here's just one example of why buffers are important. We're looking for alternative energy. We're trying to develop alternative energy. There's this idea of creating fuel cells that employ microbes. These little red circles are microbes here. There are microbes like shewanella that will live, adhere, to electrodes. Will live on surfaces of electrodes, metal electrodes. And they will eat things like sugar and organics. And they will respire electrons into the metal electrodes. So the electrons go in and you create an electric current and you can do-- have a fuel cell. So it's a way of generating an electric current.

And then people have other ideas that some like some microbes live in electrodes, other microbes like moorella thermoacetium, they live on carbon dioxide. They convert carbon dioxide to things like acetyl CoA, which is a fuel. So you throw those in there and then you like

pump in CO₂ and you make electric current. So there's a lot of great ideas of using microbes.

So some of my research relates to understanding the fundamentals of these pathways. And every once in a while I venture to hear one of these big energy talks about how is the development coming of these ideas.

And so I heard one talk and I was listening I wanted to know is this really working? Are people getting this to work? What's the status? And they talked about a lot of technical difficulties of getting it to work, but they had discovered something amazing. Something that might really change the ability to do this. And it turned out that when you're generating all this negative charge you need to have positive charge around, like H⁺, for example. And so you need to have protons, but it mattered, the concentration of those protons. And they kind of had to be kept constant and they discovered buffers.

Fifty minutes of my life. This was a talk at MIT. The person discovered buffers. I just felt like writing a letter to Washington saying, can I have their research dollars because I already know about buffers. I don't need to do a big research project to discover that buffers keep things at constant pH. And that when you're using living organisms and doing experiments and doing reactions, pH matters. I already knew that. Everyone who takes 5.111 already knows that.

And so this is part of the reason I'm teaching you this. Because some of you will not go on and study chemistry. You'll be doing engineering. You'll be doing alternative energy. Doing all sorts of things and you can be the person in the room that raises your hand to go, it's called a buffer. And that is going to change the speed of that research. They're just like right away they're going to be using buffers. And when you do Problem Set 7, you're going to know how to make a buffer. So you cannot only raise your hand and say, it's called the buffer, you can tell people how to make a buffer to use in their experiments.

So this is why the material in teaching was really important. I go out there and I hear these talks of people who are trying to do these innovative things, but they're lacking the fundamental chemistry knowledge that's hindering their ability to do it. So I want all of you to have this knowledge whether you study chemistry anymore or not, so that you can be the person who brings the case of chemical principles into the design process.

And I care a lot about alternative energy. It's going to be super important in the future. I care that we don't destroy our planet going after some forms of energy. And this idea of using microbes is a great one, but we just need people who know how to work with them to get it to

go right.

All right, so buffers. What are buffers? You've got to know about buffers. A buffer consists, an acid buffer, consists of a weak acid in its conjugate base. They're often supplied as a salt, which means you have a counter ion that comes with it, like sodium plus or Cl^- . And it buffers on the acidic side of neutral. A base buffer or a basic buffer has a weak base in its conjugate acid, often supplied as a salt, and it buffers on the basic side of neutral.

So the key to a buffer is that it has a conjugate acid. It has NHA . But it also has the conjugate base. It has A^- . If it just has HA , it's a weak acid. That's not a buffer, that's a weak acid. If you just have A^- , you just have your base. That's not a buffer. You need to be both an acid and a base, a base and an acid, an acid and a base.

On the exam people do buffer problems and they just have one, they don't have the other. That's not a buffer. And I'm going to write on your little exam, remember me twirling around the room. It was an acid and a base. I don't think you can ever forget this. This will be in your brain forever. Buffer has an acid and a conjugate base, a conjugate base and a conjugate acid.

OK, let's look at some examples. So if you mix acetic acid and acetate salt, it's conjugate base supplied in the form of a salt. So here we have the acetic acid. Here we have the acetate, the conjugate base often will be supplied. There are probably going to be some NA around. And you get this dynamic equilibrium. It goes forward, it goes back, it goes forward, it goes back.

So when you have this, if you added a strong acid to this solution, you put in more acid into this. And you had equal amounts of this and this, then your conjugate base is going to react with the strong acid. And you're going to go in the back direction. And you're going to neutralize that acid that was added and the pH should stay more or less the same if you did a good job making your buffer.

So the buffer can respond to the changes in pH by shifts in different directions to use up the extra added acid or the other way, the extra added base. So in this case, the acid that's added is effectively removed and the pH stays the same. So a buffer can respond to add acid. A buffer can also respond to added base.

If you add a base, a strong base or any kind of base, and in this case hydroxide ion, would then remove a proton from the weak acid from the acetic acid forming water and some more

of the conjugate base. And it's effectively removed as well and those OH ions are effectively removed. And again, if you did a good job designing this buffer, the pH should stay constant. So that's why you need the conjugate acid and the conjugate base.

You need the acid to react with the base that's added and keep the pH constant. You need the base to react with the acid that's added and keep the pH constant. If you just have one, it's not going to be a buffer.

So buffer action. Again, weak acid transfers, its protons, its H plus, to OH supplied by the base. So here we have added base and it's going to be reacted with the acid to be neutralized. The conjugate base, A-, can accept protons from a supplied acid. If you add an acid, it will take those and will neutralize the acid that's added.

So let's think about what type of acids and conjugate bases are going to work to make a good buffer. A strong acid in its conjugate base does not make a good buffer. Why don't you tell me why.

Yeah, so 67%. So it's really about the fact that the conjugate base of a strong acid is really not a base at all. It's ineffective as a base. And that's why it's not going to work. Buffer solution has to be in a dynamic equilibrium. You have to be able to push it both ways, otherwise, it's not going to work. So a conjugate base of a strong acid is ineffective as a base. And so if you added acid, it won't be neutralized and the pH will change.

So you need to have something that works as a conjugate base. Something that's able to interact with the hydro ion or the acid that's added and take its proton to neutralize it. If this doesn't happen, the pH will be affected. So you need to have weak acids and weak bases in your buffers. They could be moderately weak or very weak or whatever, but you have to have a conjugate set that's going to be able to push both directions where the acid can interact with the added base and the base can interact with the added acid.

All right, so all of this is really the same for a basic buffer. So we can look at an example here of ammonia plus water going to ammonium ion and hydroxide ion. And we can think about the same things. When you add a strong acid, the base will accept the protons and make more of your conjugate acid. When a strong base is added, the conjugate acid will donate its proton. And it will form NH_3 again, that conjugate base, and water and the pH will stay the same.

So it's the same idea, the only real difference between an acidic buffer and a basic buffer is whether it pH's in the acidic range or in the basic range. But the buffers work the same way. So I can redraw this picture to have our different symbols on it, but the idea is the same. The weak base will take the proton supplied by the acid and the conjugate acid BH is going to probate the OHH- and again keep the pH constant.

So the idea again of the buffer then is that a buffer is a mixture of weak conjugate acids and bases. Again, they're weak because its partner needs to be effective as an asset or a base. It can't be ineffective. Weak acid base mixtures that stabilize pH by providing a source or a sink for protons. It either adds protons or takes protons away. It can respond to add acid. It can respond to add base.

So again, pH is important and buffering is important. Our body has its own buffering system. So we have carbonic acid and bicarbonate buffering agents in our blood. And our blood has to be kept in a sort of neutral range over here. If it gets too acidic, that is very unhealthy for us, leading to some pretty severe symptoms and too much leads to death. If it's too basic, that's really bad. Also, we have death and notice these are not all that far away.

There are a number of different medical conditions that can affect the pH, diabetes, there are metabolic diseases. Something else that is under your control, hydration, you need to drink enough water. And as the weather gets colder in Boston, people so often stop drinking as much water or start drinking like hot beverages, which don't hydrate as well. So keep hydrated. If you're not hydrated, if it's gets really bad, it can start affecting the pH of your blood, which is really not good. So buffering, very important.

All right, so let's do a sample buffer problem. So sample buffer problem-- and this is important. I actually know of at least one professor that if you want to do a UROP with them or come to their office and they're going to say, write down how you would design a buffer for me and do those calculations.

So I can tell you later who that is, maybe I won't, I don't know. But this is one of the tasks that someone uses to see if they want you as a UROP. OK, so here we have one mol of formic acid and 0.5 mols of the conjugate base supplied in the form of a salt with sodium ions. And those are added to water and diluted to a total final concentration of one liter. And you're given the K_a and told to calculate the pH.

So the first step is to write out the equation. So we have an acid and water going to hydronium

ions and a conjugate base over here. And we want to think about what's there now and what's at equilibrium. So initial molarity, change in molarity and your equilibrium molarity. So it's important this word molarity. Don't put mols in here, put molarity in here. But I made it really easy for you, because we have one mol and one liter so the molarity is 1. 0.5 mols and one liter, the molarity is 0.5.

And this is also really important. You're so used to only putting things here. When it's a buffer problem, you've got to put something here, too. So you're adding the acid with the conjugate base at the same time. This is not zero. This is 0.5.

So now as this dynamic equilibrium goes you're losing some of this and gaining some of these. So at equilibrium we have one molar minus x . X is our hydronium ion concentration, which is what we want to know to calculate pH. And our conjugate base our formic ion is 0.5 plus x . We're given a K_a and we've written this expression as acid in water so we can use K_a . The equilibrium constant is for the expression as written so we can put that in and we can fill the rest out.

We have our products. We have the concentration of hydronium ion times the concentration of formic ion, the conjugate base, over the concentration of our formic acid, and again water does not appear in the expression because it's the solvent. Hydronium ion concentration is x . The conjugate base concentration is 0.5 plus x and the conjugate acid concentration is 1 minus x .

So we can now try that assumption that x is small or we can use the quadratic equation, but why don't you just try that assumption. I'm going to take this expression-- if you haven't written it all down yet, put it right up here. And now with the clicker why don't you tell me, if we use the approximation that x is small compared to 1 and 0.5, what does this simplify to?

All right, 10 more seconds.

So 70 something percent. Yep, so let's take a look at that.

So here we're making the assumption that x is small compared to 0.5, compared to 1. So that means that we drop the plus x from the 0.5 term and drop the minus x from the one term. So we're saying that these are going to be small enough that it's still going to be pretty much 0.5 and 1. And then we have to test that in a minute. So if we use this, we can calculate x and it

comes out to 3.54×10^{-4} , and then we can check the assumption.

And before you told me how to check assumptions. And that was I take x and I'll divide it by 0.5, which is the smaller of these two, and times by 100% and we get 0.69%, which is less than 5% so the assumption is OK. And we don't have to check it against 1, because if the assumption x is small compared to the smaller number is valid, it will also be valid for the bigger number. So you only check it for the smaller number and then we can solve.

So we have to think about-- we solved for x . We're happy with x . Our assumption was OK. But then we have to remember what x is and x is the hydronium ion concentration and you always want to make sure to think about this, because if it's hydroxide ion that's different. So we can calculate pH. pH is minus log of 3.54×10^{-4} , which is equal to pH of 3.45.

And here we have two significant figures after the decimal point, because the volume we had before only had two significant figures. Everything else had three, but the volume was just 1.0. So that is our answer there.

All right, so I'm going to just briefly start what happens when you-- actually we'll do-- this is how you would design the buffer for this. Next time we'll see what happens if we stress the buffer we design by adding acid to it and see what the new result is.

All right, so today we're going to finish lecture 22. So take out those lecture notes on acids and bases. And when we're done with that, we'll just continue with acids and bases. And we're going to continue with some acids and bases on Wednesday. We should finish on Wednesday and move on to oxidation reduction and that will end exam three material. So exam three is sneaking up on us and it'll have thermodynamics, chemical equilibrium, solubility, and acid base.

So you should have already filled in your handout with all the information. The parts that you were filling in are in bold here, but I just want to remind you of what we were talking about. So we had a sample buffer problem. We had one mol of the conjugate acid and a half a mol of its conjugate base supplied in the form of a salt, were put in water and diluted into one liter.

So we calculated what the hydronium ion concentration would be and therefore, the pH, using information that was given to us about the K_a , the acid ionization constant. So we got a pH of 3.45. Someone asked me after class, but isn't this conjugate base also reacting with water and forming some of this weak acid. And the answer is yes. That we are writing this as a problem

of acid in water, because we can use the K_a .

But we could've also written it the other way. And written it, and this is not in your notes, but I just want to let you know, that the weak base and water could be written that way forming a conjugate acid and hydroxide ions. And so then it would be $0.5 - x$ and $1 + x$ and x . Use K_b then, because it's a base in water to solve for x and calculate pH from P_{OH} and if you try it, you get 3.45.

So you can do these problems either way. You can think about them as a weak base problem or a weak acid problem. You just have to remember that this is not zero when you start. The conjugate has some amount. That's what makes it a good buffer. So this can work either way, but you also want to remember if you write it as an acid in water, use K_a . If you write it as a base in water, use K_b . Because those equilibrium constants are telling you about those ratios of the conjugate acid and the conjugate base at equilibrium.

So within the K_a and the K_b is information that you need about this dynamic chemical equilibrium. So both of these ways work and by the end of, sort of halfway through today's lecture, you'll see yet another way to solve buffer problems. And probably will be for most of you, the preferred way to do it.

So there's a number of different ways which makes grading the exam lots of fun. And we have option 1, option 2, option 3-- to make sure that all the options are possibly accounted for. All right, so the purpose of a buffer is to keep the pH pretty much constant. So you can add a strong acid to it and the acid will be neutralized, keeping the pH constant. You can add a strong base to it and the base will be neutralized, keeping the pH pretty constant.

So what you want in a buffer is to have a weak acid conjugate base pairing that allows it to be a source or sink for a strong acid or a strong base to keep the pH constant. So now in this problem we're asked to calculate what would happen to the pH if 0.1 mols of the strong acid had been included in our 1 liter solution. And because 0.1 mols of our strong acid would react with equal number of mols, all of that conjugate base, that's what the conjugate base does in a buffer, it reacts with the strong acid that is supplied. And it will form equal mols then of the conjugate, its conjugate acid.

So we have to do some subtraction. So for the conjugate acid, we had 0.5 mols. For the conjugate base, we had 0.5 mols. We used up one of that, 0.1 of that, reacting with the strong acid and we have 0.4 left. So we have a new concentration for our conjugate base, 0.4 divided

by 1, keep the math simple, 0.4 molar. So for our conjugate acid, we had one mol to begin with, but we formed 0.1 more when that strong acid was added.

So now we have 1.1 mols and a new molarity. So now we have to go back and we can use this expression again and determine what x is now, what the hydronium concentration is now using K_a . So why don't you tell me how I would solve this. What is the correct expression for K_a ? You can fill in your little table as you do it.

All right, let's just do 10 more seconds.

All right, so let's just fill in that table if you haven't already. So here now, we can write this as an acid and water problem. Again, again, you could have done the base in water and used K_b , but we'll just do it the same way we did before. So we have our acid 1.1 molar. Now remember, this is molarity. So you don't want to put mols in here, you want to put a concentration and some of that will be minus x .

Then we have our 0.4, 0.4 plus x . We can fill out the K_a . The K_a again, weak acid and water problem. We have products-- hydronium ion times our conjugate base over our conjugate acid equals 0.400 plus x times x , these 2, and 1.1 minus x on the bottom. So you can always solve then for x , which will tell you about the pH by using the K_a . And you just have to remember molarity and remember these are the new molarity after the reaction has occurred.

All right, so we can use the approximation that x is small compared to 1.1 and 0.4 to simplify this. Or we could use the quadratic equation. If we simplify it, we calculate x as 4.87 times 10 to the minus 4. And remember again, that the approximation is you get rid of the plus x and the minus x here.

And then, you have to check it with the 5% rule. If you did that, if you used the quadratic, then you don't have to check. But if you use the 5% rule, then you're asking is this number 4.87 times 10 to the minus 4 within 5% of the smaller value, which is 0.4 and it is here. It's 0.12%. So the assumption is OK. That's less than 5%. x is small. And then we can solve for the pH.

So pH is minus log of the hydronium ion concentration, which here is 3.31. This only has two significant figures after the decimal, because if you remember, back on the other page, the volume only had two. So actually all these numbers here really just have two significant figures. We carried an extra, but it really just had two.

All right, so our buffer was pretty good so we added 0.1 mols of a very strong acid. And we only changed the pH. We only lowered it from 3.45 to 3.31. So that was a pretty good buffer that we had designed there.

All right, so that is how you do a buffer problem. And there are other kinds of things that you can be asked about with buffers. In particular, you can also often be asked to design a buffer. And when you design a buffer, you must consider the following things. The ratio of your conjugate acid base pair and that they should also be weak conjugate acid base pairs-- the pKa and the pH. OK, so here comes a derivation.

So here is our expression that should be familiar to you at this point, for a weak acid, HA and water, going to hydronium ions and our conjugate base, A⁻. It should also be familiar to you that you can write the equilibrium expression for this acid in water as hydronium ions concentration times the concentration, the conjugate base, over the concentration of the conjugate acid. Water, which is our solvent, doesn't appear in the expression.

We can rearrange this expression now and solve for hydronium ion concentrations. We can take a log of both sides, and get this, log of hydronium ion concentration, log of Ka, plus log of HA over A⁻, multiply by negative to get this. And so we have minus, minus, minus, and minus the log of the hydronium ion concentration is what? pH minus log of Ka is pKa and this is the same as that.

So that gives us this expression that pH equals pKa minus the log of HA over A⁻. Now it's important to point out that these are equilibrium concentrations of HA and A⁻, because we derived this expression from Ka and that's an equilibrium constant. So these are equilibrium expressions. And that makes this particular expression slightly less useful, because we often don't want to have to calculate the equilibrium concentration. We know how much we added and so we often want to use initial concentrations.

But we can consider whether the initial concentrations are actually pretty similar to the equilibrium concentrations i.e. the x is small, less than 5%. So we know that a weak acid typically only loses a fraction of its protons, hence the definition of weak acid. Weak acid in water doesn't ionize that much. And a weak base typically only accepts a fraction of the protons that it could. It's a weak base.

So the initial concentration is often approximately equal to the equilibrium concentration and

that's what we've been finding in a lot of the problems. We've found that the 5% rule works pretty well. It's usually less than 5%. X is usually less than 5% of the initial concentration we had of HA or A^- . And so therefore, we can say that the pH is in fact, approximately equal to the pKa minus the log of the initial concentration of your HA over your initial concentration of A^- . And this expression is known as the Henderson-Hasselbalch Equation.

And so this equation is only valid when your hydronium ion concentration is small compared to HA and A^- , i.e., less than 5%. So this 5% rule must apply to use the Henderson-Hasselbalch Equation. The Henderson-Hasselbalch Equation is a great equation to use for buffer problems. And so, we've showed you a couple different ways of doing buffer problems. This is the final way I'm going to show you using the Henderson-Hasselbalch Equation, but you can only use it if x is small.

But most of the time, x is going to be small, because buffers are only buffers when you have a weak acid with a conjugate weak base. And when you're talking about weak acids and bases, x is small. They don't ionize that much. And importantly, and I'll emphasize this, this equation only works for buffers. Don't apply it for just regular weak acid in water or weak base in water, a strong acid in water, a strong base in water-- it only applies for buffers. Buffers, buffers.

Now I know that MIT students love equations and they love doing math, and so they try to apply this equation to every type of acid-base problem. Don't do it. Buffers, buffers. You'll remember that now, right? Because I'll make noises again if you don't. You remember that now, right?

All right, so let's use the Henderson-Hasselbalch to design a buffer then. So say we want to design a buffer of pH 4.6. Say you're interviewing for a UROP position and the UROP supervisor, the PI says, tell me how you would design a buffer pH 4.6. And you might go to the shelf and see what was available and then look up what the K_a and the pKa are, because a buffer solution is most effective in the range of the pKa plus or minus 1.

In fact, the closer the pH you want is to the pKa, the better the buffer is going to be. So we can look and see what's in the range. There are several that are close to 4.6 that we can choose from. And probably would end up choosing acetic acid, because that would be on the shelf, whereas, some of the others of these would not be there. All right, so acetate is going to work. It's a pretty common buffer. So we can use acetic acid with a suitable pKa of 4.75.

Then we can use the Henderson-Hasselbalch Equation because we're designing a buffer. So

we can use that equation and figure out what the ratio of acetic acid to its conjugate base should be. So we can rearrange this expression. We know the pKa and we know the pH that we want, and so we can subtract those. And we get that the log of the ratio should be 0.15. And then inverse log will tell us that the ratio then of the acid to the conjugate base should be 1.4.

So you should use things with that ratio. So for example, you could use 1.4 molar of the acid to one molar of the conjugate base and the total amounts are often less important than the ratio. The ratio is very important, but if you go too low in concentrations, then that will affect what's known as the buffering capacity, which is the ability of the buffer to resist changes. So if it's too dilute, and a lot of strong acid or a lot of strong base is added, then it won't be a good buffer anymore.

So the ratio is very important. The amounts are important such that you have some resistance to change. So the higher concentrations, the more resistant to change. And also, if you use too low a concentration, the Henderson-Hasselbalch Equation is no longer valid. So you could be asked to calculate sort of what the minimum concentration is that you would need to use. And so for a pH 4.60, you can back calculate what the hydronium ion concentration is. And it's 2.5×10^{-5} .

So for our 5% assumption to hold or to be valid, that this number, the hydronium ion concentration, is less than 5% of either one of these. The concentrations here would have to be greater than 5×10^{-4} . So if we use one molar or something, that's way above this, but that would be the minimum. If it's less than that, that 5% doesn't really hold and you would not have a very good buffer in that case. It wouldn't be very resistant to change. X would be big compared to those numbers. So that's how you go about designing a buffer.

And in that, there were two things that are really common mistakes. When I'm reviewing a paper for publication, two of the things that I see the most often is that people one, do not use the right buffer for their experiment. They say, oh, I'm at pH 8. And they'll use a buffer that is in fact, not a good buffer at pH 8. So who knows what their data is telling us. And the other thing that people will do is that they'll say, oh yes, it was buffered. And the pKa might be right, but the concentration of the buffer is so low that you don't really imagine the buffer's doing anything.

So now you know how to avoid both of those pitfalls.

