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**CATHERINE  
DRENNAN:**

So where are we in our grand list of our five types of problems? We've done weak acid in water, weak base in water, salt, and buffer. We only have two left. And that's what we're going to talk about right now-- strong acids and strong bases. And we're going to talk about them in terms of acid base titrations.

So switching to today's handout, so titrations-- how many of you have done a titration in a laboratory? OK, a lot of people. If you haven't, I have to say, you're not missing anything. It is really-- it's like watching paint dry for most of the time during the titration.

So here in an acid base type titration, you have the addition of, say, a base of known concentration to an acid of unknown concentration. And you can use this by figuring out what volume you need to reach the equivalence point. You can figure out the concentration of that acid or base.

If you know the concentration of two things you, can often use it to figure out a  $K_a$  or calculate a molecular weight. But that's the purpose of the titration. So let's look at the shape of these titration curves.

So here we have a strong acid with a strong base. So we start out. All we have at point 0 is the strong acid. So we should have a very low pH here. And then it should change slowly. Then it changes very rapidly and then changes slowly again.

So what is this point S? So that point S has many, many names, which are all equivalent. It's called the equivalence point, and we had the clicker question in the beginning was mentioning that. The S here really stands for the stoichiometric point. Both of these are the same thing. And it's the theoretical volume and which that base that you've added, the number of moles of that base is equal to the number of moles of acid you had.

So it's the point of which the moles are equal to each other. And so that stoichiometric 1-to-1, or equivalence. The moles are equivalent. So all these names are the same. They all mean the same thing. Don't get tricked if problem say one thing or the other.

You also might hear end point. That's often the result of the experiment that you do, where you figure out what volume you needed to add to have a color change. So the way these work usually is you have this, and you go drip, drip, drip, and you look for a color change. And at that point of the color change, the first little hint of the color change is where you want to stop and measure the volume.

But often you get very frustrated, and you go from totally clear, you're very, very slow, and you're right in here. And then you can't stand it anymore. You jump right up here, and you have to do it over and over again. But it should be that the end point should equal the equivalence point.

So if you're good at these kinds of problems, you might be able to do a quick and dirty, estimate what the value is, and then figure out exactly how much you can add before you have to go slow, i.e. you can cheat, which I highly recommend in doing these kinds of laboratory exercises. So knowing how to do the math is really valuable of these problems. So we add a strong acid and a strong base. Here's the same curve for a strong base with a strong acid, where we're adding the strong acid into the strong base.

Again, now we're going to start in the beginning at point 0 before we've added any acid. We have a basic pH. It goes slow, goes fast through point S, the equivalence point or stoichiometric point, and then goes slow again.

So how do you know? And the TSs are going to come down and do a little demo for you now about pH indicators. How do you know? And for those of you who have done these experiments in lab, again, you have this color change. And usually you're clear. You go a little bit more. You have a little bit more, and you go to this.

But as I was saying, what happens most of time is you go from this clear, all the way to the really dark, and you have to start all over again because you missed the end point. So these pH indicators are able to tell you that there's this change in pH. So the TAs are going to show you, using a pH-- come on in. Set up.

I'm just talking while you set up. Over there-- you can use the document camera if you need it. So our demo TAs have created a natural dye from red cabbage. And this dye, when it's in acid, has a slightly different structure than in base, which causes it to have these two different colors.

So we can tell which things are acidic and which things are basic by the color of the indicator. And I'm just going to hand over a mic if it's on.

**TEACHING ASSISTANT:** Is it on? Yes? Yes? OK, great. So we've got our solutions here. This is lemon juice. Did I put water in here? Right? Yeah, water, vinegar, I think. Maybe it vinegar-- this is vinegar.

Don't do that. Don't do that in lab.

**CATHERINE DRENNAN:** In the lab you should always label your containers.

**TEACHING ASSISTANT:** Yes, indeed. So we've got lemon juice, water, vinegar, and ammonia. Did you add some water into that? Can you?

So we're going to add a little bit of the indicator. The indicator came from red cabbage. So the dye in the red cabbage, it is a molecule that can be protonated. And when the molecule gets protonated, basically it's double bonds start moving around. And when you do that, it absorbs light differently.

So what we're going to see when we pour into there is that you'll see this, which is the acid forms a nice pinkish color. This was the water. And when you pour it into the water, nothing really happens. And you can kind of understand that because the indicator itself is a water-based solution. So it's going to be purple.

This was the vinegar. And as we did last time, the vinegar is acidic. And this was the ammonia. And I'm going to add little bit of water. Can you add a little bit of water into this one? You added it? OK, great. And then we're going to kind of do a little excursion here.

So what this, this is a piece of-- oh, it's cold-- a piece of dry ice, which is just solid CO<sub>2</sub>. And what I'm going to do is I'm going to drop it into there. So this is kind of a bit of a--

**CATHERINE DRENNAN:** [INAUDIBLE]?

**TEACHING ASSISTANT:** Yeah, put it over here. So this is an interesting demo because-- oh, that's not useful at all.

**CATHERINE** Yeah, actually we can change--

**DRENNAN:**

**AUDIENCE:** Can we change that?

**CATHERINE** Maybe.

**DRENNAN:**

**TEACHING** Oh, maybe not. Oh, well, it's fine. Oh, man.

**ASSISTANT:**

**CATHERINE** I think we can do that. But this is beyond my ability [INAUDIBLE].

**DRENNAN:**

**TEACHING** Well, what I was talking about was basically when you drop the CO<sub>2</sub> into this mixture, what's

**ASSISTANT:** happening is that the CO<sub>2</sub> actually decomposes, and it forms something called carbonic acid.

Good idea.

Carbonic acid is an acid, so it will actually change the pH of the solution as we're talking. And what this is relevant for is really for global warming. So we know about companies when they make-- I mean, it's true.

When we have companies and they make lots of kinds of chemical compounds, they'll release CO<sub>2</sub> into the atmosphere. And when the CO<sub>2</sub> gets released-- is it working or no?

**CATHERINE** Upside down! That's even cooler.

**DRENNAN:**

**TEACHING** Oh, look at that. So when the CO<sub>2</sub> gets released into the atmosphere, basically, by Le

**ASSISTANT:** Chatelier's principle, you add all this CO<sub>2</sub>. It will force the reaction to start making carbonic acid. And that will react with the water vapor and start making the water in the air very acidic.

Wow, that's not useful at all. And the color's not really changing. But it was supposed to.

(LAUGHING)

**CATHERINE** We have time. We can keep an eye on it.

**DRENNAN:**

**TEACHING** I think we may have added too much base. But we can keep an eye on it and watch the color

**ASSISTANT:** change while it's upside down, which is really useful.

**CATHERINE** Yes, because that's really cool.

**DRENNAN:**

**TEACHING** But anyway, yeah, that's how the indicator works. And, yeah, that's that, I guess.

**ASSISTANT:**

**CATHERINE** OK, great.

**DRENNAN:**

[APPLAUSE]

**CATHERINE** So we can leave this here. I'll switch the document the camera back. And you might add a little more. It's very concentrated still. See if we can get a little bit more without too much overflow. I think it's changing a little bit actually. Yeah.

**DRENNAN:**

Well, we'll keep an eye on it. So let's go through and calculate some points on a strong acid and base curve. So we can check off those two final types of pH problems.

So here, when we're calculating strong acid and strong bases, say we have a strong base that's 2.5 molar, NaOH being traded with a strong acid, HCl at 0.34 molar. So first, we want to calculate the pH before the equivalence point, when we've just added, say, 5 mLs of our strong acid to the solution which was 25 mLs of our strong base.

So the first thing we're going to do is calculate how many moles of base that is. So how many did we have in here? And since this base is strong, the number of moles of sodium hydroxide added equals the amount of hydroxide formed. That's the definition of a strong base. And it is hydroxide, so pretty much that's how much you get.

So all we have to do is know how to calculate the number of moles. And that is the volume that we had, and we're converting that to liters times our concentration. And so that gives us 6.25 times 10 to the minus 3 moles.

So we know how many moles of OH we have. Now we need to figure out how many moles of acid we added when we added 5 milliliters of the acid. So it's a strong acid. So the moles of acid added equal the number of moles of our hydronium ions that are formed-- definition of strong acid. And so we had 5 milliliters. We convert to liters times our concentration. That gives us 1.7 times 10 to the minus 3 moles.

So now we need to figure out what the new amount of hydroxide is. So we're going to convert. Some of our hydroxide will react with the amount of acid added because the stoichiometry is one-to-one, you're going to react equal numbers of OH with H<sub>3</sub>O<sup>+</sup>.

So we had 6.25 times 10 to the minus 3 moles. We've added this number of moles of acid. So that many moles are going to be formed into salt. And we're left with this minus this, or 4.55 times 10 to the minus 3 moles of OH<sup>-</sup> left.

So at this point, this is a strong base and water problem. All we have as hydroxide ions left in our solution. We've converted all the acid that we added into salt because it reacted with the base. And so this is a strong base now.

So for strong base, all we have to do is calculate the molarity and then calculate pOH and pH. So for molarity, We have the number of moles left, 4.55 times 10 to the minus 3, in our new volume. And this is the part where people forget. We had 25 mLs. We added five more. So our new volume is 30 mLs. And so we have a new concentration. And then from that, we calculate pH.

First we do pOH, plugging in our hydroxide ion concentration. and then calculate pH, using the fact that at room temperature-- and all these problems are room temperature-- that would be 14 minus the pOH is the pH. And we have a point somewhere around here, point B, on our titration curve after we've add 5 mLs of strong acid. Our pH is still pretty basic-- 13.18 left.

So strong base in water problem-- all you have to do is calculate the concentration of OH<sup>-</sup> minus, then the pOH, and then the pH. So you don't have to have any of these minus and pluses in terms of setting up our tables and using Ka's and Kb's For a weak base in water problem, it's a concentration of hydroxide ion-- pOH pH.

So let's move on now and think about what volume we would need to get to the stoichiometric point. So you're often asked to calculate the volume of the strong acid needed to get to the stoichiometric or the equivalence point. And to do this, you need to think about how many moles of OH you have, because at the equivalence point, you have equal numbers of moles of acid.

So we had 6.25 times 10 to the minus 3 moles of OH originally. And at the equivalence point, then, how many moles of acid do we need to add? We have to add that exact same number, by definition. So the equivalence point, it's the stoichiometric point. So if you know how many

moles of the base you had, that's going to be equal to the moles of acid you need to add.

So now we want to figure out the volume that that's needed. We know the number of moles that we need, and we know the concentration, so now we just have to calculate the volume. So we have the moles. We use the concentration of the acid to figure out the volume that has to be added. And what would be the pH at this point? It would be 7.

So this is a really fast question to ask on an exam, because all you have to do is say, if it was a strong base in a strong acid, they're going to form a neutral salt in water, so the pH is 7. And that's it. No calculations needed. You can answer that question very quickly-- so strong acid, strong base, at the equivalence point, equal number of moles. You're going to get a salt that's neutral.

In the salt here, we have HCl and NaOH is just NaCl, salt. So remember, at the equivalence point, strong acid, strong base, the pH is going to be 7. So now let's go down here and try point D so just beyond the equivalence point. So here we want to calculate the pH after 1 mL of strong acid has been added after you have reached the equivalence point. So you went 1 mL too far in your titration, and this is a strong acid in water problem, so our last type of problem here.

So first what you want to do is figure out how many moles of this acid were added due to this 1 mL extra. And again, it's a strong acid, so the amount of acid added is going to be equal to the hydronium ion concentrations formed-- definition of strong acid. So we had a concentration of 0.34 of our strong acid. We added 1 mL extra, so we have 3.4 times 10 to the minus 4 moles of H<sub>3</sub>O<sup>+</sup>.

Now we need to calculate the molarity of that, and that's a clicker question. So the trick here is just to think about what is the volume at this point. And if we look over here-- do you want to just-- you can it out. We're trying a couple of different variations of the experiment over here.

But we'll just see if we can get it over time. Maybe we'll come back to that at the end. We'll just leave it there and say, OK. Or did you want to say something? Why don't you talk about it briefly, and then we'll look at the--

**TEACHING**

We did the experiment again with a less concentrated solution, added several pieces of dry

**ASSISTANT:**

ice. And as you can see, the color-- yeah, we can put it on the camera. I don't know if we can. It's fine. But the color's changing very slowly, which is a lot slower than we expected it to

change.

But you dilute the concentration, and this is turning blue. And it will eventually turn into a yellowish-pink, which is when it will officially become an acid. So we'll just leave that there.

**CATHERINE**

We'll keep an eye on it for the next few minutes. So the trick here was to figure out the volume.

**DRENNAN:**

So you had 25 mLs to begin with.

You needed 18.4 to get to the stoichiometric or the equivalence point. Then you added one more past the equivalence point. And if you remembered to add those three volumes together, then you will get the right concentration. And when you get the right concentration, the rest of the problem is very easy. And I'll just mention also, significant figures here.

We have three here because we had three there. And so then you just take the pH of this. This is the hydronium ion concentration. And that will give your answer. And it'll be pH 2.116 with all of those significant figures, which you can never measure that accurately. But nonetheless, that's what the rules would tell us. So a strong acid in water problem is you just calculate the hydronium ion concentration and then pH. So this is a pretty simple part.

So if we go back now to our diagram, we've measured a couple of parts. We measured point B. And so we had a pH of 13.18. This was like a strong base in water problem. At a point S, we calculated that we needed 18.4 mLs of strong acid, and our pH is 7. And so the trick to doing this problem was just to remember that the moles of strong acid equal the moles of strong base at this point. And then from point D, 1 mL past the equivalence point, the pH was 2.116, and this is like a strong acid in water problem. And notice how dramatic it is.

Up here you're at pH 7. You add 1 mL too much, and you're already at pH 2. So this is a very rapid change. This is why a lot of these experiments are so frustrating. That you add a little bit too much, and you're just way, way, way beyond the stoichiometric point.

So in one titration curve here, we have three types of problems. But as we get into weak acid in weak base, which we'll do now, you'll see that a titration curve is actually all five types of problems. So this is why one wants to start problems set 7 early.

So we've done all of these now. And now we can apply all of these types of problems while doing weak acid strong base part. And we'll just start this, and we'll continue it later. But let's go through the curves now.

So this is in your handout. This is the curve for the weak acid in strong base. And I just want to remind you what we just talked about, which is strong acid in strong base. So for weak acid in strong base, the curves look quite a bit different.

So here we start at a higher pH, because it's a weak acid. Here's lower. It's a strong acid. Then we go up. The pH levels off. And this is called the buffering region. There's no such buffering region with a strong acid strong base, because strong acids and strong bases don't form good buffers.

But weak acids and strong bases can generate good buffering region because a strong base can convert some of the weak acid to its conjugate weak base, and that creates a buffer in this region. Then the pH starts to change again. It's constant in the buffering region, starts to change again.

You get to the equivalence point. The definition of equivalence points are the same-- equal number of moles of acids and base at the equivalence point. But now the equivalence point is not at pH 7 anymore. It's greater than pH 7 because we've converted our weak acid to its conjugate base.

So up here we have conjugate base, which makes it more basic. And so the pH is greater than 7. And then the curve goes up again. We also have something that's special for a weak with strong titration that doesn't exist with strong -strong, and that's called the half-equivalence point.

The half-equivalence point is the point where half the volume and half the number of moles needed to reach the equivalence point have been added. So that's the half-equivalence point. It's half of the equivalence point.

So let's just look at these-- a couple of different points here. And look at this figure here, and we'll end with this. And I'm just going to have my TAs come down and just help me with this last part.

So let's see if we can get two more. We already have someone with a hat. You have a hat. We have two more TAs. So these are all weak acids over here. So we have just our weak acids, and we have four of them.

Other TAs who want to come down, can help out. This is volume equals 0. So this is like a

weak acid in water problem. So now let's bring our moles of strong base over here. So now, Amanda, you're a strong base, so you're 1. So you're going to react just with one of these weak acids deprotonate it and form a conjugate base. There we go. And then you can go off and form your salt and water.

So now we have a buffer situation. And we have a buffer situation when we have some conjugate acid and some conjugate base. We have a special type of category of buffer at the half-equivalence point, where you have half the conjugate S and half the conjugate A.

So another mole of strong base comes in and deprotonates one of our acid. So why don't you be-- yeah, and you go off and form a salt. And so then we have half the weak acid and half the conjugate base.

Now, as we go on, we're going to reach the equivalence point. And now we've added an amount of strong base that will fully deprotonate our weak acid. So why don't we have two more strong bases come along and deprotonate. And so now we have only weak bases left.

There are just weak bases left because we added equal numbers of moles of our strong base as we had weak acid. So now we have conjugate base. So this is like a weak base in water problem. And then at the end, if we add more strong base, and a strong base comes over, there's nothing to do.

He's just strong base in solution. And so this is a strong base in water problem. So the point is one titration problem is really five different types of acid base problems. So start problem set 7 early. See you on Wednesday.

Let's just take 10 more seconds.

I have a feeling that more people understand how to do this, but it's just a matter of thinking about the sign of things. So the trick here-- you have a pH of 4, pKa of 4.19. And so, obviously, it's the difference. But you have to think about if you want the ratio to be A minus 2 A, which expression you're going to use here to give you the correct one. So just pay attention to your sign. Always show all your work on an exam.

So today, we're going to finish the lecture notes from last time on titrations, continue with titrations. And toward the end of the class, we're going to start the next unit, which is oxidation reduction. So we want to take out lecture note 23, top of page 4, where we had this curve.

So as we were finishing last time, we saw the curve for a titration of a weak acid with a strong base. And this is the curve for a weak base that's being titrated with a strong acid. And drawing curves on an exam-- that's one of my favorite exam questions. So make sure you know how to draw these types of titrations.

So things that you should pay attention to in drawing them, if it is a weak base that's being titrated with a strong acid, you would expect that before you've added any acid, that you're going to have a basic pH. So at point 0 here, you would expect a basic pH. So then the pH starts decreasing as you're titrating in the strong acid. And you go into this region of constant pH, where that's the buffering region.

So the pH is changing very little. It plateaus. It's flat. So when you're drawing a region like this, make sure that in the curve it looks kind of flat, because the idea of a buffering region is that the pH isn't changing much. Here you have the conjugate acid and the conjugate base, so it's a buffer-like problem.

Then when you get out of that buffering region, the pH drops rapidly, which is often one of the funs in doing these titrations in lab. Nothing's changing. Nothing's changing. Nothing's changing. And all of a sudden, you're down here.

So at the equivalence point here, the equivalence point is going to be below pH 7 because at this point, you have added the same number of moles of acid as the weak base. So you've converted all of the weak base to its conjugate acid. So the pH is below 7, and then it drops off rapidly.

So again, in these titration problems, there are really five different types of problems within them. When you have the volume of zero, it's a weak base in water problem. In this buffering region here, it's a buffer problem. And there's a special kind of buffer problem at the half-equivalence point, where the number of moles of the conjugate acid formed equal the number of moles of bases. And then we get to the equivalence point, and now we've converted all the weak base to its conjugate acid.

So this is just a weak acid in water problem. And then down here, it's a strong acid in water problem. So again, the trick in doing these is to recognize where you are in the curve and figure out what type of problem it is. Once you figure out what type of problem it is, it's usually not so bad to solve it because you can all figure out how to solve these five types of problems.

It's recognizing what type of problem it is at various times during the titration. and in some of the problem set problems, you'll have all of the various points to do. But in an exam, you're going to just be thrown into the middle of a titration and have to think about where it is in the midst of titration what type of problem is it.

So now we're going to go through and do an example, work point by point for a titration. And the titration we're going to do is a weak acid in a strong base. So that's the curve here. So we start at low pH and then go up.

So the particular problem we're going to work-- and we're going to work all these points. And then we're going to have a bonus point E at the end-- is formic acid. And we have 25 mLs of 0.1 molar formic acid. And we're titrating with a strong base, sodium hydroxide, 0.15 molar. And you're often going to be given the  $K_a$  of the acid.

So the first point, point A, is volume zero. You haven't added any of your strong base yet. So you can write the expression for what's going on there. You have your acid plus water going to hydronium ion concentration, and you're forming the conjugate base of that weak acid.

So this is, again, a weak acid problem. So you know how to do weak acid problems. So titrations are just a collection of problems we've already talked about how to do. So just very briefly, we'll go through this pretty fast at this point.

So we have our weak acid in water. We had 0.1 molar, and we had none of the other to begin with. So we're at zero volume here. So as the equilibrium is reached, we have 0.10 minus  $x$ ,  $x$ , and  $x$ . So because this is a weak acid in water problem, we can use  $K_a$  to solve the problem, which is our acid ionization constant. It's  $1.77 \times 10^{-4}$  for this particular one.

We can set this up it's products over reactants at equilibrium. So  $x^2$  over 0.10 minus  $x$ . Again, water doesn't fit in. That's our solvent, so it's not in our expression. We can solve this with the quadratic, or we can assume that  $x$  is small, which, again, is a pretty good assumption usually for a weak acid problem. And by assuming  $x$  is small, that means this minus  $x$  drops out.

So we're saying  $x$  is small compared to the concentration that we started with. And then we can solve for  $x$ . If we do that here, we get 0.00421, and that we can check, and we find that it is 4.2% of 0.1, so that's under 5%. So that assumption is OK. Again, I'm using the 5% rule. And then we can solve this.

x is our hydronium ion concentration. So we can plug that in and get an answer. But now I want you to tell me how many sig figs this has. And to do that, you have to figure out how many sig figs were actually in this number here. So you have to go back and look at the problem and figure out the total number of sig figs.

See how easy that was to fix? So it is two, because this had two, and the concentration was limiting here to two significant figures. So there were two here, which means there are two after the decimal point here. And I have to say I was looking a problem set 7, and some of those problems are just like if you love significant figures, they're a joy because you've got adding and subtracting. And then you had division, and then you have logs.

It is the triple whammy of sig fig love-- so two after the decimal point. So we have 0.1. We have a pH that's acetic. That's good because at the beginning, all we have is a weak acid. So we have a pH of 2.38, so that's point A.

So now let's look at this region here in the buffering region. And again, the buffering region is when you have added volumes of your acid that are greater than zero but less than the volume needed to reach equilibrium. And so in this particular problem, we're going to calculate what happens when 5 mLs of our strong base are added. So this is basically point B here. And because it's a strong base, it's going to react with all of the same number of moles of our weak acid.

It's much stronger than the conjugate base. So it's going to react pretty much completely with this. So we can write out that the weak acid plus our base are going to be converted over to the conjugate base of this weak acid. So we can just figure out the moles and then subtract them to understand how much is left and how much is being formed.

So first, then, we need to figure out how many moles we had initially. So for our acid, we had 25 mLs of 0.10 molar. So we have 2.5 times  $10^{-3}$  moles. For our hydroxide, our strong base, we've added 5 mLs. And it was a 0.15 molar solution. So we 0.75 times  $10^{-3}$  moles.

So now there's going to be this reaction. So we want to think about what happens after you have the reaction of the strong base with the weak acid. And so just to emphasize this point, say we have 8 moles of our acid here and we added just 1 mole of our strong base. That will react, pull off, deprotonate, and form water, and form the conjugate base.

So net we had eight. We added one of the strong base. So we have seven left. And we've formed one of the conjugated base. And so I'm just showing this here because so often on exams, I see people just plug the initial moles into the later part, and they forget that there's a reaction happening. And so I was hoping if I would show this, I'm going to get people used to thinking about, OK, I'm adding strong base. What's happening? How much is being converted? And if you're not subtracting things, there's a problem with the way you're doing the problem.

So here, these are less easy numbers to visualize.  $2.5 \times 10^{-3}$  moles, how much we had of our weak acid. We have added a strong base at  $0.75 \times 10^{-3}$ . So we have  $1.75 \times 10^{-3}$  moles of our acid left. So we subtract the amount that's converted due to the addition of the base. And so why don't you tell me how much, then, we're going to have of our conjugate base being formed.

So I kind of tried to fool you there. But 70% of you were not having it. So here, it's going to be equal to the number of moles of a OH that's added because that's how much is going to be converted. That's how much of the conjugate acid is converted to the conjugate base.

Now, we have moles. We need molarity if we're going to use a  $K_a$  to solve the problem, because the expression for equilibrium constant has molarity, not moles. So then in converting to molarity, the thing you have to remember is the volume.

So we had 25 mLs to start with, and now we've added 5. So we need to make sure that we have the correct number of liters in our expressions. So we can calculate  $1.75 \times 10^{-3}$  moles for our weak acid, volume concentration of weak acid. We have  $0.75 \times 10^{-3}$  of our conjugate base. And then we have a concentration there.

Now, there are two ways to solve this problem. And option one uses  $K_a$ . It doesn't involve Henderson-Hasselbalch. Option two will involve Henderson-Hasselbalch, and it's OK to use this because this is a buffer problem.

So option one now for calculating point B-- so we can set up this expression. And always remember you're talking about molarity here, so don't put in your moles in this expression. Only put in molarity. So that's why the volume's really important.

So we can put in our concentration 0.0583, and it'll be minus  $x$  for equilibrium plus  $x$  for our

hydronium ion concentration and also our concentration of the conjugate base  $0.0250 + x$ . So this is like a buffer problem, using option one. And so we can use  $K_a$ , plug in our values. Here we have our conjugate base concentration at equilibrium times our hydronium ion,  $x$  over the equilibrium molarity of our weak base.

We can, again, assume  $x$  is small, which drops out the plus  $x$  and the minus  $x$ . We solve for  $x$ . We get  $4.13 \times 10^{-4}$ . We can check the assumption. And sure enough, it's much smaller, 1.7%, 0.7% of these two. And you really only need to check one.

The smaller one-- assumptions OK. And we can calculate then by putting in  $x$ , which is hydronium ion concentration, into the equation  $\text{pH} = -\log$  of the hydronium ion concentration equals the  $\text{pH}$  3.38. We can also use Henderson-Hasselbalch, because it's a buffer problem. It's allowed.

You were given the  $K_a$ . You can calculate  $\text{p}K_a$  minus the log of  $K_a$  and put that number in, put in the concentrations that you determined. So you still need to subtract the moles. You can skip that step. But you can skip the volume step. Because when you use Henderson-Hasselbalch, the volume would cancel out if you had moles per volume moles per volume. The volume's the same.

So you can skip the calculating molarity step here-- that simplifies the problem-- and solve. And you should get the exact same number, or something was wrong. Both of these should work equally well-- 3.38.

But you'll often be asked to check the Henderson-Hasselbalch assumption. And remember there was an assumption here, because we solved the Henderson-Hasselbalch from an equation that use  $K_a$ , the equilibrium constant. So really this expression is at equilibrium, but we're plugging in values that are not at equilibrium. They're the initial values that we're putting into this equation.

So we still need to check, and we're using the 5% rule. So to check the Henderson-Hasselbalch, then, we have to back calculate  $\text{pH}$  of 3.38 equals a hydronium ion concentration of  $4.2 \times 10^{-4}$ . And then you want to check that that number is less than 5% of the smaller number. And we checked that assumption when we looked at option A. So it's still good for option B. And we can use the HendersonHasselbalch.

Now, if it was greater than 5%, then you can only use option one. And you must use the

quadratic equation. But this doesn't happen very often because a buffer is usually not a very good buffer if  $x$  is not small. A buffer's a good boss for when you have a weak conjugate acid pair. And when you have weak conjugate acids and bases, then usually  $x$  is small. It doesn't ionized much in water.

So most of the time these assumptions hold. But if you're asked to check an assumption, that's what you need to do. So we have point B two ways, and we got the same answer. It's 3.38. And that's point B, and we're in the buffering region there.

What about point C? Point C is the half-equivalence point. So let's think about what the pH would be at the half-equivalence point. So at the half-equivalence point, by definition, you've added half the number of moles you need to reach the equivalence point, or half the volume of the strong base that you need to reach the equivalence point. And at this point, the number of moles of your weak acid equal the number of moles of your conjugate base.

So when that is true and we look at the Henderson-Hasselbalch expression, we see that this term becomes 1, and so therefore pH equals pKa. So if you weren't given the pKa and you were just given the Ka, that's no problem because you can calculate it-- minus log of Ka. And so that's minus log of  $1.77 \times 10^{-4}$  for this problem, which gives us a pH about 3.75.

So if you were just given the pKa, which is for this 3.75, and it's really not much more significant than that, honestly. And there actually not a lot of significant figures when it comes to measuring pH or pKa's. If on a test it said, the pKa of this is 3.75. What is the pH at the half-equivalence point? You could write down 3.75 and nothing else.

You do not need to prove to me that this expression here is true at the half-equivalence point. It's just a way to ask a question that tests your knowledge of titrations. So this is a good problem that involves very little work, so you should be extremely excited if I'm asking you about the pH at a half-equivalence point, because that's going to be a real easy problem.

Don't spend a lot of time on it. So we got point C, 3.75-- very close. We're sort of in this region where the pH is changing not that much. So that's the end of that lecture. But the beginning of the next one starts where we left off. As I said, acid base titration problems take a long time. They're in two handouts, and we're just going to continue now with the next handout and point S, the equivalence point.