Quantitative Methods in Chemistry

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Lecture-31

Standards And Volumetric/Gravimetric Titrations Part 03

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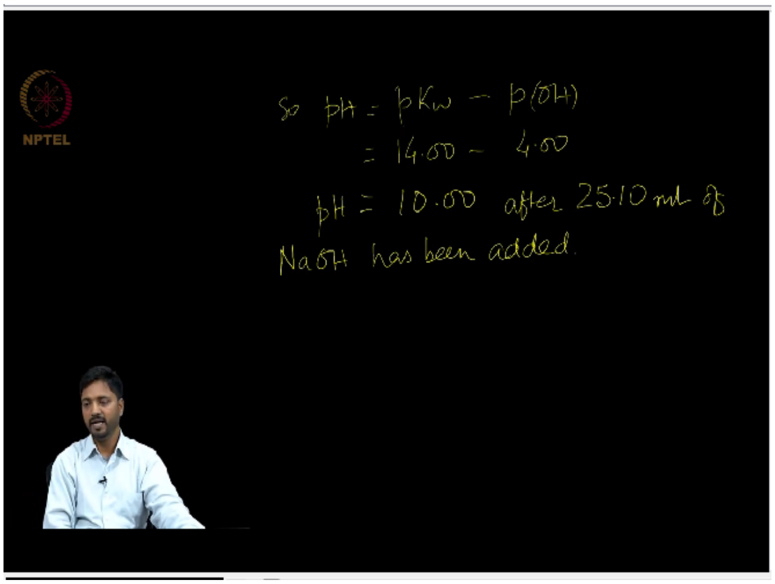

So $pH = pK_w - p(OH)$

$= 14.00 - 4.00$

$pH = 10.00$ after 25.10 ml of NaOH has been added.

Now, let us go back to the presentation.

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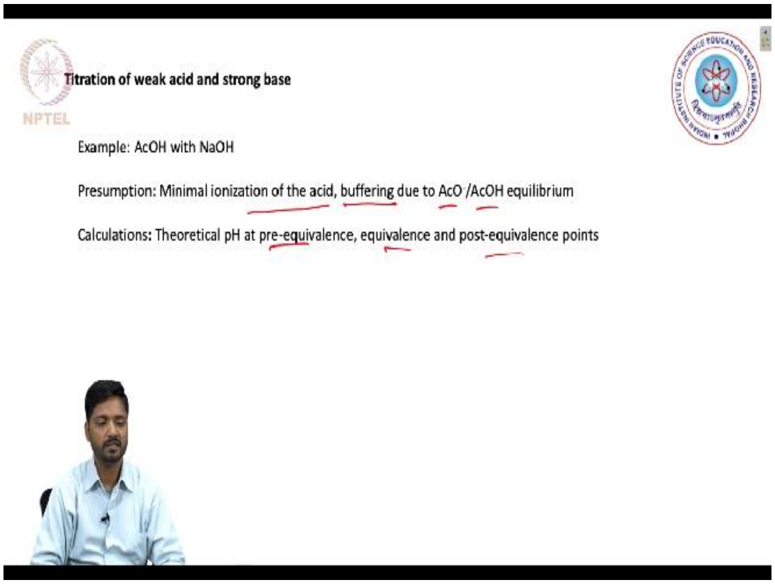

Titration of weak acid and strong base

Example: AcOH with NaOH

Presumption: Minimal ionization of the acid, buffering due to AcO /AcOH equilibrium

Calculations: Theoretical pH at pre-equivalence, equivalence and post-equivalence points

And observe what happens when we titrate a weak acid and a strong base. Now a typical and in fact the most common example of a weak acid would be acetic acid or formic acid and both are readily available and a strong base again sodium hydroxide. So, there are a few things that we need to consider are assumed here, first of course, is that the acid being weak, it undergoes minimal ionization.

And another very important aspect that will become irrelevant when we are titrating a weak acid and a strong base is the concept of buffering that happens due to the presence of the salt and the acid in equilibrium during the titration. So, this will induce slower decrease or increase in the pH. And so what we need to do now is to calculate the pH again at the pre-equivalence point, the equivalence point and the post-equivalence points. So, let us go back to the board and start doing some calculations.

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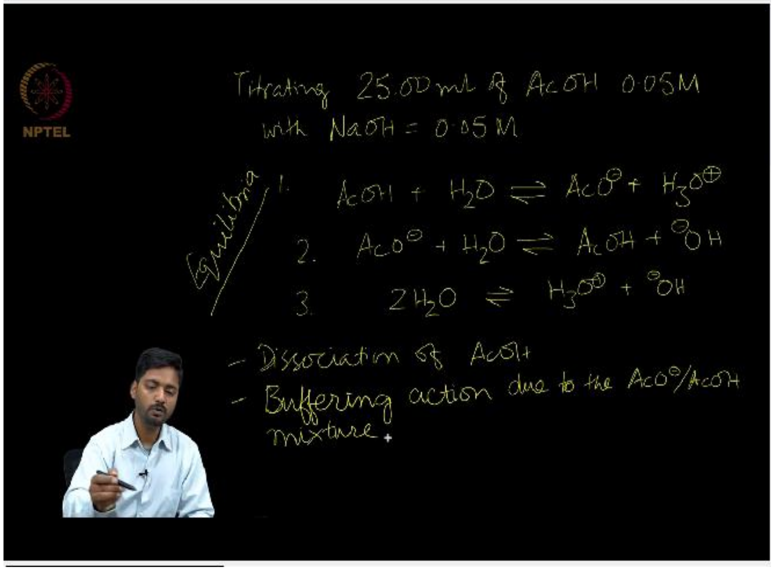

Titrating 25.00 ml of AcOH 0.05M
with NaOH = 0.05 M

Equilibria

1. $AcOH + H_2O \rightleftharpoons AcO^{\ominus} + H_3O^{\oplus}$
2. $AcO^{\ominus} + H_2O \rightleftharpoons AcOH + {}^{\ominus}OH$
3. $2H_2O \rightleftharpoons H_3O^{\oplus} + {}^{\ominus}OH$

- Dissociation of AcOH
- Buffering action due to the $AcO^{\ominus}/AcOH$ mixture.

In this case, what we are doing is we are titrating again 25.00 ml of acetic acid and its concentration is again 0.05 molar just to make quick comparisons, so this we are titrating with sodium hydroxide of the same concentration which is 0.05 molar. Now, when we are titrating, a weak acid and a strong base, we need to consider 3 different equilibria that may be in existence. The first one is the acetic acid undergoing dissociation into the acetic and then and release it into hydronium ion.

The second one is the reverse process where the acetate ion being a weak base reacts with water and accepts its proton to convert back to acetic acid and generate hydroxyl. And the third equilibrium that may be of relevance again is the self dissociation of water. So, these are the 3 equilibria that we need to consider and we will also be considering the dissociation of acetic acid and the buffering action due to the acetate acetic acid make sure present in the media.

Now with these points let us try to calculate what are the pH values at different point on nitration of acetic acid with sodium hydroxide So, firstly first is to calculate the initial pH.

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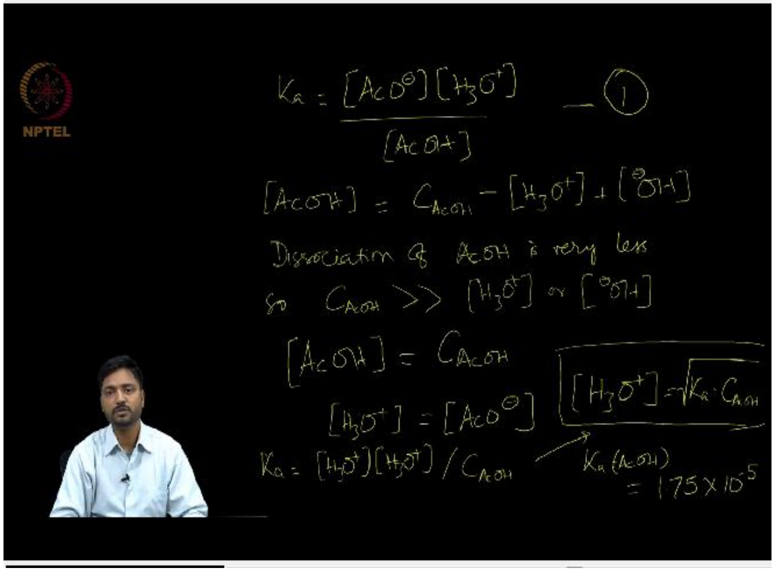

$$K_a = \frac{[AcO^{\ominus}][H_3O^+]}{[AcOH]} \quad — ①$$

$$[AcOH] = C_{AcOH} - [H_3O^+] + [^{\ominus}OH]$$

Dissociation of AcOH is very less

so $C_{AcOH} >> [H_3O^+]$ or $[^{\ominus}OH]$

$$[AcOH] = C_{AcOH}$$

$$[H_3O^+] = [AcO^{\ominus}]$$

$$\boxed{[H_3O^+] = \sqrt{K_a \cdot C_{AcOH}}}$$

$$K_a = [H_3O^+][H_3O^+] / C_{AcOH}$$

$K_a(AcOH) = 1.75 \times 10^{-5}$

So, before that, let us quickly write down the K value, which will be nothing but the dissociated form divided by the undissociated form of the aid. We also understand that if we look at the equation in the previous page, what we observe is that the acetic acid concentration will be reduced by undergoing dissociation in water to form the acetate and it will be increased when the acidity takes up water and forms the acetic acid.

And for each acetic acid that undergoes dissociation we create a hydronium ion. For each acetate and ion undergoing protonation we create a hydroxyl and ion. So based on this, what we can say is that the concentration of acetic acid at equilibrium will be the initial concentration of acetic acid minus the hydronium ion concentration because the hydronium ion is coming from the dissociation of acetic acid plus the hydroxyl ion concentration.

Because the hydroxyl ion is coming from the reformulation of the acetic acid from that acetate and ion in equilibrium proof. Now, we also make a presumption that the dissociation of acetic acid is very less. So, the concentration of acetic acid that we begin with is much greater than either the hydronium ion concentration or the hydroxyl ion concentration. So, not much changes here. And what we believe is, or what we presume is that the equilibrium concentration of acetic acid is similar to the original concentration of the acetic acid.

So another presumption that we have is that the hydronium ion concentration is equal to the acetate and ion concentration, because acetic acid dissociation is going to be our key source of the hydronium ion in the medium. Now, when we plug in these into our equation 1 which is the acidity constant equation, what we observe is that K a turns out to be equal to the hydronium ion concentration again into hydronium ion concentration divided by the original concentration of the acetic acid that was made.

Now, when we reorganized this, this turns out that the hydronium ion concentration is nothing but square root of the dissociation constant into the concentration of the acetic acid that was traditionally taken. This is the equation that we can use to calculate the initial pH of the medium. So, let us go ahead and do that. Now, at this stage, it is also important to convey that the K value of acetic acid is known to be 1.75 into 10 power of – 5. So, indeed it is weakly dissociating acid.

Now with the K value and the concentration of acetic acid originally taken available to us, it would be straightforward to calculate what is the hydronium ion concentration of this medium.

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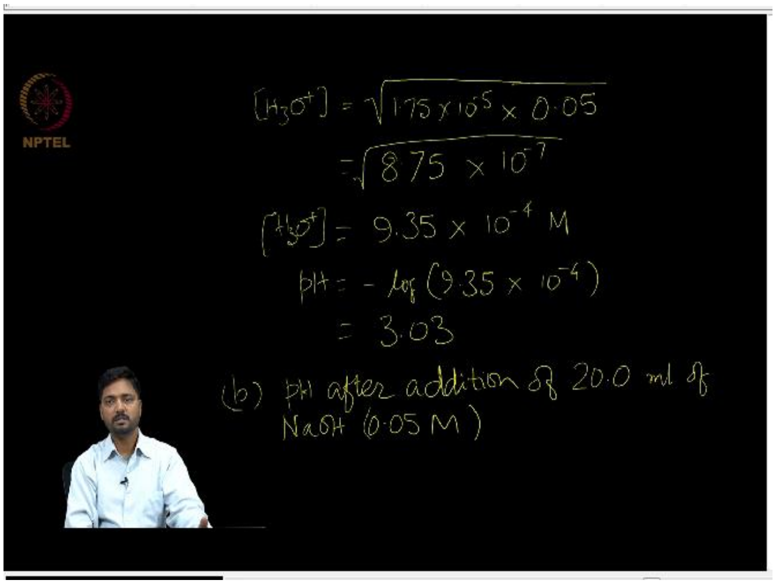

$$[H_3O^+] = \sqrt{1.75\times10^{-5}\times0.05}$$

$$= \sqrt{8.75\times10^{-7}}$$

$$[H_3O^+] = 9.35\times10^{-4}\ M$$

$$pH = -\log(9.35\times10^{-4})$$

$$= 3.03$$

(b) pH after addition of 20.0 ml of NaOH (0.05 M)

So, let us do that what we observe is the hydronium ion concentration is equal to 1.75 into 10 to the power of – 5 which is the K value into now the concentration of the acetic acid that was taken originally and this is 0.05 molar, when we solve this out this turns out to be 8.75 into 10 power of – 7 square root and this ultimately salts out to be 9.35 into 10 power of – 4 molar hydronium ion concentration.

With this it would be straightforward to calculate the pH which will be negative log of 9.35 into 10 power of – 4 and the pH of the medium now turns out to be 3.03. So, as we can observe here, when we are taking a weak acid, the initial pH is already 3.03 value and now let us calculate or let us see what is the pH value when we start adding the sodium hydroxide into this medium. So, let us take an example where we have added pH after addition of 20.0 ml of sodium hydroxide, which was again 0.05 molar. So, we need to calculate what is the pH of the medium at this stage.

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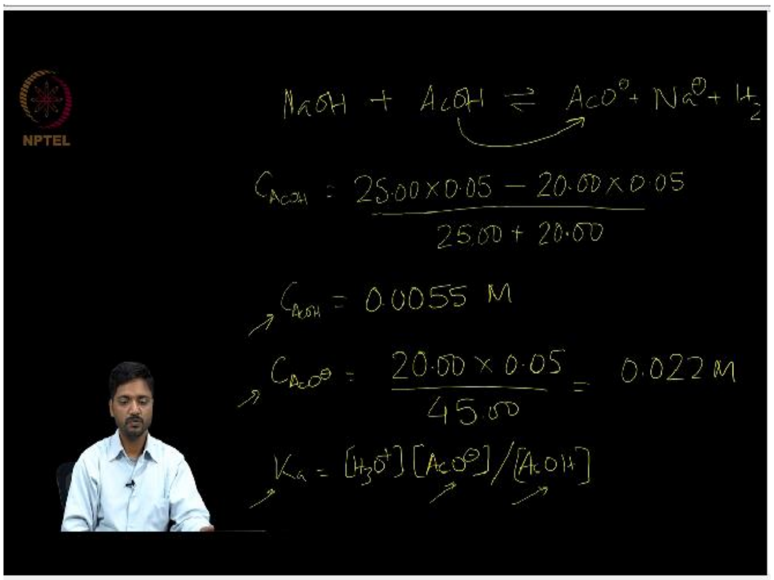

$$NaOH + AcOH \rightleftharpoons AcO^{\ominus} + Na^{\oplus} + H_2$$

$$C_{AcOH} = \frac{25.00 \times 0.05 - 20.00 \times 0.05}{25.00 + 20.00}$$

$$C_{AcOH} = 0.0055\ M$$

$$C_{AcO^{\ominus}} = \frac{20.00 \times 0.05}{45.00} = 0.022\ M$$

$$K_a = [H_3O^+][AcO^{\ominus}]/[AcOH]$$

So, what we need to consider is the following that sodium hydroxide being a strong base will react in a stoichiometric amount with the acetic acid and convert it into an acetate ion and sodium ions and water, sodium hydroxide addition will convert acetic acid into acetate enhance. So let us calculate now the concentration of acetic acid in the medium which will be the original amount minus the added sodium hydroxide divided by the total volume of the medium now, which is 25.00 + 20.00.

So, at this stage what we observe is that the concentration of undissociated acetic acid in the medium would be 0.0055 molar. Now, from here we can we will also be able to calculate, what is the concentration of acetate and ions in the medium which will be nothing but the amount of sodium hydroxide that has been added to the media divided by the total volume of the medium. And this turns out to be 0.022 molar.

So, with the acetic acid and associated and acetate and concentrations available to us. We will plug these in our equation of K which is nothing but the hydronium ion concentration into acetate ion concentration divided by the term dissociated acetic acid concentration. Now, when we do that we know that K value, we know the acetate ion concentration and we know the acetic acid concentration.

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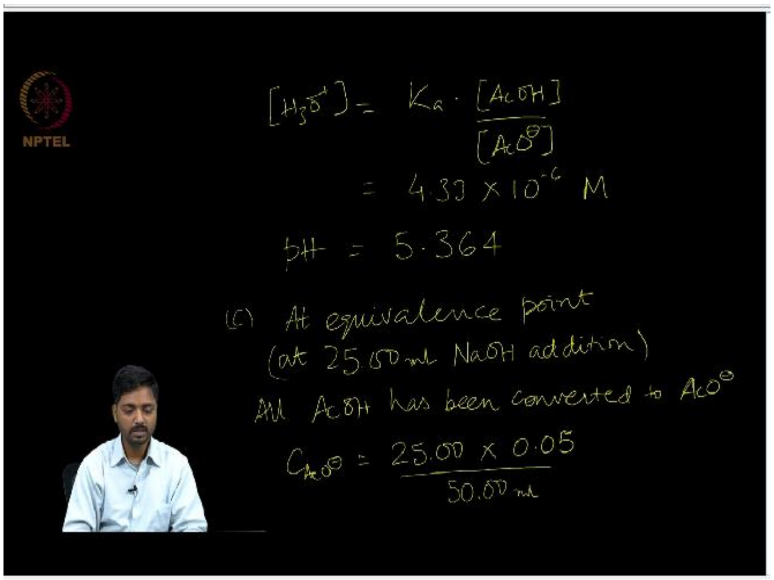

$$[H_3O^+] = K_a \cdot \frac{[AcOH]}{[AcO^-]}$$

$$= 4.33 \times 10^{-6}\ M$$

$$pH = 5.364$$

(c) At equivalence point
(at 25.00 ml NaOH addition)
All AcOH has been converted to AcO^-

$$C_{AcO^-} = \frac{25.00 \times 0.05}{50.00\ ml}$$

So, this will help us get the hydronium ion concentration which will be equal to the K value into the undisassociated acetic acid divided by the acetate and concentration present in the medium. This solves out to be 4.33 into 10 power of – 6 molar and from here the pH value can be calculated and the pH has already risen to 5.364. So at the beginning of hydration the pH was 3.03.

And even after incomplete addition of sodium hydroxide, the pH has already increased to 5.364. Now, let us see what happens as we keep adding sodium hydroxide into this medium. So, at equivalence point so, let us see the third condition, which is going to be at equivalence point. At equivalence point that is at 25.00 ml sodium hydroxide addition, we will have all acetic acid has been converted to acetate and ions.

And the pH of the medium will now be dependent upon what is first the concentration of acetate and ions which will be nothing but 25 into 0.05 divided by total now 50.00 ml.

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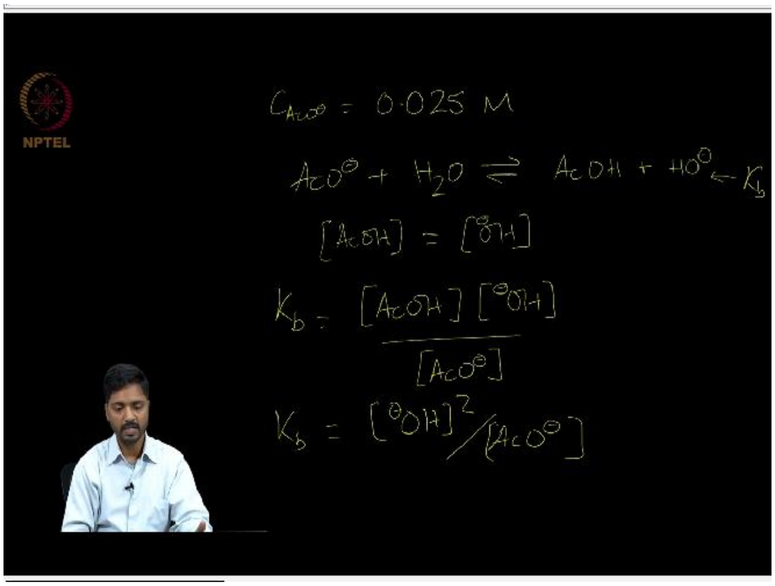

$$C_{AcO^{\ominus}} = 0.025\ M$$

$$AcO^{\ominus} + H_2O \rightleftharpoons AcOH + HO^{\ominus} \leftarrow K_b$$

$$[AcOH] = [{}^{\ominus}OH]$$

$$K_b = \frac{[AcOH]\,[{}^{\ominus}OH]}{[AcO^{\ominus}]}$$

$$K_b = [{}^{\ominus}OH]^2 / [AcO^{\ominus}]$$

And this then solves to the concentration of acetate and ions being equal to 0.025 molar because the volume is doubled, the concentration is half. Now, 1 equilibrium to be considered here is when we have acetate and ions present, they can also take up protons from water and convert back through aspartic acid and produce hydroxyl ions here. And what we believe is that the acetic acid concentration is equal to the hydroxyl ion concentration that is what the actual equivalence point will have.

So, we can write a K b value, which is nothing but the undisassociated acid into the hydroxyl ion concentration divided by the acetate ion. So, this equation will give the K b value for us. And as we have already seen that the acetic acid concentration and the hydroxyl ion concentration are the same. So, we can write this as K b is equal to hydroxyl ion concentrations square divided by acetate ion concentration.

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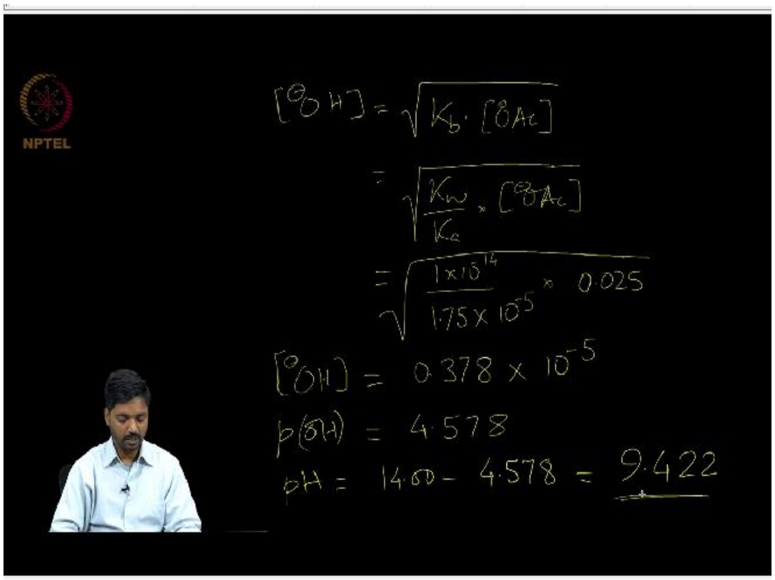

$$[{}^{\ominus}OH] = \sqrt{K_b \cdot [{}^{\ominus}OAc]}$$

$$= \sqrt{\frac{K_w}{K_a} \times [{}^{\ominus}OAc]}$$

$$= \sqrt{\frac{1 \times 10^{-14}}{1.75 \times 10^{-5}} \times 0.025}$$

$$[{}^{\ominus}OH] = 0.378 \times 10^{-5}$$

$$p({}^{\ominus}OH) = 4.578$$

$$pH = 14.00 - 4.578 = \underline{9.422}$$

Now, as we solve this, what we get is that the hydroxyl ion concentration is nothing but square root of like K b into the concentration of acetate and ions. And the K b value can be calculated as K w by K a into the acetate and ion concentration and the K w value is 10 power of - 14 K a value we know for acetic acid it is 1.75 into 10 power of – 5 and acetate and ion concentration that we calculated here was 0.025 molar.

Now, when we resolve this, what we get is that the hydroxyl ion concentration turns out to be 0.378 into 10 power of - 5. In other words, the P OH value for this system now comes to be 4.578 and the pH value will be 14.00 - 4.578 which is close to 9.422. So, it is important to note here that the pH at the equivalence point for this medium or the system is quite basic. So, we should be able to use say phenolphthalein as our indicator in this case.

And at equivalence point the pH value turns out to be 9.422. Let us see what happens when we add a little further of sodium hydroxide to this solution.

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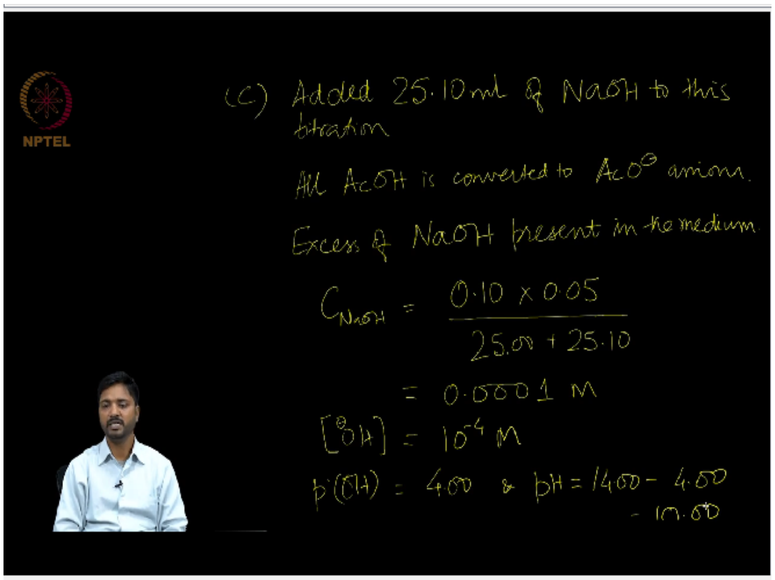

(C) Added 25.10 ml of NaOH to this titration

All AcOH is converted to $AcO^{\ominus}$ anion.

Excess of NaOH present in the medium.

$$C_{NaOH} = \frac{0.10 \times 0.05}{25.00 + 25.10}$$

$$= 0.0001 \text{ M}$$

$$[\overset{\ominus}{O}H] = 10^{-4} \text{ M}$$

$$p(\overset{\ominus}{O}H) = 4.00 \text{ \& } pH = 14.00 - 4.00$$

$$= 10.00$$

So, let us take a condition where we have added 25.10 ml of sodium hydroxide to this titration. Now, when we have added excess of sodium hydroxide what we have is that all free acetic acid is converted to acetate and ions and we have a little excess of sodium hydroxide which is present in the medium. Now, under these cases, the excess sodium hydroxide concentration would be nothing but 0.10 ml in 2.05 molar sodium hydroxide that has been added divided by the total volume which is 25.00 + 25.10 ml that has been added.

And this solves out to be almost equivalent to 0.0001 molar NaOH which is present. Now, when we have this concentration of hydroxide, hydroxyl and ions present we have P OH value of 4.00 and hence pH value is equal to 14.00 - 4.00 which is nothing but 10. So, of course, as we add a little excess of sodium hydroxide, the pH increases and becomes even more basic. So, we have seen how a variety of volumetric titrate or pH metric titrations are undertaken.

Now, in the rest part of this week, we will be focusing on how we can use gravimetric titrations for our analysis and we will understand what are the principles involved in gravimetric titrations.