JOCELYN: Hi. Jocelyn here. Today, we're going to go over fall 2009 final exam problem number five.

As always, we're going to start by reading the question. The skeletal structure of the amino acid alanine is given below as it exists in its neutral zwitterion. To the right is shown its titration curve in aqueous solution. The abscissa expresses concentration in terms of degree of protonation so that a value of 0.5-- that the neutral ion is the only species present. At a value of zero, alanine is totally deprotonated and at a value of one, alanine is totally protonated.

So let's move to part A. What is the hybridization of each of the three carbons in alanine? So to begin with this one, I would start by rewriting the structure of alanine because as it's written now, it's not as clear what the hybridization of the alpha, beta and gamma carbons are. So starting with the alpha carbon, connecting the beta carbon-- and here is the gamma carbon-- and of course, we don't want to forget the amine group.

So this looks fairly similar to what is on the page, but I've kind of expanded the structure so that it's more straightforward for us to determine the hybridization. The alpha carbon is the central carbon here and we see that it has four bonds and four electron domains. If we go back to the beginning of the class, we learned that when you have four electron domains around a central carbon, we have Sp3 hybridization.

Going to the beta carbon here, we see that it also has four bonds, but one of them is a double bond to oxygen. So we need to remember from our earlier lessons that the double bond only counts as one electron domain. Therefore, this carbon has three electron domains. And going back to our hybridization rules, we know that this gives us an Sp2 hybridization.

Lastly, we have our gamma carbon and it gives us one, two, three, four bonds and four electron domains. Therefore, our gamma is also Sp3 hybridized. This problem on the final was dealing with first beginning material, but then in part B and C, we're going to move on to the material we've learned more recently.

So moving to part B-- we are now are dealing with the titration curve that is given to us. So this looks hopefully fairly similar to what is on your page and the question-- it's asking us to indicate on the titration curve-- one, the PKA for protonation of the zwitterion. Two, the PKA for deprotonation of the zwitterion. And three, the isoelectric point.

So before we start that, let's talk a little bit about this titration curve here. What is it showing us? What is it depicting? What I like to do is-- we see that we have two buffered regions. That right off the bat should tell you that there are two different equilibriums going on. There are two different protonation/ deprotonation reactions. So I'm going to split this right down the middle here. And that way we can think about the two protonations/ deprotonations separately.

So on the left side here, we have the more acidic portion of our titration curve and even if you didn't quite understand his description of the abscissa, we know that because this side-- the solution has a lower Ph, it's going to be dealing with the more protonated species of the alanine. This-- on the right side, we have the higher Ph, so we're going to have a more deprotonated alanine on this side. And he already told us that we had the zwitterion in the middle. So next to 0.5, we're going to write a generic term for a neutral acid. If we look back to our structure, we see that we have-- the neutral zwitterion has one acidic proton here on the amine group and it has a neutral charge. So that's why I'm going to depict that zwitterion as HA

Moving to the left, more acidic portion of the titration curve, we have-- we know that there's a protonation going on. So I'm going to write that as H2A plus because whenever we add a proton, we're adding a positive charge.

And then, at the more basic side, we have doubly deprotonated alanine and so we have just our backbone, which I'm going to call a and a negative charge.

So from the question, we should know that this is true, correct? Because he told us that we have the totally protonated alanine on the left side. We have the zwitterion in the middle at 0.5 and we have the totally deprotonated on the right side.

OK. What else can we know from this titration curve or what can we add to it so that we can understand it a little bit better? Well, let's write down the equilibrium reactions that are happening that make this buffer region here. On left side, we have the doubly protonated alanine going to proton plus the zwitterion. And that's what's creating this buffered Ph region. On the right side here, we have the zwitterion in equilibrium with-- again, a proton and the doubly deprotonated alanine.

These are things that are true for any titration curve you see. Depending upon the number of protonations-- the number of times a buffer region might change, but for each buffered region, you can always determine an equilibrium constant that is causing that stability in Ph.

OK. Now let's go to the question. We need to indicate on the curve the PKA of both this equilibrium equation and this equilibrium reaction. So to do that, we hopefully will remember the Henderson-Hasselbalch equation and that gives us a relationship between the Ph of the solution and the PKA of the acid that's in solution. So writing down

the Henderson-Hasselbalch equation-- we have-- not the Ph-- and this is the same equation that Professor Sadoway derived in lecture. And here, I've written it in the most generic form, but no matter what our equilibrium species are, we just know that we put the more basic species on top and the acid that got deprotonated on the bottom.

So for the first point of this, we are looking for the PKA of the protonation of the zwitterion. So we know that it's an equilibrium between the doubly deprotonated and the zwitterion. That is the equation we're looking at.

So let's write down our Henderson-Hasselbalch for that and I'm going to call this PK1 just to keep them separate. Remember here, my Ha is on top because we have-- our doubly protonated species is the acid in this case. Now in order to put on the titration curve where the PKA is, we look at the Henderson-Hasselbalch equation and see that where the Ph equals the PKA is when the concentration of the acid and its conjugate base are equivalent. because if Ha equals H2a plus, the log term goes to zero and we have our Ph equals PK1.

Going back to the titration curve, we see that the concentration between H2a plus and Ha is equal right in the middle. We can assume that this is a to-scale concentration abscissa here. And so there we go up and we can say, OK, this point on the titration curve here corresponds to our PK1.

So from the Henderson-Hasselbalch equation, we can see that given the titration curve, this is where our PK1 is and it's about two. For our purposes, that's-- we weren't asked to estimate it, but if I had to, I'd say it's around two.

Now we have to do the same thing for the other side of the titration curve. So if you haven't done that already, maybe you can stop now and try that on your own because it's the same process. OK. So it's do of the second one-- which again, is just the Ph is equal to the PKA when the two species are equal, except for now we have different species. So basically we're looking for-- our new Henderson-Hasselbalch equation is-- with using the new equilibrium reaction, our doubly deprotonated alanine is now on top and our zwitterion is on the bottom. So this might be a little confusing because we have the same species going from the top to bottom in our Henderson-Hasselbalch equation, but remember that we're always talking about the acid is in the denominator and the conjugate base is in the numerator here. But either way, we again want to look for where the Ph equals the PK2 and so our zwitterion concentration will equal our doubly deprotonated alanine. And that occurs right here.

So the last part of this question is to indicate where the isoelectric point is and the important thing for this part of the problem, of course, is to know what the isoelectric point meets-- and it's where the dominant species in the solution is the neutral zwitterion. And Professor Sadoway already told us where that is and it is where we're at 0.5 here, which we've already indicated as where the zwitterion is dominant. And so we just can go up here and circle that and we can call that number three.

So you didn't have to go through all of the work I did and if you were familiar with the titration curve, you could have simply put these down, but understanding where these points come from is quite important for understanding acid base chemistry and how amino acids work.

All right. So let's move to part C. In part C, we're asked to draw the skeletal structure of alanine when it is solvated in an aqueous solution at extreme acidity-- ie, Ph less than one. So I'm going to write that down and then we can go back to our titration curve and see where that is because we've already spend a lot of time understanding our titration curve and that tells us a lot about the acid base chemistry of alanine. So at the titration curve, we see that at a Ph less than one, we're going to have mostly our doubly protonated zwitterion.

That said, now we need to go back and look at the structure of alanine and we can put in the protonation. So we're given the zwitterion form of alanine, but at very low acidity-- sorry-- high acidity, low Ph. This carboxy group is going to be protonated. And so we have both of our acidic protons are on the alanine and this would be a structure of alanine at a Ph less than one.

Now moving to part D-- we are asked for an aqueous solution of alanine-- calculate the ratio of the concentration of neutral alanine zwitterion to the concentration of deprotonated anion when the Ph is 8.091. So a couple things I would write down. Ph equals 8.091 and we are asked for the ratio of the concentration of the zwitterion to the doubly deprotonated anion. When we're asked for this, hopefully you think first, Henderson-Hasselbalch-- I can use that. We're given a Ph. We can find the PKA and we're asked for the ratio and concentrations.

So let's write down the Henderson-Hasselbalch equation again. And because we're asked for the ratio, we don't need any more information except for the PKA. Luckily, from part B, we know what the PKA is of this equilibrium between the zwitterion and the doubly deprotonated anion. So moving back to your titration curve, we see that the PKA is roughly 10-- doesn't need to be our-- our estimation doesn't need to be exact, but if it's in the ballpark range, then you have the right idea. So I'm going to write that. We can plug that in just down here. Log of our concentration. That's a log term.

And from here, it's just algebra. So simplify a little bit. If we bring the 10 over to this side, we get -1.909 equals the log of a minus over-- I'm sorry. I'm getting a little bit crooked here. And then if you take both sides of the power of 10, we'll get-- the ratio equal to this. And if we take the reciprocal of this, we'll get a nicer answer. We'll get HA over A minus and it won't be a fraction over here. So I suggest that you do that and you'll see that our final answer is-- let's put it right here. 81.1:1-- the ratio of our zwitterion to the doubly deprotonated anion. And then you've answered all parts of the problem.