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Continuing our discussion of acid-base theory, I have just drawn here on the board for you the structure of a popular indicator molecule. Indicator molecules are used for titrations. And titrations will be of focus of today's lecture. This is the indicator molecule, phenolphthalein. It is easier to draw this molecular structure than it is to spell phenolphthalein, but you should know how to do both of these things, or at least recognize them. Now, how do indicator molecules work? Well, during a titration, you are mixing chemicals in a way that leads to a changing pH throughout the experiment. And an indicator molecule like phenolphthalein is, in fact, a Bronsted acid.

And, if you inspect the structure that I have drawn here for phenolphthalein, you should be able to begin to understand just how it is that a molecule like this can serve as a Bronsted acid. If I write out the formula, you will see that we have quite a number of carbons and hydrogens in the molecule. And we have oxygens as well.

Those are the three elements present in a phenolphthalein molecule. And two of the hydrogens in this molecule possess Bronsted acidity that makes them valuable for the function of this system as an indicator molecule.

And what happens is when you have this in solution at low pH, it is in this form. It is neutral.

And then, as you begin to raise the pH, at some point a base that has a lone pair of electrons comes along and takes one of these two protons in a molecule, either this one or this one. Those two protons are equivalent. And what I am now going to draw is a sequence of arrows representing the electronic flow in the phenolphthalein molecule that occurs when H plus is transferred over to the base with its lone pair of electrons.

So, I am starting these arrows at pairs of electrons and I am showing the flow of how they move.

And this is a pretty interesting rearrangement because it is complicated. It is an electronic rearrangement that is transmitted through this molecule such that here in the center, this four coordinate or sp three hybridized carbon, which is bonded to this oxygen, has a pair of electrons that migrates to it.

And, if I draw now the product of this reaction, what you should be able to see quite clearly -- And I am not always explicitly drawing out the lone pairs of electrons on each of the electronegative oxygen atoms in the molecule, but the sequence of double bonds and single bonds in the molecule has been altered in a profound manner because of the base coming along and removing a proton from one of these peripheral oxygens, namely, that one here. So, we have now a singly negatively charged system. And that charge is balanced, over here, by the base that has the proton attached to it.

That is the structure-function relationship that is typical of indicator molecules. And indicator molecules can either be naturally occurring, as they are in some plants.

Or, alternatively, they can be molecules that are synthesized to respond to factors like pH in a given way that might be desired. And, in the case of phenolphthalein, this change takes place between 8.2 to 10.0 pH units. And the color change associated with this is colorless to pink.

Looking at the structure of the anionic form of the phenolphthalein molecule that results from its deprotonation, what you can see is that this sp<sup>3</sup> hybridized carbon atom at the center of the molecule, which in the neutral form is acting as an insulator, preventing the pi-systems of the three six-member rings from communicating, is converted into a three-coordinate sp<sup>2</sup> hybridized carbon atom here at the center, -- and provides a conduit for a communication between the pi-systems of the three six-membered substituted benzene rings that are in this molecule. And that change in electronic structure is what leads to the production of this pink Chromophore in the anionic deprotonated form of a phenolphthalein molecule that is important at high pH.

All you have to do, in fact, is to change the substituents on this molecule in order to get a response at a different pH value. Bromothymol blue is an indicator with a structure similar to that of phenolphthalein, but with a sulfur here in place of this carbon. And in bromothymol blue, we also have some isopropyl and bromine substituents on the aromatic rings. And that modifies its properties such that it goes from yellow to blue as the pH rises above 6.0 to about a value of 7.6.

So, if you go to a textbook and look in a table of indicator molecules, you will be able to select an indicator that is appropriate for a particular type of titration.

And just to give you a very simple schematic of a classic type of titration, I am going to show you here -- -- the type of system that you may need to think about in connection with this next problem set.

And it is a system like this, where we have a flask down here at the bottom that contains, initially, some volume of a weak acid.

And that weak acid might be, for example, acetic acid, as we talked about last time.

And we will say, for example, that this could be 0.1 molar CH<sub>3</sub>COOH.

That is acetic acid. And the calculation that we left off with at the end of last hour is one that we will get to solving today that had to do with what is the pH of a tenth molar acetic acid solution in water?

Or, in other words, what is the pH of this solution down here containing the acetic acid at the beginning of this

titration that we are going to carry out.

We might have a weak acid down here.

We might also have our indicator present, so that we will see a color change when we pass through a particular pH. And we are going to make the pH rise by putting into this burette here, which will allow us to control a dropwise addition of a strong base solution that we are going to add in and slowly neutralize our acetic acid that is down here at the bottom.

So, this is strong base. And, for example, that might be tenth molar sodium hydroxide.

So, there is a typical titration.

And, if you think about it, because we are adding one solution to another, we are going to have a constantly changing volume in this bottom solution throughout the experiment. And so ultimately what we are going to be interested in, in our questions such as the following, as the volume increases -- And we will give the volume, for the purposes of today's lecture, the symbol the lower case letter  $m$  -- As the volume increases, what happens to the pH?

We know that we are using a strong base to neutralize an acid, so the pH is going to start out low and somehow is going to rise. But what if we wanted to predict the mathematical form of the rise in pH as a function of this increasing volume of the solution?

Then we would have to have some equations that would be useful for describing this physical property as a function of this increasing volume. This is what we often want to be able to do in chemistry. We want to be able to describe properties that change either as a function of time or as a function of some other variable, here volume, in a titration. And we want to be able to see if we can come up with a set of equations that would predict that change as a function of this variable that is changing.

And, in order to do that, here, I am going to first point out that we can put together some titration equations.

And, ultimately, we are going to want to generate a mathematical model for this titration.

And then, if you are experimentalist, you want to go ahead and take that mathematical model and compare it to actual experimental data.

But let's work on getting a model generated, here. First we are going to have a set of chemical equations. These correspond to the acid HA, which is acetic acid in our example, in water reacting to give some concentration of  $H^+$  plus the anion  $A^-$ , which is acetate ion, in this particular case. We have a strong base, which is

sodium hydroxide. And when you put sodium hydroxide in water, because it is a strong base, it ionizes completely. And I am signifying that with a single forward arrow rather than with an equilibrium arrow.

This going into water is going to be Na plus and hydroxide, OH minus. Now, at certain points in a titration curve, you would not need to necessarily go much further than this in order to have enough information to start solving for the pH at a particular value of a volume  $m$ . But at some points along that titration curve, that is not enough information.

And that is because water itself can sometimes get into the equation. Here is an interesting equation, which is  $H_2O + H_2O \rightarrow H_3O^+ + OH^-$ .

That is a conceivable reaction that could be occurring even in pure water, but the value of the equilibrium constant for that reaction is very small. And I will draw that as an equilibrium to distinguish it from the irreversible ionization of sodium hydroxide in aqueous solution.

I have a pair of equilibria that I have written.

I have one forward reaction. And I want to point out, too, that this third equation I have written here has a special name, which is autoprotolysis.

I will tell you more about the equilibrium constant associated with autoprotolysis in a moment. But because this equilibrium constant is very small, meaning that there is very little  $H_3O^+$  and  $OH^-$  present in pure water, because of that pure water itself is not a very good electrolyte. Meaning pure water itself is not a very good conductor of electricity, because the autoprotolysis reaction lies mostly over here to the left in pure water. But at certain points along a titration curve, such as the one we are going to want to develop on this panel here, we are going to need to include autoprotolysis in order to get the right answer because it is there, it can occur. Let's continue.

Another type of equation that we can use to put this into some kind of a mathematical footing is the balance of charge in a solution like the one that we are talking about in that beaker to which we are adding sodium hydroxide solution.

And the charge balance consideration tells us that the concentration of hydronium ion plus the concentration of sodium ion must be equal to the concentration of hydroxide plus the concentration of acetate ion,  $A^-$ .

Because what I have done here in the charge balance consideration is I have said okay, what are all the possible charged species in solution? I can make a list of them.

It is those four things. And I know that the number of positive charges must equal the number of negative charges because this is overall a neutral beaker in which we are putting things. But everything that you put in is charge neutral, so the positives have to equal the negatives. That is a very nice limiting equation that helps us understand how the different competing chemical reactions and equilibria will all settle down and arrive at the physical result, which will be our observable. And then, in addition to that, we have a mass balance consideration.

And in this mass balance consideration, we will be able to write that our HA initial value -- -- that is square brackets, once again, denoting concentration -- will be, at any point in time, equal to the actual value of HA plus the concentration of A minus. And that just says that when you have acetic acid and you put it into water, it ionizes partly to hydronium ion and acetate ion.

And that which does not ionize is unionized HA.

And so, the ionized A minus concentration plus the unionized HA concentration is equal to the sum total of the acetic acid that is present in solution.

And, similarly, we have another mass balance equation, which is just that the sodium hydroxide initial is equal to our sodium ion concentration because all of it is ionized. That is a little simpler than the situation with the acetic acid.

And then, in addition to those equations, we have our equilibrium equations.

And we are going to have two of these because there are two equilibria that I wrote over there under titration equations.

The first of these is going to have the equilibrium constant  $K_a$ , and that is going to be  $[H^+][A^-]$  times A minus, which is acetate in the case of acetic acid, all over HA. That is the expression for the equilibrium of acetic acid ionization in dilute aqueous solution. And I will give you a value for this in a moment. I won't write it right here.

Well, why don't I just do that. It is  $1.8 \times 10^{-5}$  for this specific example of acetic acid. And then, if you were working with some other weak acid, you would be able to go to a table and look up the  $K_a$  value for it, if it has been measured and reported and tabulated. And then, we have  $K_w$ .

And this is the equilibrium expression for the autoprotolysis reaction that I mentioned over there, the other equilibrium, which is  $[H^+][OH^-]$  times OH minus. And that is equal to  $1 \times 10^{-14}$ , so a very small equilibrium constant.

And some of you may be wondering why water is not appearing in an expression like this one or like this one.

And the reason for this is that in the expressions that I am deriving here, we are using concentrations in place of activities for these species.

In the derivation of the equilibrium constants, the activity of pure water at very high concentration is approximated as one. And so, this is simplified as shown here. And having put all these equations together, what we are going to want to do is take the following approach. We are looking at the expression for electro-neutrality here, the equal number of positively and negatively charged species in solution. And I want to get this expression rewritten in terms of things that I know at any point along the titration curve, with the exception of the one thing that I want to know, the pH.

And the pH we can calculate easily if we know the  $H_3O^+$  concentration. So, I am going to be seeking to get  $Na^+$ ,  $OH^-$ , and  $A^-$  rewritten in terms of  $H_3O^+$  and constants using the equations that I have up here on the board.

First, let's attempt to do that for  $A^-$  using this  $K_a$  expression. And I am going to rearrange it.

And it is going to be equal to  $K_a$  times  $HA$  divided by  $H_3O^+$ . But I still have a problem with this expression for  $A^-$  because I am going to need to replace  $HA$  with something that will allow me to get everything in terms of just  $H_3O^+$  and constants. And so, if I look over here at the mass balance equation, I can use this one and replace  $HA$  with  $HA_{initial} - A^-$ .

Now I have  $A^-$  written in terms of an initial concentration of  $HA$  itself and constants.

I need to rearrange this a little bit.

I am going to multiply through by  $H_3O^+$  so that I can write  $A^-$  times  $H_3O^+$  is equal to  $K_a$  times  $HA_{initial} - K_a$  times  $A^-$ .

And hopefully I have done that right. And, if so, I will be able to say that  $A^-$  is going to be equal to  $K_a$  times  $HA_{initial}$  all over  $H_3O^+$ .

Does that look good? Plus  $K_a$ , thank you.

$H_3O^+$  plus  $K_a$ .

And let's bring that down here.

Because now, I would like to go ahead and make this substitution for the charge.

We have our  $A^-$ . The other ones are a little easier. We now have this equation  $H_3O^+$ . And we were

going to replace Na plus by NaOH initial.

And we are going to recognize that we can use the equation for autoprotolysis to replace hydroxide with  $K_w$  divided by  $H^+$ . And then now we have the A minus being replaced by  $K_a \frac{HA}{H^+ + A^-}$ .

And at this point, you have actually done a really nice thing, because you have generated a general titration equation for the titration of interest in this particular case. You can see that at any point along that curve for a given volume  $m$ , we can now stop and walk along in one milliliter increments.

And, in each spot along that curve, we could go ahead and solve this equation to get the value of  $H^+$ .

And then we would just have to take the negative log of that, and we would have the pH at that position. And we are interested if this type of a model for the mathematical form of the titration curve bears any resemblance to what one sees in reality. And, if so, one could then be, at least for the time being, until your theory no longer fits, satisfied that you have accounted for the various equilibria that could be present in a system such as the one we are describing here. This happens to be a cubic equation, and it has, therefore, three roots.

And when we solve it at each of these points along the titration equation, because of the physically realistic quantities that we are going to be interested in, only one of the roots is positive.

We are talking about  $H^+$  concentration.

It cannot be a negative concentration.

The positive root is the one we want, and then we can convert that to pH and can see what kind of result we get.

And so, I will show you how we can do that using a tool available on Athena.

First of all, let me tell you that for the purposes of doing this, I am going to replace these various quantities by some simpler symbols, here. I am going to go  $x + a$ ,  $a$  is our NaOH initial, is equal to  $\frac{b}{x} + (c \times d)$  over  $(x + d)$ .

So, I am going to use those simpler symbols for this equation. I could rearrange it and show you how it is a cubic equation, you set it equal to zero, and then you solve, and you get the roots.

Just like a quadratic equation but with another term.

And, instead of doing that, we are just going to leave it in this form, which is simpler to look at.

And we are just going to use that.

And so, let's go ahead and define A.

That is the initial concentration of sodium hydroxide. We are going to go 0.1.

And remember I need to get this in terms of the quantity  $m$  here, which is the volume. And so, I am going to take  $m$ , minus 20 over  $m$ . And the reason I am doing is this is I am saying that we have an 0.1 molar solution of sodium hydroxide that we are adding. But there is a dilution factor that you have to take care of. So, at every value  $m$  we are saying that we are starting with a volume of 20 in the acetic acid flask at the bottom there at the beginning.

And then we are starting to add volume units of sodium hydroxide. And so the volume,  $m$ , is increasing. That is how I take care of that, there. And then our value of  $b$  is  $K_w$ , so that is  $1 \text{ E minus } 14$ .

That is for autoprotolysis. And then we have  $c$ , that is our initial concentration of acetic acid.

And we happen to have a dilution factor here, too, but it is simpler, just 20 divided by  $m$ .

And there is that. And then  $d$ , what did I say that  $d$  was?  $d$  is our equilibrium constant for HA,  $1.8 \text{ E minus } 5$ .

There is our acidity constant for acetic acids.

Now I have the four things in there that I need, and those are four things that I know because of the initial conditions that I am defining for this problem.

And then I am going to define my equation as being equal to  $x$  plus  $a$  is equal to  $(b \text{ over } x)$  plus  $(c \text{ times } d)$  all over  $(x \text{ plus } d)$ . There is my equation.

And this nice calculator, all I have to do, in principle, is tell it what the value of  $m$  is. And then it is going to solve that cubic equation, give me back the three roots.

I take the positive one and I take the negative log of it, and then I know the pH at that value of  $m$ .

I can develop a whole titration curve based on the equations that we have been discussing. And so let's choose a value of  $m$  here to start with, and I am going to choose 30.

We are starting at 20. At the very beginning of the titration, we are at 20. Let's see what happens at 30 given the particular value of  $m$ . Here is what I do.

There may be other ways to do this.



I am defining this thing called the solution set.

Because the solving of that equation is going to give us three values. And then I want to be able to pick the one that I want. We would use sol-set is equal to, we are going to solve that equation, and we want  $x$ , which is our  $H_3O^+$  concentration.

And sometimes it chokes. Let's see what happens.

Sometimes it is a little slow. But it takes a lot longer if you actually try to work it all out by hand.

I have a picture of an image of this that I grabbed.

I can show you if this fails on me.

Don't fail on me. There we go.

You can see it got the answer. And so here is a positive root, and then there are two negative roots to this cubic equation in  $x$ . And I want to find out the pH.

When we are up to 30 volume units,  $m$  equals 30.

And so, I will define  $p$  here as equal to the negative log base 10 of the first of the answers in my solution set, sol-set one, which is the positive  $x$  value.

And, bingo, there is the pH, 4.745 whatever dot, dot, dot. That is now the pH at a volume of 30. Now, you figure I am starting with 20 volume units of 0.1 molar acetic acid.

And by the time  $m$  equals 30 volume units, that means I have added ten volume units of strong base, enough to quench half of my acetic acid.

And what if I had just only quenched none of it?

I can change  $m$  now. Once you have this in here, you don't have to retype these things.

I can go back here and say let  $m$  be 20.

And, if I do that, now I am actually at the zero point, before I add any strong base.

And there is the pH now, The answer to the expression that we had at the very end of class last time that was going to tell us what is the pH of tenth molar acetic acid, there is the answer, 2.87, because that is what we have when we start.

Now you can see that you could just go through and use that to get the pH at any value of  $m$  along this titration curve.

And when you do that, let's show you what the result is, now what you see here is a set of data.

I start at 20. And I'm going up in single volume units, 21, 22, 23, and 24, I am showing what the pH is at each of those choices of  $m$ .

And I have gone all the way from 20 to 60.

And you take that data set -- And then you can take a file, like the one I just showed you, which just had values of  $m$  and corresponding values of pH.

And you can go ahead and just plot that thing.

And, when you do that, you get the form of the titration curve here, which is the classic form of a titration curve for titrating a weak acid with a strong base.

And you see that here,  $m$  was 20, and we let it increment through all the way up to 60.

And what you see initially, and you are going to need to study this one and the other cases of titration curves that are in that chapter of your book, is how the little subtle features differ from one case to another.

They do differ. A much simpler titration curve than this one is obtained if you titrate a strong acid with a strong base. This is titration of a weak acid with a strong base. And you see that initially, we have that 2.87 initial pH value, that it kind of shoots up quickly here at the beginning. There is a steep rise, initially. And then it kind of levels off.

And in this region here, the pH is not changing very rapidly at all as you are adding more sodium hydroxide.

Until you get out here, and the pH just shoots up.

And you will notice that it is around where we get to 40.

Because we started with 20 mLs of tenth molar acetic acid.

And, when we get out to  $m$  equals 40, we have added 20 mLs of tenth molar sodium hydroxide. At that point the pH just shoots up. And then over here it turns over and just goes kind of slowly for a minute.

And it just approaches an asymptotic limiting value over here on the high pH side of the scale.

One thing you will notice here is that at this point where we have added the same number of equivalence of sodium hydroxide molecules as we had acetic acid molecules to start with, this occurs over here at greater than 8.0 pH units rather than at the neutral value of And I would like you to think about why that might be.

And that will be something that will be covered in recitation, but it is important. If we had derived here today the expression for the titration of a strong acid with a strong base, then at 40 we would be right at 7.0, but when we were using this weak acid, acetic acid, it comes up here over 8.0 pH units.

This point where we have added as many strong base molecules as we started with, weak acid molecules, is called the equivalence or the stoichiometric point in the titration. Moreover, where would your indicator molecule change color? At what point, at what value of  $m$ , for example?

It would be close to there. It would be because, in the case of phenolphthalein, it changes between right in here. It might change right around maybe 41 or so.  $m$  equals 41 might be where the color change from colorless to pink occurs, for the reasons that we have discussed. And then right here, it turns out at this value of  $m$  equals 30, the pH is equal to the pKa of acetic acid. And that is a relationship that I would like you to think about. And it is a relationship that comes into play very strongly when we talk about the preparation of buffer solutions according to the Henderson-Hasselbach equation. At  $m$  equals 30, the pH value of the titration is the pKa of acetic acid, which is right here at about 4.7 or so.

We did that one a moment ago. We found out what that value was. And, in plus or minus 1.0 pH units of that, we have the part of the titration curve that is called the buffering region.

In here we have generated a buffer in situ.

And buffers help the pH not to change too much when acids or bases are added in solution. That is what buffers do.

They try to help you keep in a constant pH range because lots of things are dependent upon a particular pH for proper functioning. And you know that this is important in the world's oceans, it is important in our environment, and it is important in our bodies.

So, the pH considerations for aqueous solutions are quite important. And I hope that today I have been able to give you a nice way of thinking about some of the math that goes behind a titration curve.

Have a nice Halloween.