

Quantitative Methods in Chemistry
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Lecture-30
Standards And Volumetric/Gravimetric Titrations Part 02

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pH metric titration of a strong acid and a strong base

Sharp decrease in pH close to the equivalence point.

This change of pH is often visually observed by addition of indicators such as phenolphthalein, bromothymol blue etc.

Phenolphthalein
 $pK_a = 9.74$
8.7-10.7

$HIn + H_2O \rightleftharpoons In^- + H_3O^+$ (acid-type indicator)
 $In + H_2O \rightleftharpoons InH^+ + OH^-$ (base-type indicator)

$K_a = \frac{[H_3O^+][In^-]}{[HIn]}$ — ①
 $K_b \frac{[HIn]}{[In^-]} = [H_3O^+]$ — ②

We get most visual response when $\frac{[HIn]}{[In^-]} = >10$ or <0.1

Indicator pH range = $pK_a \pm 1$

So, let us look at some pH metric titrations that can be performed using acids and bases as our first example, we will be considering the titration of a strong acid with a strong base. And what I have plotted here is the change in the pH of the solution of the base to which acid has been added. So, the pH keeps decreasing as the more and more acid is added to the base solution, and what we observe is that in this regime, the change is the maximum.

And around this regime only the equivalence point will be applied. Now, sometimes what we do is and that is in fact what you would have done in your school and colleges is to add indicators such as phenolphthalein or bromothymol blue to this titrating solutions and observe the color changes in them as an indication of completion of the titration or achievement of the equivalence point.

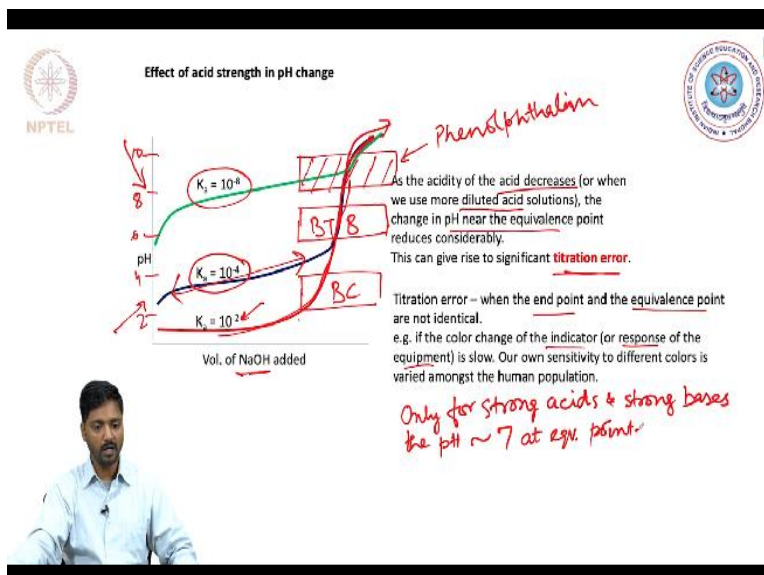
Now, it is important to understand that our indicators can be of either acid type, where the indicator is in a protonated form, and at appropriate pH, it gets converted to an ionic form, or our indicator can as well be in the basic type where the indicator accepts a proton and converts into a cationic species based on the pH of the medium and the ionic or the cationic species of the indicator or dynamic or the cationic forms of the indicator have a different absorbance or emission profile, which becomes our indicator of the completion of the titration.

Now, since this is an equilibrium reaction for an acid type indicator, we can describe dissociation constant K as given here in this equation 1 and this describes the changes in the amount of the anionic form and the neutral form of the acid type indicator that will be present as the H_3O^+ ion concentration varies, because K value for every indicator is fixed. So, we simply observe the differences in the anionic and neutral forms as the pH has changed.

And this equation 1 can be transformed into equation 2 where the H_3O^+ concentration can be described in terms of the K value of the indicator and the concentrations of its neutral and the anionic forms. It is important to remember here at this point that for an indicator to show the maximum visual response, we require the concentration of the neutral form by the anionic form to be either greater than 10 or less than 0.1.

So, the best pH range for an indicator would be its pK_a value ± 1 . So, let us consider the most common acid type indicator, which is phenolphthalein and phenolphthalein is known to have a pK_a value of 9.74. So, what this indicates is that the phenolphthalein will undergo the maximum color change in the pH regime of 8.7 to 10.7. So, phenolphthalein is a basic indicator and it will work best when the pH of the medium is basic and it is in the range of 8.7 to 10.7.

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So, when we titrate an acid and a base, the acid strength has a very clear influence on the type of titration curve that we will generate during this titration. For example, in this graph here, I have plotted 3 different acids of different strengths, which are being titrated against the same concentration of sodium hydroxide. And what we observe is that for the strongest acid, we obtain the strongest profile, which is indicated as the red profile.

And what we see here is that there is a tremendous change in the pH of the media as more and more NaOH is added. However, when the acid strength is reduced for example, when we take a K value of $10 \cdot 10^{-4}$, the acid is weaker than the acid, which is having a K when they have 10^{-2} . And in this case, we observe this regime where the pH increases, indeed, slow rate is some sort of a buffering regime.

And, more importantly, the change in the pH of the medium is much lower than what was happening with the first acid where the K value of 10^{-2} as we work with even weaker acid, for example, one with K value of 10^{-6} , we observe that the change in the pH of the medium is really negligible and it would be difficult to discern the equivalence point of this titration. So, what we observe is that as the acidity of the acid being implied for the titration decreases or when we use more dilute acids, the concept remains similar that the change in pH near the equivalence point reduces considerably.

And when that happens, we start generating what is known as a titration error. What is titration error, titration error is when the end point of titration and the equivalence point of the titration theoretically are not identical. So, the end point is practically determined by the equivalence point can be determined theoretically and when these 2 did not have the same value, then we say that our titration is having some error.

And one very common source of generating a titration error is the small change in the color of the indicator or small change in the response of the equipment which we are utilizing to figure out our titration and sometimes this change can also be slow and that will also dictate the errors that may creep into our titration. And further when we are using visual indicators, such as phenolphthalein or bromothymol blue, then our own sensitivity to different colors is varied amongst the human population.

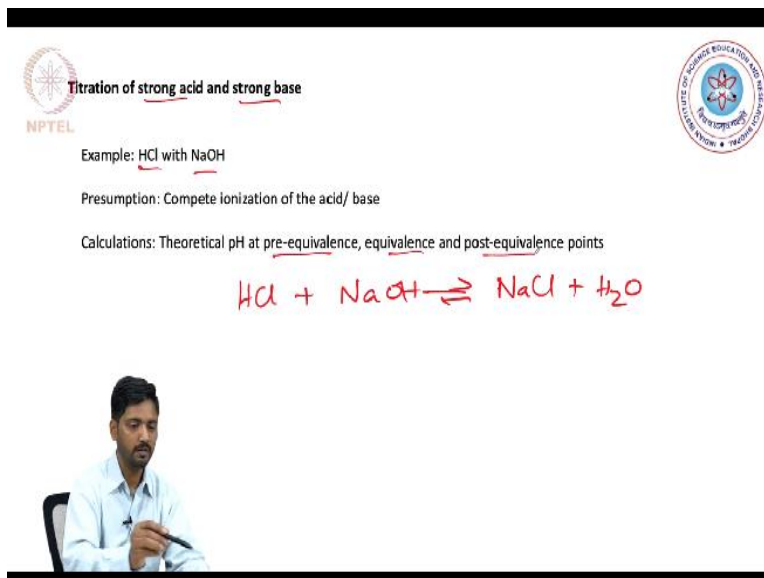
So, our ability to discern the anionic form from the neutral form will be vary from individual to individual and this may again generate titration error. Now, it is important at this point to think what indicator would suit best for titrations that are shown in the profile here and I will give you 3 typical examples of indicators that are used commonly and then explain this important point. So, one indicator which we already talked is phenolphthalein.

And it was supposed to have if this is the region of 10⁸, 4, 4, 2, so, if this is the pH value, then this is the regime where phenolphthalein will work best. So phenolphthalein will work best when our the pH of the medium is basic. However, if we take bromothymol blue that works best in the pH regime of 6 to 8 and that is shown here. So, bromothymol blue would be our indicator of choice when we are titrating the blue curve with our K value of 10 power of -4.

When we are dealing with a more acidic acid we can choose a different indicator. For example, in this case, we can use the bromocresol which has a pKa value of 4.7. So it would work best in the acidic regime and will be useful when we are titrating strong acid with a strong base. Now, one very important point to remember here is that only for strong acids and strong bases the pH is close to 7 at equivalence point.

Then we are dealing with a weak acid and a strong base a strong base will dominate and at equivalence point the pH will be basic. Similarly, if our acid is strong, but the base is weak, the pH at the equivalence point will be acidic. So, please keep this important point in your mind when you are thinking of titrations.

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The slide features a title "Titration of strong acid and strong base" with "strong acid" and "strong base" underlined. It includes the NPTEL logo on the left and the Indian Institute of Technology Bombay logo on the right. The text on the slide reads: "Example: HCl with NaOH", "Presumption: Complete ionization of the acid/ base", and "Calculations: Theoretical pH at pre-equivalence, equivalence and post-equivalence points". A handwritten chemical equation in red ink is shown:
$$\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$$

Now, let us take a few quick examples of pH metric titrations. The first example that we can take is of titration of a strong acid and a strong base. A common example would be simply type question of HCl and NaOH and they will undergo stoichiometric reaction there this equation describes the chemistry happening between the acid and the base. So, we have stoichiometric formation of sodium chloride in the reaction between the hydrochloric acid and sodium hydroxide.

So, let us go to the board and try to calculate theoretically what would be the pH when we titrate at HCl with NaOH and we will take known concentrations of the acid and base and see the theoretical pH at the pre-equivalence, equivalence and post- equivalence points. So, let us go to the board.

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Titrate 25.00 ml of 0.05M HCl with NaOH 0.05M. What are the theoretical pH values at

- No NaOH has been added
- 20.00 ml of NaOH
- At equivalence point (25.00 ml NaOH)
- After addition of 25.10 ml of NaOH

- $\text{HCl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}^-$
- $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$

Presumption → All H_3O^+ comes from dissociation of HCl.

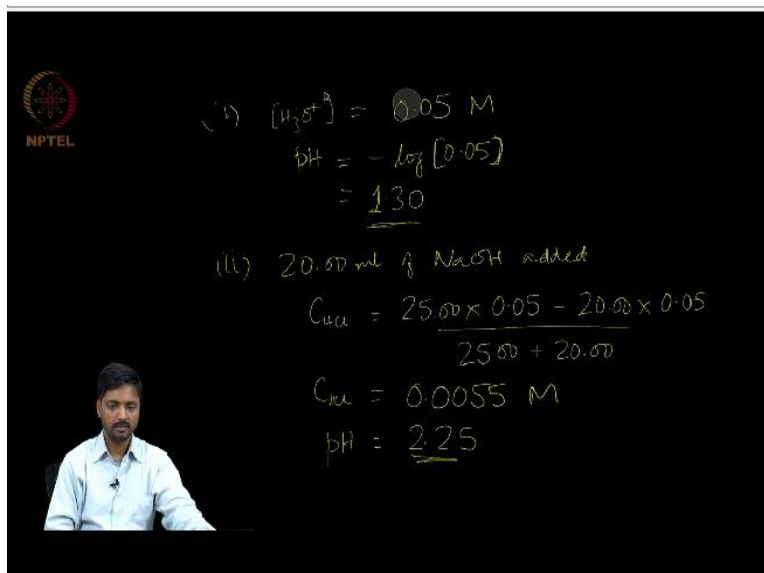
So, what we are doing here is so, we are going to titrate 25.00 ml of HCl which is 0.05 molar with NaOH whose concentration is also 0.05 molar. And what we would want to calculate is what are the pH values, what are the theoretical pH values at first, when no NaOH has been added then at pre-equivalence points say, when we have added 20.00 ml of NaOH. Then we will also calculate the pH at the equivalence point which will come again on addition of 25 ml NaOH.

And finally we will calculate the pH post-equivalence and that would be at after addition of 25.10 ml of NaOH, so, these would be the 4 conditions that we will calculate the pH at. So, let us begin let us first see what are the equilibria that we need to consider. The first equilibrium is the dissociation happening of the hydrochloric acid into hydronium ion and chloride ions.

And the second equilibrium that may be of relevance here is the self dissociation of water into hydronium ions and hydroxyl ions. Now, obviously, when we are talking about strong acid, the dissociation of the acid will dominate over the self dissociation of water. So, what we will presume is that all the hydronium ion in this case is being generated from the hydrochloric acid present in the solution.

So, let us calculate based on this presumption, so let me explicitly write the presumption all H_3O^+ comes from the dissociation of HCl. Now, when we take this presumption, we can calculate the pKa value or the pH value of the solution at the initial instance.

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(i) $[H_3O^+] = 0.05 \text{ M}$
 $pH = -\log(0.05)$
 $= 1.30$

(ii) 20.00 ml of NaOH added
 $C_{HCl} = \frac{25.00 \times 0.05 - 20.00 \times 0.05}{25.00 + 20.00}$
 $C_{HCl} = 0.0055 \text{ M}$
 $pH = 2.25$

And that means that the hydronium ion concentration would be equal to 0.05 moles, which is the concentration of the HCl that we are using. And when we calculate the pH from this, that would be negative log of 0.05. And this comes out to be 1.30. So, we see that initially we are dealing with a very low pH of 1.30 which should be the case when strong acid like hydrochloric acid is solubilized in water. Now, let us take the second case where we have added 20 ml of NaOH.

So, since the reaction between the sodium hydroxide and hydrochloric acid is stoichiometric the concentration of hydrochloric acid that will be present will now become the initial amount of HCl present minus the amount of sodium hydroxide added and the volume change now would be 25 plus that 20 ml that has been added of the sodium hydroxide. So that 25.00 is the initial volume and 20 ml is the sodium hydroxide that has been added to this titrating mixture.

And when we solve this, what we get is that the concentration of HCl now becomes out to be 0.005 molar and from this we can calculate the pH value and the pH is still quite acidic with a pH value of 2.25. Now, we can see that even after adding 20 ml of sodium hydroxide, the pH change is only about in fact less than 1 pH unit. Now, let us look at the case what happens at the equivalence point.

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(iii) At equivalence point
 All HCl is converted to NaCl
 NaOH " " NaCl

No excess $[H_3O^+]$ or $[OH^-]$ is present
 in the titrating vessel.

$$[H_3O^+] = [OH^-]$$

$$[H_3O^+] = \sqrt{K_w}$$

$$= \sqrt{1 \times 10^{-14}}$$

$$= 10^{-7}$$


pH = 7.00

So, at equivalence point essentially all HCl is converted to NaCl and similarly, all NaOH that has been added is also converted to NaCl. So, we essentially do not have any hydronium ion or hydroxyl ion present, no excess hydronium ion or hydroxyl ion is present in the medium in that titrating vessel. So, in that case we have the hydronium ion also equal to the hydroxyl ions and they both are being contributed by the dissociation of water.

So, water what we have is the hydronium ion concentration is equal to the square root of K_w and we know that the K_w is 1×10^{-14} and when we take the square root this turns out to be 10^{-7} and hence the pH value at this point is exactly 7. So, as I indicated earlier also when we are titrating strong acids and strong bases, we can expect only in these cases that the pH is equal to 7 at the equivalence point.


Now, let us look at what happens in the fourth and the final case here that is when a little excess of sodium hydroxide is present, but before that, I want to also highlight it here that when we added initial 20 ml of sodium hydroxide, the pH change was less than 1 pH unit. However, the next 5 ml of sodium hydroxide addition suddenly increased the pH by about 5 pH unit. So, we can see a very rapid change in the pH of the medium as we approach the equivalence point. Now, let us see what happens as we cross the equivalence point.

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(iv) Beyond equivalence point
25.10 ml of NaOH

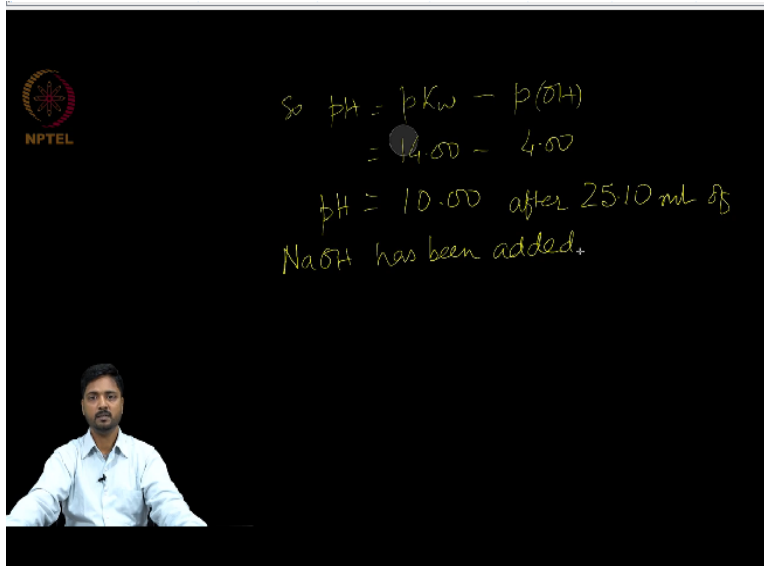
No free HCl left.
Slight excess of NaOH in the medium.

$$C_{\text{NaOH}} = \frac{25.10 \times 0.05 - 25.00 \times 0.05}{25.10 + 25.00}$$
$$C_{\text{NaOH}} = 0.0001 \text{ M}$$
$$[\text{OH}^-] = 10^{-4} \text{ M}$$
$$\text{p}(\text{OH}^-) = 4$$


And so beyond the equivalence point, that is when we have added say 25.10 ml of sodium hydroxide. Now in that case we have no free HCl left. In fact, there is a slight excess of sodium hydroxide in the medium and what is the concentration of sodium hydroxide. So, we can calculate the concentration of sodium hydroxide as the total amount of sodium hydroxide that was added minus the initial amount of X here that was present this mole divided by the total volume of the medium now, which is 25.10 + 25.00.

Now, when we calculate this we get the concentration of NaOH as approximately 0.0001 molar and this turns out that the hydroxyl ion concentration is 10 power of - 4 molar or p OH, which is the negative log of the H concentration is 4. Now, from this it is very straightforward to calculate the pH of the solution.

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The image shows a video frame with a presenter in the bottom left corner and a blackboard with handwritten text. The blackboard contains the following text:

NPTEL

$$\text{So } \text{pH} = \text{pK}_w - \text{p(OH)}$$
$$= 14.00 - 4.00$$

$\text{pH} = 10.00$ after 25.10 ml of NaOH has been added.

And so pH is equal to pK_w - p OH. So, the pK_w is 14.00 and the pH is 4.00. So, the pH value turns out to be 10.00 after 25.10 ml of NaOH has been added. So, we see here that only 0.1 ml addition of sodium hydroxide in excess suddenly increases the pH of the medium by about 3 pH units. So it is amply clear from this that near the equivalence point we see the strongest changes in the pH of the medium as the strong acid and the strong base are titrated.