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5.111 Principles of Chemical Science, Fall 2008 Transcript – Lecture 24

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PROFESSOR: Please settle down and take a look at this question. OK, let's take 10 seconds. I think that it's a simple math mistake is between one and two at least. So, the trick here is you know the p h and the p k a and you want to find the ratio so you can subtract and do the log. So maybe we'll have this question later or something similar and we can try this one again.

So we're going to talk about buffers again today.

I just feel the need to take a moment and reflect on the historic events of the last 24 hours, and talk about how it will affect chemistry. So some of you may have voted for the first time. Some of you may have worked on a campaign for the first time. Some of you may have been very active in a campaign for the first time, either for Obama or McCain, that you got involved. And I thought just to put this election in a little bit of the historic perspective in terms of about being an undergraduate student or a student and working on a political campaign or being part of a political movement.

So, my father was very active as a political student activist. But the difference between some of you and my father was that he was a political activist at the University of Hamberg in Germany in the 1930's in Hitler's Germany. So he was the leader of the left wing student organization. That was something that put one's life at risk to take on that role at that time.

So, things were heating up a little bit and the gestapo were discussing some of the activities with the left wing student leaders at college campuses in Germany. And some of them, after the discussions, no one knew where they went, they seemed to disappear. Now my father was very concerned about this and he decided to lay low for a while, and so he thought I'll do a semester at another university. And he told his parents that if the gestapo came looking for him, that they should send him a telegram saying "Your Aunt Millie is sick." Since he did not have an Aunt Milly, he knew that that would mean get out now.

So he went to another university and he was doing a semester there, and someone he knew told him you really need to go into hiding. But he didn't really trust this person, so we packed a bag with a few clothes and some toiletries, but he didn't actually leave. Then the next day he came home and there was a telegram under his door. So, you can guess what the telegram said. He grabbed the bag that was already packed and headed down the stairs.

The gestapo was coming up the stairs. My father's name was Heinz Leopold Lushinski and the gestapo said to him, "Do you know Herr Lushinski? And my father said, "Yes, of course, he lives on the top floor." The gestapo went up, my father went down, and he didn't go back to Germany for 30 years. So he came to the United States as a political refugee and became a citizen. He voted in every election, every possibility, he was very, very active. My family was very, very active in politics. He gave money every year to the American Civil Liberties Union to protect civil liberties, and he also gave money to the American Rifle Association. He always liked to have a plan b.

So, it was sometimes a little humbling to be the only child of this man. He was in his 50's when I was born, and I thought how can I live up to something like this? Am I ever going to risk my life for what I believe in. If given that choice would I do the right thing? And I don't know if I'll ever get an answer to that question, but I talked to my father about this and he said all I need to do is work hard, find something that I love doing, some way that I can contribute, and that's what's really important -- contributing is really important.

So I was drawn to teaching, and I love teaching here at MIT because you all are so talented and smart, and it is really an honor and a privilege to be involved in your education. But I feel that in the last 24 hours, we have all received an additional call to service. That president elect Obama said in the campaign that his top priorities are going to be scientific research, coming up with clean energy technologies, and improving healthcare. He called to scientists and engineers. And last night the American people said yes, we like that vision, and they elected him president. So we have been called, you have been called, he has reached out to students and said, students of science and engineering, you need to contribute. And it's been a while since any president has really called to action, scientists and engineers. And last time that happened, a man went on the moon. So let's see what we can do this time.

The next challenge is clean energy, healthcare. It's going to be really important for sciences and engineers to get involved, and at the core an energy technologies, and at the core of medicine is chemistry. So you are in the right place right now. You are going to be the generation that needs to solve these problems, because if you don't solve the energy problem and don't come up with clean alternatives, there isn't going to be much of a planet left for another generation to try to solve those problems. So it's going to be your job and your job is starting right now with the education that you can get at MIT.

So, it's actually somewhat interesting that today, the day after this election, we are going to talk about one of the units that students in this class have had the most difficulty with over the years, acid based titrations. This has been the undoing of some chemistry individuals. It has been the undoing of some grades of A. It has been the undoing, perhaps, of some interest in chemistry. But I would like to say today, at this moment, it will not be your undoing, it will be your triumph.

Every year I challenge students to do the best job on acid based titration ever, and people have been doing well. This might be the last time I teach in the fall. You have actually had the highest grades so far in this class, in the history of the class that I know of, and so this is the challenge. So right after this election, your challenge is to conquer chemistry starting one acid and one base at a time.

So, ready to do some acid based titrations? Who are the naysayers in this crowd? Just a few people up there. All right. I have to tell you that what I'm going to tell you about acid based titrations will seem like it makes pretty good sense as I'm saying it. But often, people inform me that when they actually go to work the problems on the test, it's a little less clear on what they're supposed to be doing. So the key to acid based titrations is really to work problems. And so we have, for your benefit, assigned problems for the problem-set due Friday. And so after today, you should be set to do all of the problems on the problem-set. And in terms of acid based titration, you will need a lot of this knowledge again in organic chemistry, biochemistry, if you go to medical school -- I used to TA medical students, they didn't know how to do this. And I said "Who taught you freshmen chemistry?" So it's good to learn to this now here today, work problems, take the next test, and guaranteed it'll be on the final again. So you'll learn it now, you'll get lots of points, both on the final and the third exam.

All right, so acid based titrations, they're not that hard, but there are not a lot of equations to use, and I think that people in chemistry are used to what equation do I use. No, it's really about thinking about what's going on in the problem, and as the problem proceeds, as more, say, strong base is added, the problem changes. So it's figuring out where you are in the titration and knowing what sort of steps to apply.

So here are some titration curves, and one thing you may be asked to do is draw a titration curve, so you should be familiar with what they look like. So we talked last time about strong acids and strong bases. So if you have a strong base, you're going to have a basic p h, and then as you add the strong acid, you will go to the equivalence point, equivalence point when you've added the same amount of moles of acid as there is base or base as there is acid, equal number of moles. And when you mix a strong acid in a strong base, you form a salt, and the salt is neutral in p h, because the conjugate of a strong acid or a strong base, is ineffectual, it doesn't affect the p h, it's neutral. So we have p h 7, and then you continue to add, in this case, a more strong acid, and the p h goes down. So for the other titration it's pretty much the same, except you start at acidic p h's, go up to neutral p h, and then go basic.

So we talked about these last time and we worked a couple of problems, but now we're going to move into the slightly more difficult type of problem, which has to do with when you have a weak acid or a weak base being titrated. So let's look at the difference of the curve to start off with. So here we have the strong acid and the strong base, and here we have a weak acid and a strong base. One thing you may notice right off is that the equivalence point has a different p h. So, a strong acid and strong base again, mix, you form a salt that's neutral, p h 7. But if you're titrating a weak acid in a strong base, the conjugate of the strong base will be ineffective, but the conjugate of the weak acid will act as a base. So the p h then, at the equivalence point, when you've added equal number of moles of your strong base as you had weak acid, then you'll have the conjugate base around, and the p h will be greater than 7.

So in working the problems, if you get an answer with this type of titration problem that's different than that for p h at the equivalence point, you're going to know that you did something wrong, you need to go back and check your math.

Another big difference has to do with the curve shape down here, and so you notice a difference over here than over there. And in a titration that involves a weak acid in

a strong base, you have a part of the curve that's known as a buffering region, and the p h is fairly flat in this buffering region as shown down here. So that's in contrast, there's no such buffering region on this side. So here the p h will go up, it'll level off, and then go up again. And this, for some of you, is probably the frustration in doing acid based titrations in lab, because you're adding and nothing's happening and nothing's happening, and you're in this region, then all of a sudden you add just a little more and you're up here.

So notice how steep that is over here. So sometimes when you're in the buffering region, it seems like you're never going to reach the end of the titration and then it'll happen all too quickly. So buffering region, remember a buffer is something that has a conjugate, weak acid and weak base pair, and then in a buffering region, the p h pretty much stays fairly constant in that region. It acts as a buffer, neutralizing the p h, maintaining the p h by being a source or sink of protons, and so here the p h then is staying constant in that buffering region. So those are some of the differences between the type of curves.

Another point that I will mention or term I will mention that has to do with weak acid in strong base or a weak base in strong acid is this 1/2 equivalence point concept. So 1/2 equivalence point you've added 1/2 of the amount of strong base that you need to get to the equivalence point, and that's right in the middle of that buffering region. So that's another point where you'll be asked to calculate the p h.

So now let's look at different points in a titration. So, first let's walk through and just think about what is happening. So when we start in this titration of a weak acid in a strong base, before we've added any of the strong base, all we have is a weak acid. So it is a weak acid in water type problem. And so here I've drawn our acid, and the acid has its proton, which is going to give up when you start doing the titration. So that's what we have at zero volume.

Then we start adding our strong base, and the strong base is going to react with the acid, one-to-one stoichiometry, it's a strong base. It'll pull off protons off the same number of moles of the strong acid as the number of moles of the strong base that were added. And so then, you'll start to have a mixture of your conjugates, your weak acid and your conjugate base. So the base is a minus here. And so if you have a mixture of a weak acid in its conjugate base, that's a buffer, and so you'll move in to the buffering region here. So that's at any volume that is greater than zero and less than the equivalence point is going to be around in that region.

Then we have a special category of the buffering region, which is when you've added the volume to get to the 1/2 equivalence point. And when you've done that, you will have converted 1/2 of the weak acid it its conjugate base, so you'll have equal number of moles of your weak acid as moles of the conjugate base -- 1/2 has been converted. And so that's a special category right there.

Then you get to the equivalence point. At the equivalence point, you've added the same number of moles of strong base as the number of moles of weak acid you have, so you've converted all of your weak acid to it's conjugate base. So all you have is conjugate base now, and so that's controlling the p h, so the p h should be greater than 7. So that's a weak base in water problem.

And if you keep going, then you're going to end up with a strong base in water problem. The weak base will still be around, but it will be negligibly affecting the p h

compared to the fact that you're dumping strong acid into your titration. And so that's this part of the curve.

So you see that in one type of problem, one titration problem, you actually have a lot of sub problems, or sub types of problems, you'll have weak acid buffer, special category of buffer, a conjugate base or a salt issue, and then a strong base. And this is one of the things that people have trouble with in the titrations, because we may not ask you to do all the points, we may just sort of jump in somewhere, and say okay, what is the p h at the equivalenced point, and you need to think about what's happened to get to the equivalence point. Or we may jump in and ask you about a region that would be in the buffering region, and you have to remember that at that point you should have some of the weak acid and also some of the conjugate bases being formed.

So, it seems like there are a lot of different things, but there are only five types of problems. But in a titration curve, you run into a lot of those different types at different points in the problem.

So now let's go the other direction and consider titration of a weak base with a strong acid. So here's what that curve would look like. You're going to start basic, of course, because you're starting with a weak base, you haven't added any strong acid yet. As you add strong acid, the p h will decrease. Because it is a weak base, you will be forming some of its conjugate as you add the strong acid, and so you'll go through a buffering region again where the curve would be flat, where the p h will be pretty much the same for region of time. Then the curve will drop again and you'll get to the equivalence point. At the equivalence point, you've added the same amount of moles of strong acid as you had weak base, so all of your weak base is converted to its conjugate acid, and so you should be acidic at the equivalence point, and then the curve goes down.

So again, we can think about this in terms of what is happening. In the beginning it's just a weak base in water problem, but as you add strong acid, you were pronating some of your base and forming its conjugate acid here, and you're in the going to be in the buffering region. Then at the 1/2 equivalence point, you've added enough moles of strong acid to convert 1/2 of the weak base to its conjugate, so those are going to be equal to each other -- the number of moles of the weak base and the number of moles of its conjugate acid. At the equivalence point, you've converted all of the weak base you started with to its conjugate acid, so it'll be a weak acid in water problem, and then at the end it's strong acid.

So the trick is to recognizing what type of problem you're being asked to do, and a lot of times if people get a question and they just write down OK, at this point in the titration curve, it's going to be a weak base in water problem. And just writing that down, most of the time if you get that far, you do the rest of the problem correctly. So just identifying the type, there are only 5, of problems gets you a long way to getting the right answer.

So let's do an example. We're going to titrate a weak acid with a strong base. We have 25 mils of 0.1 molar acid with 0.15 moles of a strong base, n a o h, we're given the k a for the acid. First we start with mils of the strong base added. So what type of problem is this? It's a weak acid problem.

So we know how to write the equation for a weak acid or for an acid in water. We have the acid in water going to hydronium ions and a conjugate base. So weak acid. For weak acid, we're going to use our k a, and we're going to set up our equilibrium expression. So here we have 0.1 molar of our acid. We're going to have some of that go away in the equilibrium, forming hydronium ion and some conjugate base, and so we know we have expressions for the concentrations at equilibrium. And we can use our k a, k a for acid, it's a weak acid problem, and we can look at products over reactants.

So, see, now we're doing a titration problem, but you already know how to do this problem because we've seen a weak acid in water problem before. So we have x squared over 0.10 minus x here. We can assume x is small, and get rid of this minus x, and then later go back and check it, so that just makes the math a little bit easier. And we can solve for x and then we can check -- we can take this value, 0.00421 over 0.1 and see whether that's less than 5%, it's close but it is. So that assumption is 0K. If it wasn't, what would we have to do? Quadratic equation.

All right, so now, here's a sig fig question. Tell me how many sig figs this p h actually has. OK, 10 seconds.

So, in the first part of the problem we had a concentration that had 2 significant figures, the 0.10 molar. Sometimes later, people have extra significant figures that they're carrying along, but we had those 2, and so we're going to have 2 after the decimal point then in the answer of the p h. So again, the number of significant figures that are limiting are going to be the number after the decimal point.

All right, so we have one p h value, and now we're going to move on. So let me just put our one p h value down. We have volume of strong base, and p h over here, and we're starting here with zero moles added. We have a p h of $2 \cdot 38$. It's a weak acid, so it should be an acidic p h, which it is.

All right, so now let's move into the titration problem, and now 5 . mils of the strong base have been added, and we need to find what the p h is now. So it's a strong base, so it's going to react almost completely, that's our assumption. If it's strong, it goes completely. And so, the number of moles of the strong base that we add will convert all of the same number of moles of our acid over to its conjugate. So we can just do a subtraction then.

So first, we need to know the initial moles of the acid that we had. We had 25 mils, 0.10 molar. We calculate the number of moles for the hydroxide added, we added 5 mils, it was 0.15 molar, and so we can calculate the number of moles of the strong base that were added. So the strong base will react completely with the same number of moles of the weak acid. And we're going to do then -- we have the moles of the weak acid here, minus the number of moles of the strong base we've added, and so we're going to have 1 . 75 times 10 to the minus 3 moles of the weak acid left. So, then how many moles of the conjugate base will be formed by this reaction? What do you think?

Same number. So 0.75 times 10 to the minus 3. So always remember that in these titration problems, nothing has been added yet, you're at zero mils added. Some amount of some subtractions are going to have to occur because something has happened. You've converted something, things are different than when you started.

All right, so now we have weak acid and we have moles of its conjugate, what type of problem is this? If you have a weak acid and its conjugate base -- buffer, right. So we're going to do a buffer problem and we need to know the molarity first. So we have moles over volume -- again, the volume, you had 25 mils to begin with, you added 5 more. So you have to have the total volume 30 mils, and we can calculate then the concentrations of both.

Now we can set up our equilibrium table, and this looks like a buffer problem because it is, and by looking like a buffer problem you something over here, you have your weak acid over here, but you have something over here now, it's not zero now, we're starting with some conjugate base. So we have 0.0583 minus x on one side, and we 0.025 molar plus x on the other side.

We can use k a again. This is set up as an acid in water going to hydronium ions and conjugate base, so we can use our k a, set things up, and we can always say let's see if x is small, make an assumption, check it later. That'll simplify the math. So we get rid of the plus x and the minus x. Again, we're saying that if x is small, the initial concentrations are going to be more or less the same as the concentrations after the equilibration occurs. And we can calculate $4 \cdot 13$ times 10 to the minus 4, as 4, that is a pretty small number. And we have to check it, and yup, it's small enough, it's under $4 \cdot 13$ times $4 \cdot$

So now we can plug this in. X is our hydronium ion concentration minus log of the hydronium ion concentration is p h, and we can calculate p h to 3 . 38 -- again, we're limited by two significant figures in the concentration. So now we've added 5 mils down here, and our p h has gone up a little bit, it's now at 3 . 38 over here.

There's another option for a buffer problem. What's the one equation in this unit? Our friend Henderson Hasselbalch. And yes, you can use that here too, assuming that you check the assumption and it's OK. Most people will prefer to do this because it is a bit easier. So, you weren't given, though, the p k a in this problem, you were given the k a, so pretty easy to calculate -- minus log of the k a is the p k a. So you can calculate that, put that in. You have your concentrations and it should be concentrations, but you may notice that if you actually had moles the volume would cancel here. So here are the concentrations, but with the same volume, the volume term does cancel. It makes this a little faster and it gives the same answer, which is great. To use Henderson Hasselbalch you also need the 5% rule to be true, because Henderson Hasselbalch is assuming that x is small. It's assuming that the initial concentrations and the concentrations after equilibrium are about the same.

So we can check the assumption. We can back-calculate the hydronium ion concentration, which would be x, and see if it's small, we already know it is, so it's OK. So there are 2 options for buffer problems, but do not use the Henderson Hasselbalch equation when it isn't in the buffering region, it doesn't hold then.

So again, you check the assumption, and if it's OK, it's fine. If not, you need to use option one and you need to use the quadratic equation.

All right, so buffering region. Now we're at the special kind of problem in the buffering region, the 1/2 equivalence point. So here you've added 1/2 the number of moles of the strong base to convert 1/2 the moles of the weak acid to its conjugate. So at this point, the concentration of h a equals the concentration of a minus -- equal number of moles in the same volume, those are equal. You can use Henderson

Hasselbalch here, and find that if they're equal, you're talking about minus log of 1, so the p h is going to equal the p k a. And you're done with this type of problem.

I have been known to put 1/2 equivalence problems on an exam, because exams are often long, you have only 50 minutes, there's lots of different type of problems, and this problem should not take you a long amount of time. You do not have to prove to me that this is true. All you need to remember, 1/2 equivalence point, p h equals p k a, and if you calculate the p k a, you're done. So this is a short type of problem. If you remember the definition of 1/2 equivalence point, it's easy to do. So now we have another number, so 3.75, and we're working on our curve.

Now let's move to the equivalence point. At the equivalence point, you've added the same number of moles of your strong base as you had weak acid. So you've converted all of your weak acid to its conjugate base. So the p h should be greater than 7. Now all you have is conjugate base, that's basic, p h should be greater than 7.

So when you are doing this titration, you have your weak acid and your strong base. You're going to be forming a salt here, and a salt problem, you can tell me about salts. And so, just remind me, what does the n a plus contribute to the p h here. It's going to be neutral. And what about this guy down here? Yeah, so it's going to be basic. So, the sodium, anything group 1, group 2, no effect on p h, they're neutral. But if you have a conjugate base of a weak acid, that's going to be basic. Salt problems, really just part of what you already know about.

So always check your work. If your p h doesn't make sense from what you know, you might have made a math mistake. So let's calculate the actual p h at the equivalence point. We know that it should be basic, but what is it going to be? So first, we need to know how much of the strong base we had to add, because we need to know about all the moles. So how much of this did we need to add.

So we needed to add enough of the strong base that you converted all of the moles of the weak acid to its conjugate. So we had 2 . 5 times 10 to the minus 3 moles of our weak acid. So that's all going to be converted to the moles of the conjugate base, and so that's going to be equal to the number of moles we needed to do it. So we needed 2 . 5 times 10 to the minus 3 moles of our strong base to do that complete conversion. We know the concentration of the base was 0.15 . So we would have needed 1 . 67 times 10 to the minus 2 liters of this concentration added to reach the equivalence point.

So then the total volume that we're going to have at the equivalence point is the 25 mils that we had to begin with, plus this 16 . 7 mils to make this final, total volume. And remember, you always need to think, what is the total volume, how much has been added to get to this point in the titration curve. Then we can calculate molarity, so we know how many moles of conjugate base have been formed, and we know the new volume, so we can calculate the concentration of the conjugate base.

So now, you can help me solve this problem. Set up an equation for me to solve it. Let's take 10 seconds. That's the best score we've had today. Yup. So now we're talking about a conjugate base. So we have converted all of the weak acid to the conjugate base, and so it's a weak base in water problem, so we're going to talk about a k b. If you were only given the k a for this problem, how would you find k b - what interconnects k a and k b? K w, right. So you can calculate, here it's given to

you, but you could calculate it if you had a calculator, and you would find that this is true. Now it's a weak base in water problem. We're not in the buffering region anymore. We've converted all of our weak acid to the conjugate. So it's a weak base in water problem. So we have x squared, 0.06, that was the concentration we calculated, minus x.

So again, think about what type of problem it is. So again, weak base in water problem -- x squared over 0.06 minus x. And we can assume that x is small, and calculate a value for x, which is 0.83 times 10 to the minus 6, and then we're going to calculate p o h, because now x is the hydroxide ion concentration. Because in a weak base in water problem, here in this type of problem, the base, and here is your acid -- the conjugate of this acid is the base, hydroxide, and the conjugate of this weak base is its conjugate acid over here, so now when we are solving for x, we're solving for hydroxide ion in concentration, so we're calculating a p o h, which then we can calculate a p h from. So we can take 14 minus 5 . 74 and get our value. And it's bigger than neutral, it's 8, it's basic, and that makes sense, it is a weak base in water problem. So, let's see, it's 8 . 26, so now we're up here in our curve, and we're at 8 . 26, and that's going to be greater than 7 for this type of problem. So that makes sense, it's good. Greater than 7 is what we want to see.

So now, you've gone too far -- you've passed the equivalence point, and you keep adding your strong base in. Now you still have some of the weak conjugate base around. So you still have this around, but you only have 1 . 83 times 10 to the minus 6 molar of it. So very little amount -- x is small. So your p h is going to be dictated by the amount of extra strong base you're adding. So this is similar, then, to a strong acid or strong base in water problem.

So if you're 5 mils past the equivalence point, 5 mils times your concentration of a strong base, so you have extra, 7 . 5 times 10 to the minus 4 moles extra. So then you need to calculate a concentration of that, and so you remember the whole volume -- you're 5 mils past, you had 25 miles to start with, and you had to add 16 . 7 mils to get to the equivalence point. And you have, that's your total volume, you get a concentration, that's your concentration of hydroxide, it reacts completely, you don't have to do any equilibrium table here. It's going complete, it's a strong base. You could try adding that value of your other weak base to this, but remember, that's times 10 to the minus 6, so it's not going to be significant with significant figures. So you can just use this value -- plug it in to p o h, calculate it, and then calculate p h. And so now we're somewhere up here at p h 12 . 21, 5 mils past. And there we've worked a titration problem.

So let's review what we saw. In the beginning, zero mils of the strong base, we have a weak acid in water problem. We moved into the buffering region where we had our weak acid and the conjugate base of that weak acid. At the equivalence point, we've converted all of the weak acid to the conjugate base, so it's a weak base problem. And then beyond the equivalence point, it's a strong base problem. That's what we've just worked.

So, we can check these all off now. You know how to do all of these types of problems. And there are not that many, you just need to figure out where to apply what. And if you can do that, you're all set, this unit will be easy for you, and you can go through and make me very happy on the exam. There's nothing -- well, there are few things in life as beautiful to me as a perfectly worked titration problem. It really, it brings me joy, and I've had people write on the exam sometimes, "I hope

that my solution to this brings you joy." And I will often write, "Yes, it does," and put a smiley face. Because it really is nice to see these beautifully worked. I know, I'm a little nerdy and geeky, but after yesterday, being smart and a nerd and a geek is cool again.

All right, so let me just tell you where we're going. We have five more minutes, and actually that's perfect, because I can get through some rules in those 5 minutes. So let's do 5 minutes of rules.

Oxidation reduction doesn't have a lot of rules, so five minutes is actually all we need to do that. Oxidation reduction involves equilibrium, it involves thermodynamics. I like it because it's really important for reactions occurring in the body, and acid bases as well -- p k a's are really important to that. And so, between acid base and oxidation reduction, you cover the way a lot of enzymes work.

So let me give you five minutes of rules, and that will serve you well in this unit. Some of these are pretty simple. For free elements, each atom has an oxidation number of 0, so this would be 0. So, oxidation number of in a free element. For ions that are composed of one atom, the oxidation number is equal to the charge of the atom, so lithium plus 1 ions would have an oxidation number of plus 1. Again, pretty straightforward.

Group one and group two make your lives easy. They seem to have a lot of consistent rules. Group one metals in the periodic table have oxidation numbers of 1. Group two metals have oxidation numbers of plus 2. Aluminum is plus 3 in all its compounds. Pretty simple.

Now we get to things that are a little more complicated but still useful, oxygen. Oxygen is mostly minus 2, but there are exceptions to that, such as in peroxides where it can have an oxidation number of minus 1, and if it's with a group one metal, it can be minus 1. Remember, group one, and actually group two here, that's plus 1, always plus 1, always plus 1, always plus 2, and so hydrogen has to accommodate that. So usually plus 1, except when it's in a binary complex with these particular metals that are in group one or group two.

Fluorine, almost always minus 1, or always minus 1 -- other halogens, a chloride, bromide, iodide, also usually negatives, but if they're with oxygen, then it changes. So, here is an example. And in neutral molecules, the sum of the oxidation numbers must be 0. When the molecule has a charge, the sum of the oxidation numbers must be equal to that charge. So, let's do a quick example. Hydrogen, in this case, is going to be what? Plus 1, so it's not with a group one, group two metal here. So what does that leave for nitrogen? And that makes the sum, plus 1, which is equal to the sum of that molecule, so that works. So we might not have known nitrogen, but we can figure it out if we know the rules for hydrogen and we know what it all has to equal up to.

And so, this unit is sometimes a relief after oxidation reduction, because it's all about simple adding and subtracting, it's not so bad.

OK, oxidation numbers do not have to be integers. Example here, you have superoxide, what would its oxidation number be? Minus 1/2.

And those are the rules, and then on Friday, we'll come back and we'll look at some examples.