Quantitative Methods in Chemistry

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Lecture-05
Problems on Acid-Base Equilibria, Calculation of pH of Strong and Weak Acids

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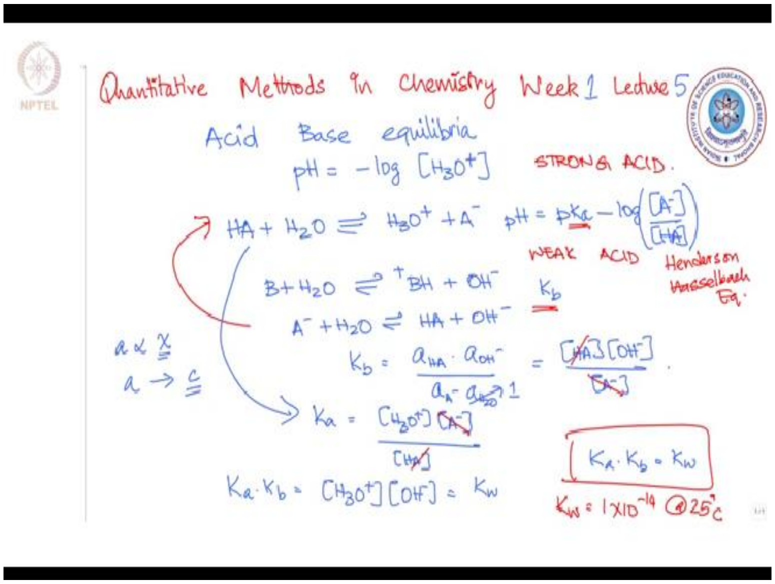

Quantitative Methods in Chemistry Week 1 Lecture 5

Acid Base equilibria

$pH = -\log[H_3O^+]$ STRONG ACID.

$HA + H_2O \rightleftharpoons H_3O^+ + A^-$ $pH = pK_a - \log\left(\frac{[A^-]}{[HA]}\right)$

WEAK ACID

Henderson Hasselbalch Eq.

$B + H_2O \rightleftharpoons {}^+BH + OH^-$ K_b

$A^- + H_2O \rightleftharpoons HA + OH^-$

$a \propto x$

$a \rightarrow c$

$K_b = \frac{a_{HA} \cdot a_{OH^-}}{a_{A^-} \cdot a_{H_2O} \rightarrow 1} = \frac{[\cancel{HA}][OH^-]}{[\cancel{A^-}]}$.

$K_a = \frac{[H_3O^+][\cancel{A^-}]}{[\cancel{HA}]}$

$K_a \cdot K_b = [H_3O^+][OH^-] = K_w$

$\boxed{K_a \cdot K_b = K_w}$

$K_w = 1 \times 10^{-14}$ @ $25^\circ C$

In the previous class we saw some examples of how to calculate concentration in different units and also looked at how they can be interconvert it across these units. In addition, we also try to understand a little bit of how equilibrium constant can be determined for the same reaction in non-stoichiometry amounts and when they do not go to completion. In today's class, we will be looking at some examples of acid-base equilibria.

We had already defined a few parameters that we redefine them so that we get the class started, we defined pH as minus a logarithm of the concentration of H 3 O + ions, and this is for strong acids. On the other hand, for weak acids we were able to derive the Henderson Hasselbalch equation that goes to pH equal to P ka - log of A - by H A weak acid. The other parameter that can be defined of course, here we defined with a parameter called Ka, which is the acidity equilibrium constant.

Similarly, one can also define the basis of equilibrium constant. Let us say you have B, which is a weak base that abstracts a proton from water. It is defined by K b. So why do not we write the K b, so let us take a similar example as we are taken earlier. For instance, let us say you have A - H 2 O, giving H A + OH -. So similar to the acidity constant that you have seen before, so you are talking about K a and K b for the same chemical.

So in which case what ends up happening, K b can be given us in which case K b can be given as activity of HA times activity of OH - divided by activity of A - activity of H 2 O, we know that activity of H 2 O is 1, so we are not going to write it any further. And we define what is activity, activity goes as the mole fraction or the concentration depending upon the solute. So let us assume that this is such a low concentration, which will end us approximating the activity to the concentration of the solute itself.

So this ends up becoming HA times OH - divided by A -. And how was K a defined from this equation K a was defined us H 3 O + times A - divided by HA. Of course here also we assumed the activity of water is 1 because it is a pure state and we have approximated activity to concentrations. So one is able to realize if you take a product of K a times K b, what ends up happening is that in the HA terms start to cancel.

And the A - term starts to cancel and you are going to be ending up with H 3 O + times OH -, this is nothing but K w. So for a given chemical the product of K a times with K b = K w okay, so, let me also write the equation here Henderson Hasselbalch and of course, K w is 1 into 10 power – 14 at 25 degrees Celsius okay. Now that we have seen it let us take some examples.

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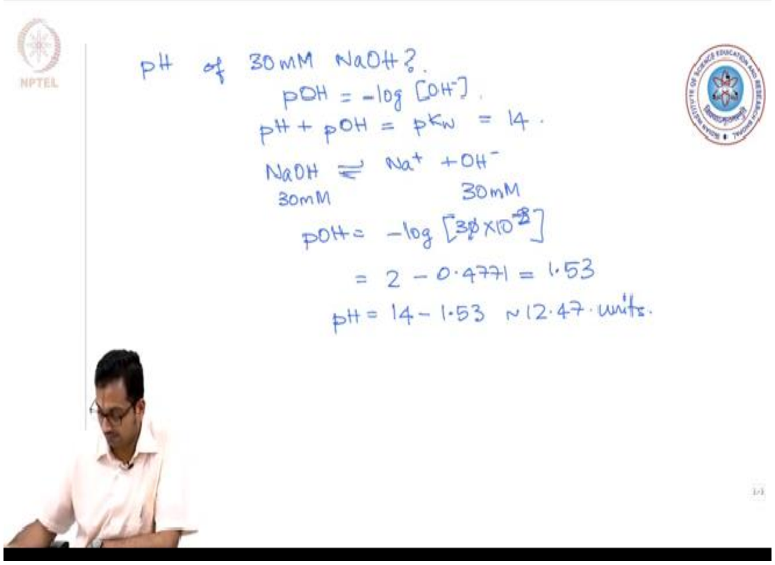

pH of 30 mM NaOH?

$pOH = -\log [OH^-]$

$pH + pOH = pK_w = 14$

$NaOH \rightleftharpoons Na^+ + OH^-$

30 mM   30 mM

$pOH = -\log [3\cancel{0} \times 10^{-2}]$

$= 2 - 0.4771 = 1.53$

$pH = 14 - 1.53 \sim 12.47$ units.

What is the pH of 30 millimolar NaOH, as we are able to realize P OH is like a definition of pH, which has given as negative logarithm of OH - ions. Simple math and our intuition clearly says pH + P OH which will be equal to P K w, which is nothing but 14. So now we know that for NaOH it is going to completely dissociate at this concentration to give Na + and OH - ions. So if you had 30 millimolar of a NaOH you are going to have 30 millimolar of hydroxyl ions.

So therefore the P OH is going to be given by - log of 30 times 10 power - 3 since it is merely so this will translate itself to something like 3 10 power - 2. This is going to be 2 - of log 3 which is 0.4771. So that will be equal to 1.53 P OH. Therefore the pH for the solution is going to be given by 14 - 1.53. That is going to end up becoming approximately 12.47 units. What we are able to see here is for a given acid or a base you can define the pH that is associated with it.

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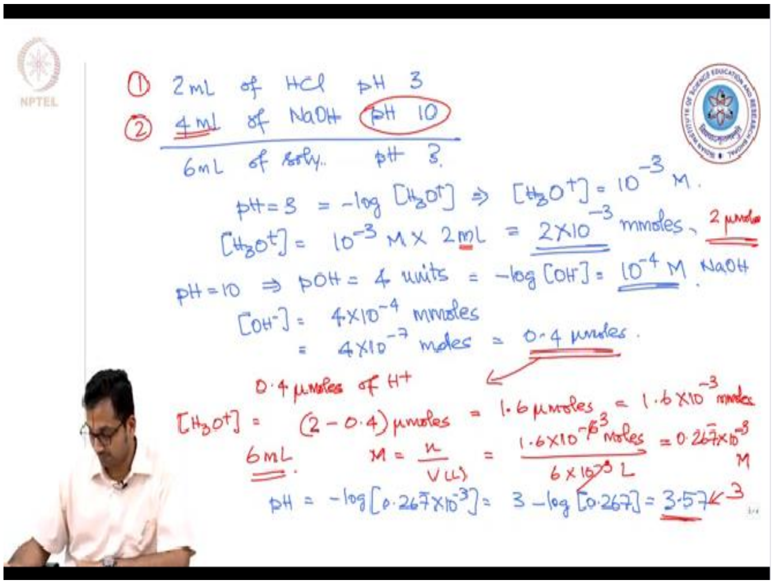

① 2 mL of HCl pH 3

② 4 mL of NaOH pH 10

6 mL of soln.. pH ?

$pH = 3 = -\log[H_3O^+] \Rightarrow [H_3O^+] = 10^{-3}$ M.

$[H_3O^+] = 10^{-3}$ M × 2 mL = 2×10^{-3} mmoles, 2 μmoles

$pH = 10 \Rightarrow pOH = 4$ units $= -\log[OH^-] = 10^{-4}$ M NaOH

$[OH^-] = 4\times10^{-4}$ mmoles

$= 4\times10^{-7}$ moles = 0.4 μmoles.

0.4 μmoles of H^+

$[H_3O^+] = (2-0.4)$ μmoles = 1.6 μmoles = 1.6×10^{-3} mmoles

6 mL $\quad M = \frac{n}{V(L)} = \frac{1.6\times10^{-3}\text{ moles}}{6\times10^{-3}\text{ L}} = 0.267\times10^{-3}$ M

$pH = -\log[0.267\times10^{-3}] = 3 - \log[0.267] = 3.57 < 3$

Let us try to see what happens when we mix acid and basis together. We are very well aware of the fact if you mix a strong acid with strong base, you get a neutral salt and water that comes of it. Let us take such an example. Let us say we have 2 ml of Hcl at pH 3 and then to this you are adding 4 ml of NaOH at pH, let us say at 10. So, this immediately implies then let us say you add these 2 things together, you get 6 ml of solution.

What is the pH. Let us try to answer this question. So let us take it step wise, when you are trying to say concentration of Hcl at pH 3 is going to be pH = 3. Assuming full dissociation, there is going to be - log of H 3 O + ions and solution 1. So I am going to call this solution 1 and the solution 2. So this is going to imply H 3 O +. It is given by 10 to the power of - 3 molar. And you have 2 ml of it.

So therefore the number of millimoles so H 3 O + concentration is going to be given by 10 to the power of - 3 moles times 2 ml which is going to be 2 into 10 to the power of - 3 millimoles okay, so this is the amount of H + that you have in your hand and let us determine what is the concentration of OH - that is present, that will end up neutralizing this acid at pH 10. We understand that the P OH which is 4 units, the P OH is 4 units, this implies - - log of OH – is this, which end up as 10 power – 4 molar NaOH which is present.

So, if 10 per - 4 is present, how many millimoles of OH - is present, that is going to be 4 times 10 to the power – 4 millimoles. Of course, I am writing millimoles because you are using milliliter here. So, this can be rewritten as 2 micromoles. So now you have a given amount of H 3 O + and given amount of OH - ions that are present okay. So this could be written as 4 into power of – 7 moles, which is 0.4 micromoles.

So you are able to realize that you have more amount of H + ions, then the OH – ion. So basically the result and solution should be an acidic. So when you are neutralizing these 2 what ends up happening, you are going to have 0.4 micromoles of H + neutralized by this 0.4 micromoles of OH -. So finally what ends up happening, the amount of H 3 O + that is going to be present is going to be 2 – 0.4 micromoles is going to end up as 1.6 micromoles.

Of course, this can be rewritten as 1.6 10 to the power of - 3 millimoles. Remember, we have to convert it back into concentration which is in molarity. So therefore what is going to end up happening how much ml, so you are having 6 ml that is going to be present? So molarity is equal to a number of moles by the total volume that you have and of course liters. So you have something as 1.6 10 to the power of – 6 moles divided by 6 ml.

So that is going to be equal to, so therefore the pH is going to be given by - log of 0.267 times 10 power - 3, this is going to be 3 - log of 0.267. This is going to be equal to 3.57 units. So basically what you are able to realize is that by addition of H + and NaOH and with NaOH concentration being a little lower, you are able to realize you are pushing the pH from 3 to 3.57. This example shows that what happens when you add a strong acid and strong base at a given concentrations.

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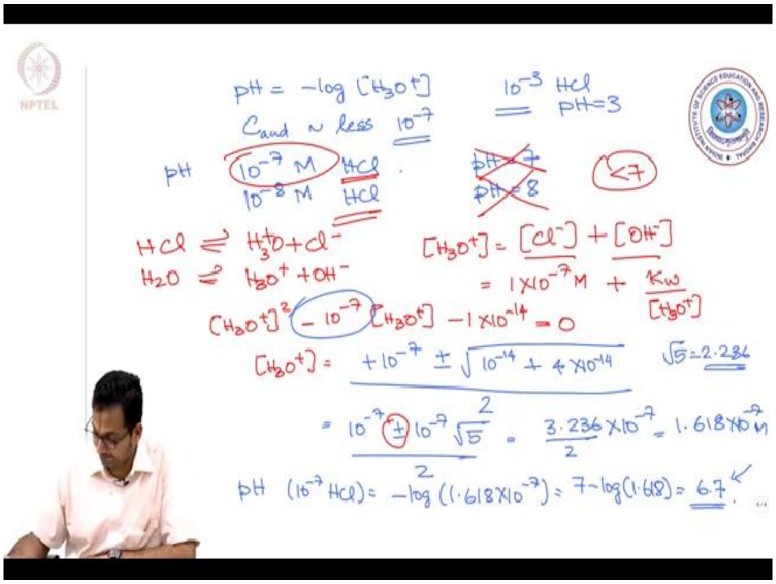

$pH = -\log[H_3O^+]$ 10^{-3} HCl $\underline{\underline{\quad}}$ $pH = 3$

$C_{acid} \sim$ less $\underline{\underline{10^{-7}}}$

pH 10^{-7} M HCl

10^{-8} M HCl

~~pH = 7~~

~~pH = 8~~

<7

$HCl \rightleftharpoons H_3O^+ + Cl^-$

$H_2O \rightleftharpoons H_3O^+ + OH^-$

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

$= 1 \times 10^{-7} M + \frac{K_w}{[H_3O^+]}$

$[H_3O^+]^2 - 10^{-7}[H_3O^+] - 1 \times 10^{-14} = 0$

$[H_3O^+] = \frac{+10^{-7} \pm \sqrt{10^{-14} + 4 \times 10^{-14}}}{2}$ $\sqrt{5} = 2.236$

$= \frac{10^{-7} \pm 10^{-7}\sqrt{5}}{2} = \frac{3.236}{2} \times 10^{-7} = 1.618 \times 10^{-7} M$

$pH\ (10^{-7} HCl) = -\log(1.618 \times 10^{-7}) = 7 - \log(1.618) = 6.7$

Let us try to ask the same question but in a slightly different way. We just defined that the pH is given by - logarithm of H 3 O + for strong acids, let us say you have 1 millimolar of Hcl immediately you are able to say the pH is 3, as we just saw in the previous example. But let us say if you are using a concentration of strong acid that is similar or less than that of 10 power – 7. So let us take an example, what is the pH when you have a 10 power – 7 molar Hcl.

It is very tempting to say the pH of this solution is 7 to obscure this point, let us say you have a 10 power – 8 molar Hcl. It is very tempting to say the pH is 8. But this is not correct. So is this you are able to realize that if you are going to add a concentrated acid, the pH has to be less than the neutral pH and at 25. The pH neutral pH is 7. So therefore, it has to be less than 7 units. So where are we going wrong, let us take this problem step wise Hcl at this concentration can be very well approximated to be completely dissociated to hydronium ions in the presence of water.

And chloride ions and water of course, undergoes self dissociation into hydronium ions and hydroxyl ions. So, therefore, the total concentration of hydronium ion in such a case is going to be given as the sum of the concentration of the chloride ion and that of the hydroxyl ion that comes from waters self dissociation. So, when you are having this case, we just took an example of 10 per - 7 molar So, you are able to realize this is going to be 1 into 10 per - 7 and OH - we know for a fact is given by K w divided by the **+** H 3 O + ion concentration.

So, doing the basic LCM we are going to get H 3 O + the whole square - 10 to the power - 7 H 3 O + - K w, I am going to write it directly as 1 into 10 to the power of - 14 = 0. So this is a quadratic equation, which we can solve by trying to find the solution H 3 0 + - - b. So it is going to be + 10 power - 7 plus + - square root of b square so that makes it 10 power - 14 – 4 times Ac minus of minus becomes plus, 10 to the power - 14 divided by 2A. So this was with quick arithmetic square root of 5 is 2.236.

This will be you have 2 solutions here, you have a plus or minus and you realize that the - 2.236 results in negative concentration of hydronium ions, which is not possible. So therefore, we are only going to take the solution where you have the plus. So therefore, this is going to end up as 3.236 into 10 to the power of -7 was divided by 2, this is going to be 1.618 10 to the power of -7 molar.

So now the pH of 10 to the power of - 7 Hcl solution is going to be given by - log of 1.618 into 10 to the power of - 7. This is going to be 7 - log of 1.618. That is going to be equal to 6.7. So, you realize that although it is very tempting to say the pH of 10 power – 7 molar Hcl is 7, it is actually wrong. It has to be less than 7. And you do see it is a little less than 7, which is at 6.7. So be very careful when answering such questions.

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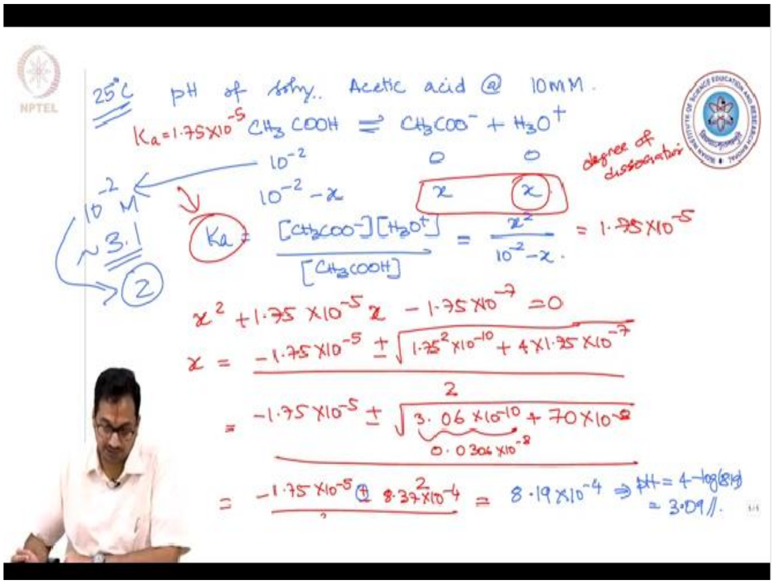

25°C pH of soln.. Acetic acid @ 10mM.

$K_a = 1.75 \times 10^{-5}$ $CH_3COOH \rightleftharpoons CH_3COO^- + H_3O^+$

10^{-2} 0 0

$10^{-2} - x$ x x

degree of dissociation

10^{-2} M

~3.1

②

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = \frac{x^2}{10^{-2} - x} = 1.75 \times 10^{-5}$$

$$x^2 + 1.75 \times 10^{-5} x - 1.75 \times 10^{-7} = 0$$

$$x = \frac{-1.75 \times 10^{-5} \pm \sqrt{1.75^2 \times 10^{-10} + 4 \times 1.75 \times 10^{-7}}}{2}$$

$$= \frac{-1.75 \times 10^{-5} \pm \sqrt{\underbrace{3.06 \times 10^{-10}}_{0.0306 \times 10^{-8}} + 70 \times 10^{-8}}}{2}$$

$$= \frac{-1.75 \times 10^{-5} + 8.37 \times 10^{-4}}{2} = 8.19 \times 10^{-4} \Rightarrow pH = 4 - \log(8.19)$$

$$= 3.09$$

So let us solve one more question to finish up the entire discussion. So, let us say we have to calculate pH of a solution that has initial acidic acid concentration at 10 millimolar. So what is the pH of a 10 millimolar solution of acidic acid of course, we are assuming it is all 25 degrees. The equilibrium experiments you are to mention the pH and the temperature at which it is being performed.

So if we do not say anything, the assignment or in the tutorials it means that you are assuming 25 degrees Celsius. So acidic acid is a weak acid and we realized that it is not going to completely dissociate to form acetate anion and the hydronium ion. So 10 millimolar can be written as 10 to the power of - 2. And let us say you started with 0 and then let us say there is a certain amount of conversion, let us assume that as x.

So it going to have K a that is going to be given by assuming at low concentrations, you can approximate activity to the concentrations. This is going to end up as x square divided by 10 to the power of - 2 - x. So now if we know the K a of acidic acid, we should be able to determine what is indeed the pH. So let us quickly calculate that it is given the K a of acidic acid is 1.75 into 10 to the power of – 5 is going to be equal to 1.75 okay.

So now that is done, let us determine what is x. So this is rearranging quick rearranging gives us therefore x is going to be given by. Why are we trying to determine x because x determines what is the pH of the solution. So this is going to end up to be, once again we are only going to take the plus solution, not the minus solution. So what we are able to realize here is that if you take a weak acid so although we are taking 10 power - 2 molar.

You finally end up with the pH of 3.09. You can you finally end up with a pH of 3.1 units, had you taken a strong acid you would have been at a pH of 2. So this clearly indicates the degree of dissociation given by the parameter K a makes you understand why pH of weak acids would end up to be a little lower at a given concentration against a strong acid.