

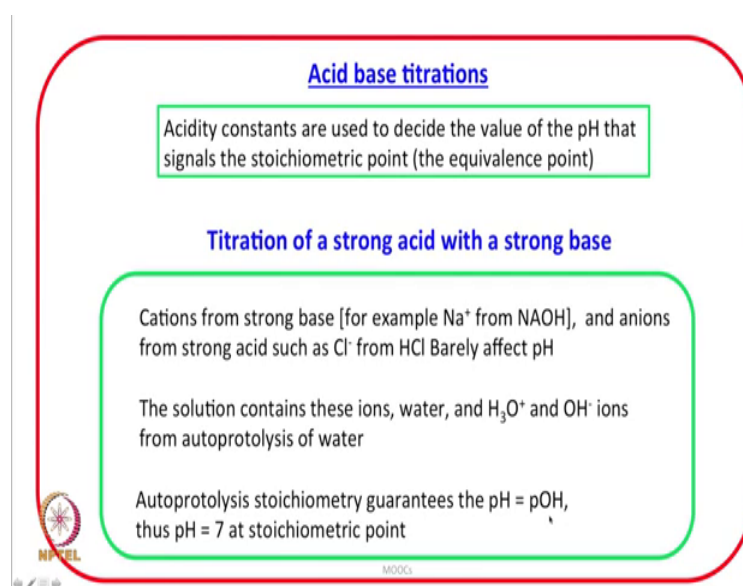
**Chemical and Biological Thermodynamics: Principles to Applications**  
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**Lecture - 36**  
**Acid-base titrations**

So far we have discussed quite a bit about the concept of equilibrium and equilibrium constant and discussed a few examples of these concepts. As I mentioned earlier equilibrium and equilibrium constant and associated thermodynamic quantities, offer a lot of applications, in the discussion of the processes both qualitatively and quantitatively.

In biological systems we are very much concerned about the pH; how to select a suitable combination of salts to prepare a specific pH solution. So, in order to understand these things in more details let us today discuss about the acid base titrations, and how we can apply the discussion on equilibrium and equilibrium constant to address acid base titrations. Acidity constants we have discussed in our earlier lectures what is acidity constant and how to write an expression for the acidity constant. Acidity constants are very useful in deciding the value of the pH that signals the stoichiometric point.

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Acid base titrations

Acidity constants are used to decide the value of the pH that signals the stoichiometric point (the equivalence point)

**Titration of a strong acid with a strong base**

Cations from strong base [for example  $\text{Na}^+$  from  $\text{NaOH}$ ], and anions from strong acid such as  $\text{Cl}^-$  from  $\text{HCl}$  Barely affect pH

The solution contains these ions, water, and  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions from autoprotolysis of water

Autoprotolysis stoichiometry guarantees the  $\text{pH} = \text{pOH}$ , thus  $\text{pH} = 7$  at stoichiometric point

MOOCs

In an acid base titration stoichiometric point is also called equivalence point we remember your school laboratory you are using a buret and a flask to titrate an acid

with a base and trying to find out the end point by using an indicator. And that end point I am referring to as tachometric point or equivalence point let us discuss a few things in detail. Let us first consider let us look at the slide we consider titration of a strong acid with a strong base an example of strong acid is HCL we discussed in the previous lecture that an acid which is completely virtually completely ionised in solution we call it as a strong acid. And strong base again an example is sodium hydroxide which is virtually completely ionised in aqua solution.

Let us consider the titration of a strong acid with a strong base and let us take a look at the slide cations from strong base for example, sodium ions from sodium hydroxide, and anions from strong acid for example, chloride ion from HCL barely affect p H then the solution contains these ions, what are these ions? Sodium ions chloride ions water H<sub>3</sub>O<sup>+</sup> plus and OH<sup>-</sup> minus ions from autoprotolysis of water. Let us recognise that when you are titrating an acid with a base you have the ions coming out from the acid you have the ions coming out from the base and you also have ions which can come out from the autoprotolysis of water. Now it is a different matter that whether the amount of hydronium ion and hydroxide ions produced from the autoprotolysis of water can be ignored or not that we will discuss and let us go back to the slide.

Autoprotolysis stoichiometry in this case guarantees that p H is equal to p OH; that means, when we are titrating a strong acid with the strong base at equivalence point p H will be equal to p OH and that is and that means, if p H is equal to p OH; that means, p H we are talking about is equal to 7 at the stoichiometric point and as I said the stoichiometric point I am referring to as equivalence point ok.

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### Titration of a weak acid (such as $\text{CH}_3\text{COOH}$ ) an strong base (NaOH)

The analyte solution becomes sodium acetate

The solution contains  $\text{CH}_3\text{COO}^-$ ,  $\text{Na}^+$ , and ions from autoprotolysis of water

Due to Bronsted base  $\text{CH}_3\text{COO}^-$ , we can expect pH to be greater than 7

### Titration of a weak base (such as $\text{NH}_3$ ) an strong acid (HCl)

The analyte solution becomes ammonium chloride

The solution contains  $\text{NH}_4^+$ ,  $\text{Cl}^-$ , and ions from autoprotolysis of water

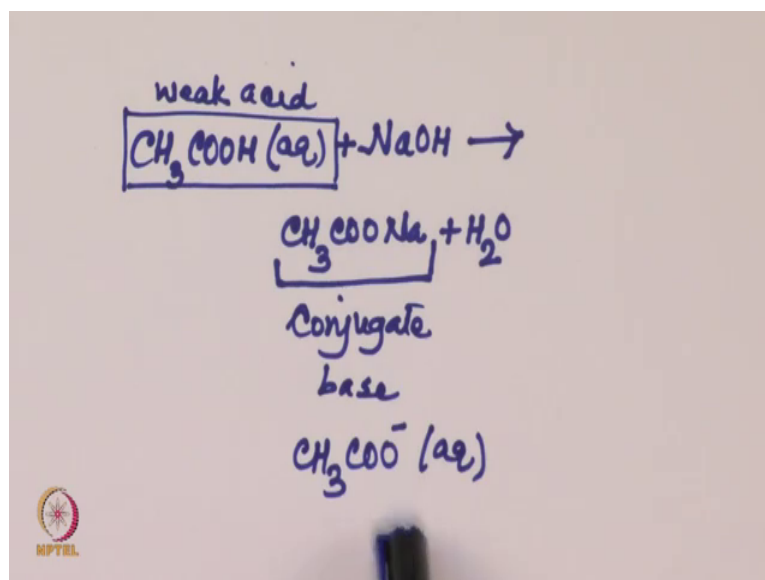
Due to Bronsted acid  $\text{NH}_4^+$ , we can expect pH to be less than 7



MOOCs

Let us talk about now titration of a weak acid with a strong base a weak acid again as we discussed in the previous lecture is not completely ionised its very weakly ionised and an example of a weak acid is acetic acid a strong base which is virtually completely ionised. So, let us take this example and go to the slide weak acid example is acetic acid. So, when you titrate what you have let us write down the equation.

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We have  $\text{CH}_3\text{COOH}$  equals plus  $\text{NaOH}$  it will produce  $\text{CH}_3\text{COONa}$  plus  $\text{H}_2\text{O}$ . So, the solution upon titration forms sodium acetate.

Let us remember since we will be connecting our discussion with the equilibrium constant and eventually equilibrium constant is connected with the Gibbs energy. If you are talking about the titration of a strong acid with a strong base the product which is formed because the reaction the ions are virtually the whatever the acid or alkali base which we are taking if it is strong that is virtually completely ionised; that means, in that case the minima in the Gibbs energy verses extent of reaction will be close to the formation of products.

And when it is weak acid and strong base, and weak acid is not completely ionised; that means, we are talking about minima which is lying close to the reactants coming back to the titration of a weak acid with a strong base like sodium hydroxide which is a strong base and acetic acid which is a weak acid the analyte solution becomes sodium acetate. So, what does the solution have as I just discussed. It will have acetate ion it will have sodium ions and of course, always you will have ions from autoprotolysis of water. So, let us go back to this, this is the weak acid and its conjugate base if I write this is the weak acid and its conjugate base this is acetate ion  $\text{CH}_3\text{COO}^-$  this is its conjugate base.

So, due to this Bronsted base we can expect the p H to be greater than 7, when we titrate weak acid with a strong base  $\text{CH}_3\text{COO}^-$  is Bronsted base it can accept a proton and therefore, we can expect the solution to have p H which is greater than 7; because p H greater than 7 is supposed to be an alkaline solution that is in which there is an excess of the base. So, that is what is commented over here in the slide that due to Bronsted base  $\text{CH}_3\text{COO}^-$  we can expect the p H to be greater than 7 this is the scenario when you titrate a weak acid with strong base.

Now, what about when you titrate a weak base such as ammonia with a strong acid such such as HCL and obviously, when you titrate ammonia with HCL in an aqua solution, the analyte solution becomes ammonium chloride in the solution you will have formation of ammonium chloride that is what is commented here the analyte solution becomes ammonium chloride, and now the solution will have ammonium ion will have chloride ion and as usual the ions from the autoprotolysis of water, and what are those ions these are hydronium ions and hydroxide ions.

Ammonium ion this is the Bronsted acid because it can donate a proton and therefore, we can expect the p H to be less than 7 over here. So, look at the comment due to the Bronsted acid NH<sub>4</sub><sup>+</sup> plus we can expect p H to be less than 7. We have taken an examples of titration of a strong acid with a strong base or titration of a weak acid with strong base or titration of a weak base with a strong acid, and discuss that at the equivalence point for the titration of a strong acid with a strong base p H is expected to be 7 because you will have a neutrality at 25 degree centigrade over there, and when you titrate a weak acid with a strong base we can expect to the p H to be greater than 7 in the solution and when you titrate weak base with a strong acid you can expect the p H to be less than 7.

What about generation of a complete p H curve when you titrate an acid with a base, how will the complete p H curve against the volume of the acid or volume of the base titrated will look like; let us discuss that. we will now discuss titration of complete p H curve.

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**Generation of complete pH curve**

Titration of a volume  $V_A$  of a solution of a weak acid of molar concentration  $A_0$  (the analyte) with a strong base MOH of molar concentration  $B$  (the titrant)

Solution is electrically neutral :  $[M^+] + [H_3O^+] = [A^-] + [OH^-]$


Total number of A groups (as HA and  $A^-$ ) is constant and equal to  $A_0 \times V_A$

$$[HA] + [A^-] = A \qquad A = \frac{A_0 V_A}{V_A + V_B}$$

The molar concentration of  $M^+$  cations also changes because the amount added at any stage is  $B \times V_B$  and the total volume of the solution is  $V_A + V_B$

$$[M^+] = S \qquad S = \frac{B V_B}{V_A + V_B}$$

The quantity  $S$  denotes the current concentrations of the salt that is the product of the reaction

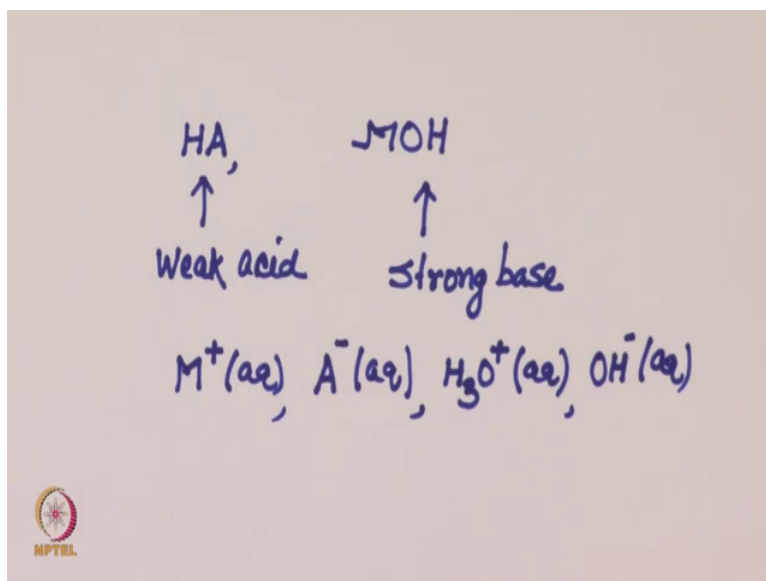

MOOCs

Let us assume that we titrate a volume  $V_A$  of a solution of weak acid and the concentration of weak acid let us take as  $A_0$  moles per litre this is the analyte, and we want to titrate it with the strong base MOH the molar concentration of strong base let us call it as  $b$  this is the titrant. So, what we are talking here is the titration of a volume  $V_A$  of a solution of weak acid with a strong base; that means, you are taking a strong base

and to that you are adding V A centimetre cube of a weak acid and then monitoring the changes.

So; obviously, we are talking about an acid what is the acid? Let us represent acid by HA this is our weak acid, and strong base we are representing by M OH.

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This is weak acid and this is strong base. So, what we will have after these are titrated what are we going to have in the solution? We are going to have M plus aquas we are going to have A minus aquas which will come from the ionisation of HA and then we will have H<sub>3</sub>O aquas and we will also have OH minus aquas.

We are going to have these ionic species in their aq form in solution. The solution is electrically neutral let us go to the slide since the solution is electrically neutral this equation will hold that is the total positive charge will be equal to total negative charge we write in terms of the concentrations concentrations of whatever positively charged species some of that has to be equal to the sum of the concentration of all the negatively charged species.

The next step is to calculate or to find out the total number of a groups or you can express in terms of amount also A groups, A groups will come from HA and A minus; obviously, A is present in HA and whatever is its extent of ionization since it is a weak

acid its extent of ionization is going to be small. So, A minus is also going to be there this is equal to a naught into V A how it comes I will explain that.

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$$A_0 \text{ mol L}^{-1}$$

$$V_A \text{ L}$$

$$\underline{V_A \cdot A_0}$$

$$N_1 V_1 = N_2 V_2$$

$$A_0 V_A = A (V_A + V_B)$$

The initial concentration was A naught of the acid and let us say I write this as mole per litre and we had V A I can express centimetre cube or litre whatever volume. So, therefore, the total number of a groups is going to be you multiply V A into A 0 these many moles, that is the amount of A groups and lets go to the slide total number of a groups is constant and is equal to A 0 into whatever is the volume of the acid weak acid added and this has to be constant whatever HA plus A minus this is equal to total number of a groups.

But also let us realize that when you are adding a to strong base when you are adding an acid to strong base the total volume is also changing imagine the titration which you do in acid base you are taking one solution in the flask and the other solution in the bear head, and when you are adding a small amount of the solution from the bear head into the flask the total volume in flask is increasing; that means, the concentrations are also getting modified we have to take into account that and let us look at the slide.

The amount of a modified when you add a to b is equal to A 0 into V A divided by V A plus V B. How do you get that you can get it by using for example, if you remember you are using this kind of equation N 1 V 1 is equal to N2 V 2 this must apply. So, if I use initially it was A 0 and we took V A centimetre cube of the acid this has to be equal to if

the final amount is  $A$  and the total volume is  $V_A + V_B$  and from this  $a$  is equal to  $A_0$  into  $V_A$  divided by  $V_A + V_B$ .

Once again from here  $A$  is equal to  $A_0$  into  $V_A$  divided by  $V_A + V_B$  and that is what is written on the slide  $a$  is equal to  $A_0$  into  $V_A$  over  $V_A + V_B$ . If the concentration of the acid changes the concentration of the  $M^+$  cations coming from the alkali from the base also changes and exactly the similar calculations can be done and the amount added and at any stage is  $B$  times  $V_B$ , and the total volume of solution as I just discussed is  $V_A + V_B$  and if I write  $M^+$  concentration that is whatever is the amount of base that we are adding base is  $MOH$ . So,  $M^+$  is coming from the base and  $M^+$  is interacting with  $A^-$  to form the salt.

So, therefore, this is equal to  $S$ .  $S$  is the salt concentration and by the same arguments as we discussed for  $a$   $S$  will be equal to  $b$  times  $V_B$  over  $V_A + V_B$ . The points to be noted in this discussion is that we are writing  $M^+$  equal to  $S$ .  $S$  is the salt concentration of salt form which will be equal to the amount of cations given by the base and this  $S$  is equal to  $B$  times  $V_B$  or  $V_A + V_B$  by the same arguments that we discussed earlier. And this quantity  $s$  denotes the current concentration of the salt that is the product of the reaction you are titrating weak acid with a strong base. So,  $A^-$  will come from the acid and  $M^+$  will come from the base will form a salt  $MA$  and  $S$  denotes the concentration of that salt form which is the product of the reaction all right

Now, let us write an expressions for the autoprotolysis constant that is  $K_a$ .



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$$K_a = \frac{a(H_3O^+)a(A^-)}{a(HA)} \approx \frac{[H_3O^+][A^-]}{[HA]}$$

$$K_w = a(H_3O^+)a(OH^-) \approx [H_3O^+][OH^-]$$

The conservation of A groups can be expressed in terms of [A-]

$$[A^-] = \frac{AK_a}{K_a + [H_3O^+]} = \frac{AK_a}{K_a + H}$$

Now express electrical neutrality condition in terms of  $[H_3O^+] = H$  alone

Solution is electrically neutral:  $[M^+] + [H_3O^+] = [A^-] + [OH^-]$

$$H + \frac{BV_B}{V_A + V_B} = \frac{A_0 V_A K_a}{(V_A + V_B)(K_a + H)} + \frac{K_w}{H}$$

Now let us write an equation for the acidity constant  $K_a$ , we always write  $K_a$  as activity of hydronium ion into activity of A minus divided by activity of HA and now let me assume the activities to be close to concentrations, that is I am assuming that the solution is very dilute then let me write another equation for the autoprotolysis constant of water that is  $K_w$  which is also activity of hydronium ion into activity of hydroxide hydroxide ion. So, let me also assume that the activities can be replaced by the concentrations assuming that there is lot of water, then if I combine these two equations I can write another expression for A minus and this comes from the conservation of A groups the conservation of A groups remember that if I go to previous one of the previous slides I was writing HA plus A minus is equal to A.

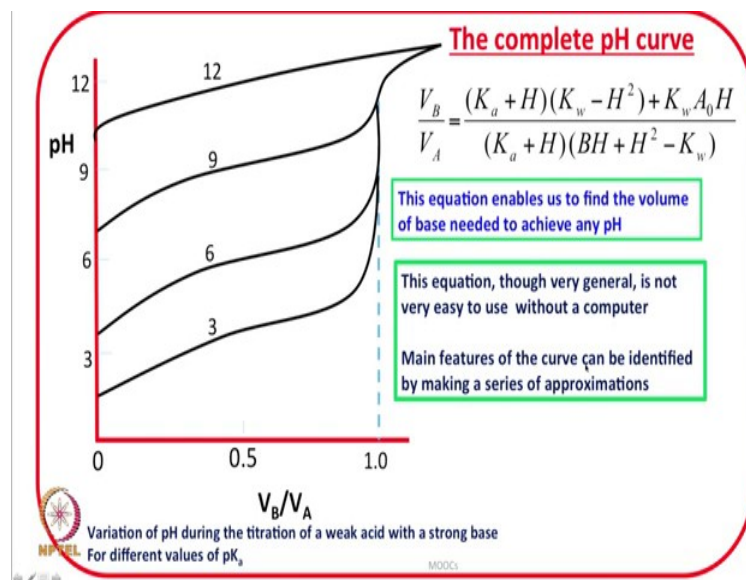
So, by using these equations I can get an expression for A minus in terms of the acidity constant and in place of hydronium ion concentration allow me to write only H. H means H is the hydronium ion concentration. So, once we have obtained this relation next we can use the electrical neutrality condition in terms of H alone. What we are doing is we express electrical neutrality condition in terms of H alone and what is that condition this one solution is electrically neutral that is the total concentration of positively charged species is equal to total concentration of negatively charged species.

We have an expression of M plus A minus and OH minus for example, we have A minus here in terms of the acidity constant ion hydronium ion concentration. For M plus and for

A minus a minus I have discussed A minus is A times K a over K a plus H and OH o h can be from here in this expression I can write in terms K w divided by h and M plus can come from the previous discussion let me just go back and show you M plus is equal to s and s also in terms of V B and V A can be written.

Once we combine all these concentrations for M plus A minus and OH minus and H3O plus I write as H I get this kind of equation. Now this kind of equation is quite cumbersome kind of equation which will actually if you try to rearrange it will come as a cubic kind of equation and to solve this.

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Equation for example, you know we if we look at lets go back if we look at this equation solving this equation is not that easy one may need computer to solve this kind of equation.

So, let me rearrange that equation and I can write that equation in terms of V B and V A because when you titrate you know the volume of the alkali added and you know the volume of the acid taken. And these volumes can be connected with H and now you try to solve again here you see it is third power of H. So, therefore, you will need definitely computer to solve this equation.

But nevertheless we will discuss that what approximations can be made, but the complete p H curve for various values of p k these are K a p K a values for various p K a

values will look like this. So, you see the p H will be expressed in terms hydronium ion concentration for various V B and V A you get hydronium ion concentration for different K a values and those hydronium ion concentrations can be expressed in terms of p H and then you generate these kind of p H versus V B by V A titration curve and for different p k values you see how the p H will vary.

So, this is the complete p H curve as the function of the volume of alkali a volume of acid are added to the alkali. So, this equation enables us to find the volume of base needed to achieve any p H since it is against V B by V A you are varying b how much base is need to achieve any p H can be obtain by this equation as I mentioned earlier that now this equation is very general it is not very easy to use without a computer because H into H square they becomes third power of H. Main features of the curve we can identify by making a series of approximations and what is what are those series of approximation.

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The pH in the course of a weak acid-strong base titration

**Approximations:**

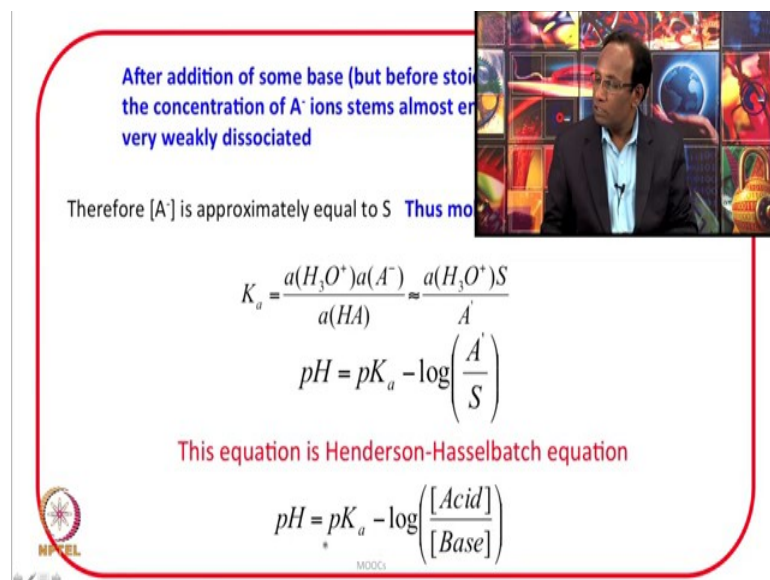
- Since acid is weak, HA is more abundant than any A<sup>-</sup> ions in solution
- When HA is present, it provides hydronium ions that greatly outnumber any that stem from the autoprotolysis of water
- When excess base OH<sup>-</sup> is present, the OH<sup>-</sup> ions it provides, dominate any that come from water autoprotolysis

MOOC

The approximations that we will use since acid is weak therefore, HA is more abundant than A<sup>-</sup> ions in solution HA is weak acid is very weakly dissociated therefore, the amount of A<sup>-</sup> ions will be very less compared to HA and when HA is present it provides hydronium ions that greatly outnumber that any that stem from autoprotolysis of water this is also assumption; that means, we will be ignoring the hydronium ions which are coming from autoprotolysis of water and we are we will be considering hydronium ions that will come from HA.

And when excess base is present the OH ions which come from the base will dominate any that come from water autoprotolysis of water these are the approximations that we are going to make.

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After addition of some base (but before stoichiometric point) the concentration of A<sup>-</sup> ions stems almost entirely from the salt as the acid is very weakly dissociated.

Therefore [A<sup>-</sup>] is approximately equal to S. Thus molar concentration of A<sup>-</sup> is S.

$$K_a = \frac{a(\text{H}_3\text{O}^+)a(\text{A}^-)}{a(\text{HA})} = \frac{a(\text{H}_3\text{O}^+)S}{A'}$$

$$\text{pH} = \text{p}K_a - \log\left(\frac{A'}{S}\right)$$

This equation is Henderson-Hasselbalch equation

$$\text{pH} = \text{p}K_a - \log\left(\frac{[\text{Acid}]}{[\text{Base}]}\right)$$

So, after addition of some base that is before the stoichiometric point is reached the concentration of A minus ions will come almost entirely from the salt as the acid is very weakly dissociated. So, you have HA which will form a which will give A ion and then you have A ion which will stem almost entirely from the salt which is present which is formed as a product. So, we will assume that after addition of some base the concentration of A ions will come entirely from the salt because acid is weakly dissociated therefore, I can approximate A minus equal to s that is the concentration of salt.

And therefore, the molar concentrations of acid new molar concentration of acid will be a whatever it was minus the S. S is the concentration of the salt. So, instead of a now I will use the molar concentration of acid HA as A prime and therefore, you write the acidic constant as usual and instead of A minus activity I will use S that is what I am saying I am approximating A as S and instead of A HA I will write a prime.

And now when you convert this into p H or p K a terms you take a logarithm on both sides and write p K as minus log K a and p H as minus log activity of hydronium ions you will get this expression p H is equal to p K A minus log A prime by S. A very

important equation this is called hasselbatch equation which in other words in other terms it is is written as p H is equal to p K A minus log concentration of acid divided by the concentration of base. This is the very important equation we will discuss more about this in the next lecture.

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The Henderson-Hasselbatch equation

$$pH = pK_a - \log\left(\frac{A}{S}\right) \qquad pH = pK_a - \log\left(\frac{[Acid]}{[Base]}\right)$$

pH = pK<sub>a</sub> when S = A'

Thus pK<sub>a</sub> of the acid can be measured directly from the pH of the mixture

But now if I take a prime equal to S that is when the concentration of acid is equal to concentration of salt then p H is equal to p K a. So that means, p K a of the acid can be measured directly from the p H of the mixture see if you know the p H if you know the concentration of a that is acid and s that is salt we can measure p k a.

So, the discussion in this lecture has led to generation or the discussion on the generation of the complete p H curve and the derivation of a very important equation the Henderson Hasselbatch equation. We will discuss more about the Henderson Hasselbatch equation in the next lecture.

Thank you very much.