

Chemical and Biological Thermodynamics: Principles to Applications

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Lecture - 37

pH curve for titration of weak acid with strong base Buffers and indicators

In the previous lecture, we discussed about the complete pH curve and we also came up with an equation which was used to generate that complete pH curve and that equation was a complicated kind of equation and we also discussed some approximations that we are going to use in further discussion, but when we talk about pH, especially with reference to biologically important systems, it becomes very important because for biologically important molecules; for example, proteins nucleic acids pH becomes very important. We will discuss later that how pH can affect their confirmation and hence their properties.

So, therefore, while preparing a solution of biologically, important systems in laboratory, we prepare a solution, we prepare a solution which is called buffer therefore, it becomes very important to understand; what is a buffer and the connection of buffer is with its resistance to change the pH of a solution upon addition of a small amount of an acid or a base and that is why pH becomes very important.

Another question is that what salts or an acid should be chosen to obtain a solution of a particular value of pH, for example, if you want to prepare a solution of pH 5 or pH 7 or pH 9 or pH 12, what salts and what acid should be taken. These are important questions and we will address these questions in today's lecture.

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At stoichiometric point the H_3O^+ ions in solution stem from influence of OH^- ions on autoprotolysis equilibrium, and the OH^- ions are produced by the Bronsted equilibrium

$$A^-(aq) + H_2O(l) = HA(aq) + OH^-(aq)$$
$$K = \left(\frac{a(HA)a(OH^-)}{a(A^-)} \right) \approx \left(\frac{[HA][OH^-]}{A^-} \right)$$

After sufficient addition of acid, well past the stoichiometric point, pH is controlled by excess base present

$$[H_3O^+] \approx \left(\frac{K_w}{[OH^-]} \right)$$

For molar concentration of excess base B^- : $pH = pK_w + \log B^-$



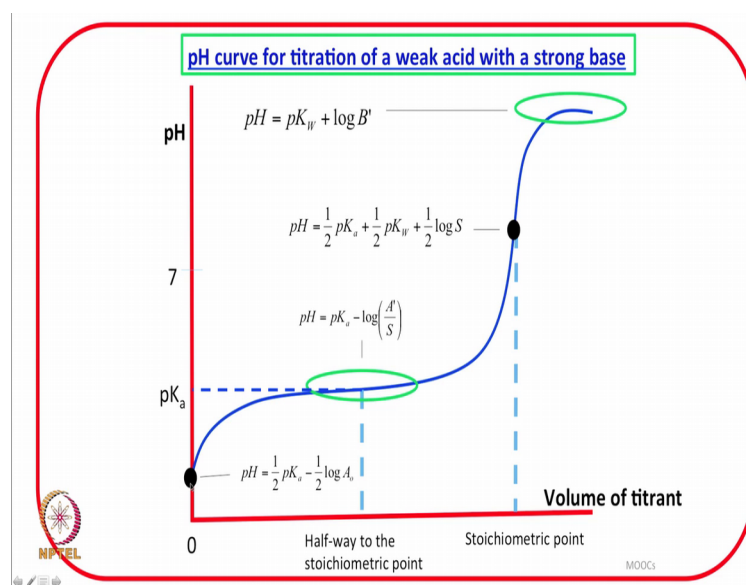
Let us start discussing about pH curve for titration of weak acid with strong base. Now what we have is at stoichiometric point the hydronium ions in solution stem from influence of OH^- ions on autoprotolysis equilibrium and OH^- ions are produced by Bronsted equilibrium, we are talking about this expression; that is the negatively charged ions. For example, the hydroxide ions and OH^- ions; you see which are produced also produced by the autoprotolysis of water and the action of A^- ions on water upon acceptance of proton because A^- ion is Bronsted base; it will accept a proton and result into the formation of OH^- ion.

And therefore, these will influence this stoichiometric point if I write equilibrium constant for this particular reaction, it will be activity of HA into activity of hydroxide ion over activity of A^- taking activity of water to be 1 and you convert these into molar concentrations you get this kind of expression you have molar concentration of HA molar concentration of OH^- and molar concentration A^- treat it as within the bracket.

Now, what happens after sufficient addition of acid; that is well passed, the stoichiometric point pH is controlled by excess base present please look at this statement very carefully, after sufficient addition of acid, well past the stoichiometric point pH is controlled by excess base present, how I can write this expression that H_3O^+ is equal to K_w divided by OH^- ion, even if I write this by using autoprotolysis of water.

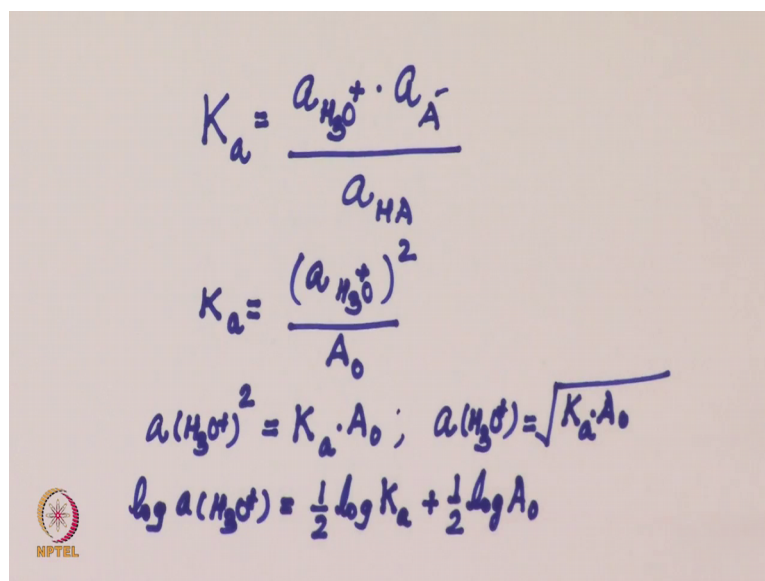
The hydronium ion concentration is approximately given by the autoprotolysis constant of water divided by hydroxide ion. So, it is the amount of OH ion, if it is in excess that is going to control the pH of the solution because H₃O⁺ will be modified accordingly then, again if I take logarithm on both sides and set minus log H₃O⁺ as pH and OH ion, concentration will result into pOH and then use pH plus pOH is equal to pK_w, I am skipping a step over here. Why I am doing it because we have discussed these things many times and eventually one will get this relation with pH is equal to pK_w plus log B prime where B is the amount of the base that is present in solution. So, that is what I was trying to comment upon that the pH of the solution is controlled by the excess base which is present in the solution.

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And let us talk about the pH curve, for titration of weak acid with a strong base, this is the type of curve that we discussed in the previous lecture that one will obtain when you titrate a weak acid with a strong base. Let us try to identify different regions, let us say here, we start with this is purely weak acid, no base added and when you keep on adding base, the horizontal axis represents volume of titrant and the vertical axis is pH and this is how the pH changes and this represents equivalence point also pay attention to the various equations which are written over here this equation. We have just derived the relationship between pH is equal to pK_w plus log B, when you have excess base that is what we just discussed, if there is an excess base, pH will be controlled by excess base and you are talking about this region you are starting with pure acid.

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So, let us see pure acid and since we are talking about a weak acid, I will write the acidity constant is equal to activity of H₃O plus into activity of A minus into divided by activity of HA that is how we write the ionisation constant or acidity constant, sorry, weak acid and let me write again K A is equal to if the acid is weak and initially there is no base present then both these have to be equivalent because the source of A minus is also. So, A and the source of H₃O plus is also HA and you are not talking about the contribution from autoprotolysis of water.

So, if I equate these 2; these 2 activities I can write this H₃O plus rise to the power 2 and this I will retain as A 0 because this is hardly dissociated, yes, it is hardly ionized, we can ignore the extent of ionization and write this approximately as the initial concentration.

So, activity of H₃O plus square is equal to acidity constant into A 0 and this is same as this equation H₃O plus is equal to square root of acidity constant into A 0 and now I can take logarithm log activity of H₃O is equal to half log K A plus half log A 0.

And the next step will be; you take a negative sign on both sides, you multiply by minus 1 convert this to pH convert this to p K and this remains, then as minus 1 by 2 log A 0 and that is what if you look at the figure, now that initially that is what is the equation pH is equal to half p K A minus half log A 0 pH is given by this expression and the pH is modified as you keep on adding alkali and half way to stoichiometric point. This equation, we also derived that when a prime is equal to S when the concentration of acid

and concentration of salt are equivalent pH is equal to pK_A and that is what is indicated over here at the midpoint halfway to the stoichiometric point pH is equal to pK_A .

And you see the region of the pH change is reasonably flat around pK_A , this flat region has a lot of significance; that means, a slight addition of an acid or a slight addition for a base is not going to change pH significantly because you see within this circled region this is a flat region and the pH of the solution does not change when you add a little more amount of the titrant and that is what is called the buffer action.

What is a buffer? Buffer is a substance which does not allow the change of pH upon addition of small amount of an acid or a base and for what pH value, it should be used, it depends on the pK_A ; that means, we should choose a substance and the region that is wherever it the value wherever it has a value of pK_A plus minus 1 pK_A plus minus ` that range can be used to be selected as the substance for preparing a specific pH.

For example, if I want to prepare a solution of pH 7 then I should pick up a salt the or an acid the pK_A of the acid should be let us say 7 if the pK_A is 7 then the pH can be 7 plus minus 1. So, on other words, if I want to prepare a solution of pH 7, then I should use an acid or the salt of that acid where the acidity constant is within a range of plus minus one of that value.

So, therefore, if the pK_A is 6, then I can use that acid and its salt to prepare a buffer of a solution of pH from 6 to 8 for a pK_A ; for a pK_A of 7 the pH can be 6 to 8, comfortably can be used and that lies in this flat region. So, please do remember this that whenever we want to prepare a solution of specific pH, it should fall within plus minus one range of the pK_A value of that acid.

Let us go back to the figure now you continue adding alkali and you see beyond this beyond this region, it is very sharply changing and we will soon derive this equation at the equivalence point and then further addition will give rise to another saturation that is the pH becomes constant over there almost constant over there unless there is another ionization further happening and this equation we also derived.

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Find an approximate expression for the pH at the stoichiometric point of the titration of weak acid with a strong base. Calculate its value for the titration of 25.0 mL of 1.0 M HClO(aq) with 0.1 M NaOH(aq).

$$K \approx \left(\frac{[OH^-]^2}{S} \right), \text{ so } [OH^-] \approx (SK)^{\frac{1}{2}}$$

$$K = \left(\frac{a(HA)a(OH^-)}{a(A^-)} \right) = \left(\frac{a(HA)a(OH^-)a(H_3O^+)}{a(A^-)a(H_3O^+)} \right) = \left(\frac{K_w}{K_a} \right)$$

$$[OH^-] \approx \left(\frac{SK_w}{K_a} \right)^{\frac{1}{2}} \quad pOH = \frac{1}{2}pK_w - \frac{1}{2}pK_a - \frac{1}{2}\log S$$

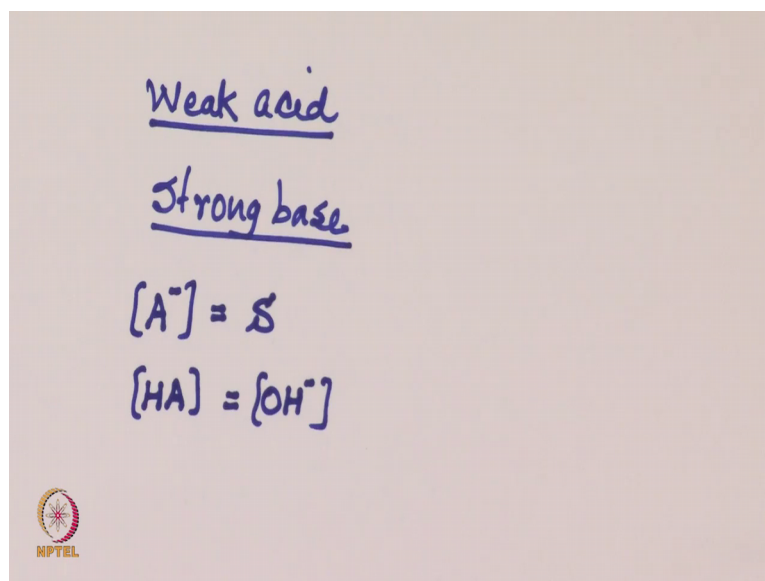
$$pH = \frac{1}{2}pK_a + \frac{1}{2}pK_w + \frac{1}{2}\log S$$

$$pH = \frac{1}{2} \times 7.43 + \frac{1}{2} \times 14.00 + \frac{1}{2} \log 0.050 = 10.1$$


Now, let us try to derive this kind of equation, this equation which is at the equivalence point, find an approximate expression for the pH at the stoichiometric point of the titration of weak acid with strong base, calculate its value for the titration of 25 ml of 1 molar HClO with 0.1 molar NAOH again, we are talking about weak acid and strong base.

And as usual, since we are talking about weak acid and a strong base, we will again use those approximations, we are talking about weak acid and we are talking about strong base.

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So, whatever is a minus A minus we are talking about anion of the weak acid, we can equate that equal to S if I use S as the concentration of the salt which is formed as a product and whatever is the concentration of HA and whatever is the amount of H₃O plus, it produces this, I will equate equal to let me write this as the concentrations OH ion these are the 2 approximations that I am going to use.

So, therefore, equilibrium constant is equal to OH minus square over S and from these, I can get OH is equal to OH minus is equal to S into K square root, from this equation K which is activity of HA into activity of hydroxide ion over activity of A minus can be written as activity of HA into activity of hydroxide ion and let me divide and multiply by activity of hydronium ion and then combine these 2 these 2 multiplication replication is equal to K_w autoprotolysis constant of water this is equal to K_w by K_A because this is K_w and K_A reciprocal of K_A is a into a of HA over A minus into A H₃O plus this is the activities A is as written as activities.

From this, if I substitute K_w by K_A for K into this expression I get expression for OH and from this, I can easily get p OH by taking logarithms and pH plus p OH is equal to p K_w therefore, I can express this equation in the form of pH and this is the expression that we were looking for and once you substitute the values of p K_A of the acid and we substitute p K_w which is fourteen at 25 degree centigrade and the concentration of salt form will be 0.05 and the final answer can be obtained as 10.1.

So, please try to solve this in a detailed way by yourself, but this method describes; how pH can be obtained at the stoichiometric point and this is the expression to be used at the stoichiometric point and that I showed in the previous figure the equivalence point that is the concentration of salt can be calculated from the given information and that please try yourself.

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Buffers and indicators

$$pH = pK_a - \log\left(\frac{A^-}{S}\right)$$

Slow variation of pH in the immediate vicinity of $S = A^-$ is the basis of Buffer Action

Buffer action is the ability of a solution to oppose changes in pH

The mathematical basis of buffer action is the logarithmic dependence in Henderson-Hasselbalch equation

The physical basis of buffer action is abundant supply of A^- ions (due to presence of salt) which can remove any H_3O^+ ions by additional strong acid

Moreover numerous HA molecules can supply H_3O^+ ions to react with any strong base that is added (examples of Le Chatelier's principle)

Now, buffers and indicators; I have discussed about the need of buffers. A buffer is a substance which resist the changes in pH upon addition of a small amount of acid and small amount of base indicator as the name suggests indicates the occurrence of the equivalence point.

Let us discuss details, this is Henderson Hasselbalch equation and this equation suggest that the slow variation of pH in the immediate vicinity of S equal to a prime signal, the basis of buffer action remember that flat region and buffer action is the ability of a solution to oppose changes in pH as I just discussed.

The mathematical basis of buffer action; what is the mathematical basis is the logarithmic dependence of this ratio of acid to salt concentration, the logarithmic dependence is the mathematical basis and whereas, the physical basis is abundant supply of a minus ions because salt is there and this A^- can remove any hydronium ion by additional strong acid that is when small amount of an acid is added and alternately or vice versa that is numerous HA molecules can supply H_3O^+ ions which can react

with strong base that is added. So, both these statements are examples of the Le Chatelier principle application of Le Chatelier's principle, alright.

The rapid change of pH near stoichiometric point in a titration is the basis of indicator detection, we will discuss more about that and acid base indicator is generally a water soluble weakly acid organic molecule; acidic organic molecule and that organic molecule should be able to exist in an acid form I write as HIn and conjugate base where proton is denoted and I write as In minus form and both these occur in different colours.

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The rapid change of pH near stoichiometric point the basis of indicator detection

An acid base indicator is generally some large water soluble weakly acidic organic molecule which can exist as an acid (HIn) or conjugate base (In⁻) form that differ in colour

$$HIn(aq) + H_2O(l) = H_3O^+(aq) + In^-(aq)$$

$$K_{in} = \left(\frac{a(H_3O^+)a(In^-)}{a(HIn)} \right) \quad \log \left(\frac{[HIn]}{[In^-]} \right) \approx pK_{in} - pH$$

The proton transfer equilibria will be this you have an acidic form of the indicator HIn, it will donate its proton form hydronium ion and will have In minus and these 2 will have different colour that is before the titration it will have colours specific to this after the titration it will have colours specific to this.

Let us write down equilibrium constant for this K_{in}, I write which is activity of hydronium ion into activity of indicator in the negatively charge form over activity of the indicator in weakly acidic form and take the logarithm and express this logarithm ratio of log HIn by In minus as p K_{in} minus pH this relation can be obtained by manipulation of this and now I can use this relation for further discussion.

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$$\log \left(\frac{[HIn]}{[In^-]} \right) \approx pK_{in} - pH$$

When $pH < pK_{in}$: indicator is predominantly in acidic form and has corresponding colour

When $pH > pK_{in}$: indicator is predominantly in its basic form

At end-point $pH = pK_{in}$

At stoichiometric point of an acid-base titration, pH changes sharply
If pH passes through pK_{in} , then there is a pronounced colour change, thus
End-point will coincide with stoichiometric point of titration

According to this relation when pH is less than pK_{in} the overall values positive; that means, the indicator is predominantly in the acidic form and has its corresponding colour and when pH is greater when pH is higher than pK_{in} then this overall it is negative; that means, indicator is predominantly in its basic form and will have its corresponding colour at the end point you have pH is equal to pK_{in} , alright; that is why it is commented over here that at stoichiometric point of an acid base titration pH changes sharply and if pH passes through pK_{in} that is when it passes through this equality there is a pronounced colour change does end point will coincide with stoichiometric point of titration.

And I am sure that this reminds you of the methyl orange or phenolphthalein which was used as indicators in the acid base titrations during your school level laboratory classes and today's discussion describes that why the colour of the indicator changes. It is just the change in the state of ionisation that each ionized state has a different colour.

So, what we discussed in today's lecture is about a very important concept and that is buffering action what is a buffer I am again repeating that in biologically important systems buffers play a huge role because several biologically important molecules have their specific activity at a particular pH value and therefore, maintaining that pH becomes very important and therefore, selection of the acids and its combination with the salts which will give us that particular pH value becomes very important and I hope

today's discussion helps in deciding that which molecules should be taken which acid which salt should be taken to prepare pH of the desired pH value.

Thank you very much.