Environmental Chemistry and Microbiology
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Lecture - 3
Acids, Bases and Salts - III

Welcome everyone, to our online NPTEL course. Environmental Chemistry and Microbiology. I am Professor Anjali Pal from Civil Engineering Department. I am covering the Environmental Chemistry part and this is my third lecture on acids, bases and salts. And in this lecture, I will cover mainly the buffer, the mechanism of buffer action and how to select the buffer.

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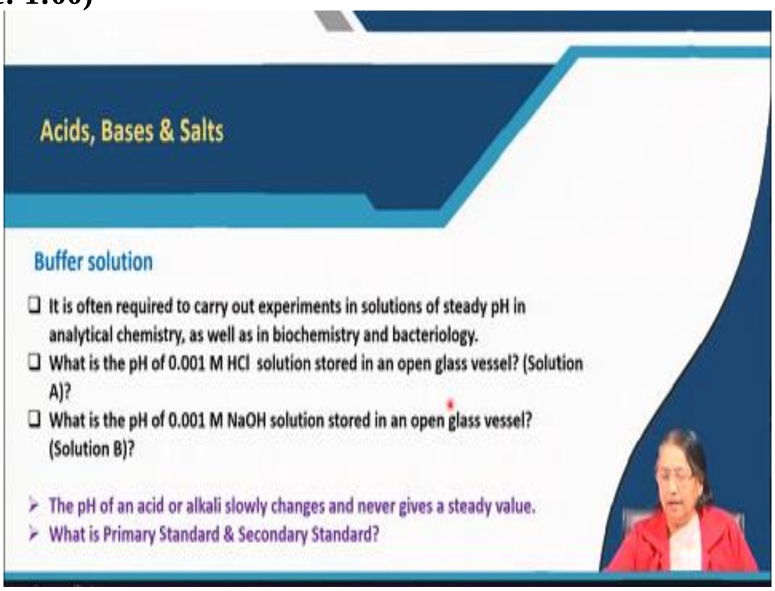

Buffer is very important in chemistry in maintaining the pH. It is often required to carry out experiments in solution of steady pH. It is very useful in analytical chemistry as well as in biochemistry and bacteriology. I will tell you some question here. What is that question? Say for example, I have a solution of 0.001 molar HCl and it is stored in your open glass vessel. Say, I have named it as solution A. I have kept it stored for quite some time. Say, for example, 7 days. Then, I measured the pH after 7 days. So, what should be the pH of that solution? I have already told you about the pH. I have given the concept of pH that pH is nothing but the $-\log_{10}[H^+]$ and I already told you that HCl is a strong electrolyte. That means it will dissociate 100%.

If I calculate pH of solution A, then it will be as follows:

$pH=-log_{10}(10^{-3})=3$........................(1)

But after 7 days also will that pH be 3 if it is kept in an open glass vessel. That is a question. Will it be 3 or it will differ?

In the same way 0.001 molar NaOH is stored in an open glass vessel. It is called solution B and if it is stored for 7 days, what should be the pH? If we directly calculate, then pH will be:

$pOH=-log_{10}(10^{-3})=3$

So, $pH=14-3=11$..................................(2)

But is that correct? Just direct calculation will give me the pH or it will be different something else that is the question. The pH of the acid or alkaline slowly changes and never gives a steady value.

Why it is changing? First of all, it will depend upon the type of glass vessel in which the solution is kept. If it is alkaline and you keep acidic solution, then some alkali will come out and react with the acid and hence pH will get changed. Secondly, an open vessel is exposed to atmosphere and hence carbon dioxide, ammonia from the atmosphere may come and get dissolved in the water. Hence it will change pH.

That means pH will not be a constant, with time it will change. That is why they are not primary standard. So, what do we know about primary standard and secondary standard? We know primary standard is something which we can weigh accurately, which is not hygroscopic, which we can accurately measure; and also if we prepare the solution, we can keep it stored for long period of time. That is primary standard. Strength is known. Strength will not change with time. But for secondary standard we know with time it may change. The weight also we cannot take it properly like this. So, in the case of HCl and NaOH that we have prepared in the glass vessel is not a primary standard because pH is changing.

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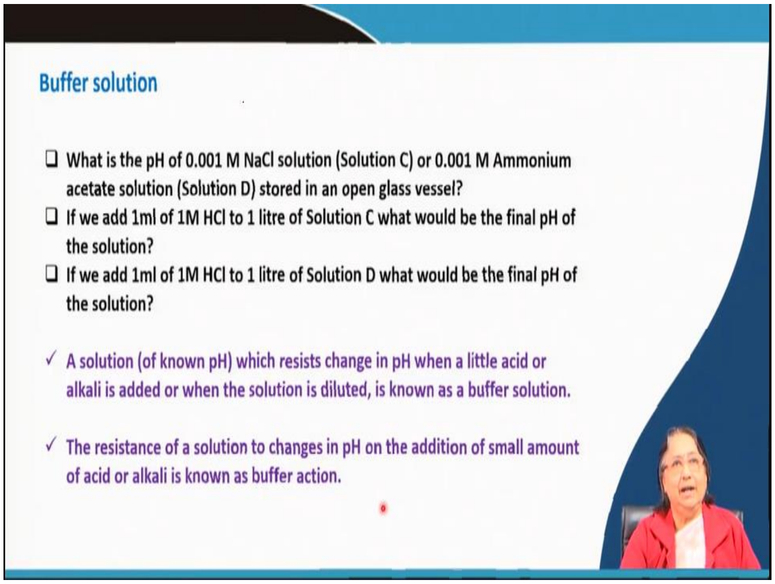

Now, here comes the function of buffer. Before going to that, I have 2 more questions. What is the pH of 0.001 M NaCl solution? I call it solution C. What is the pH of 0.001 M CH_3COONH_4? We call it solution D. Both solutions (C&D) is stored in an open glass vessel. This is very simple. You know that sodium chloride solution has a pH 7. It is neutral solution. So, it is 7 and what about 0.001 M CH_3COONH_4. For today, you think that the pH is say x. I have not calculated it. Say it is x.

Now, another question is coming if we add 1 ml of 1 molar HCl to 1 liter solution of C (that means sodium chloride solution). What should be the pH? Initially it was 7 because it is sodium chloride solution. Now, I am adding 1 ml 1 molar HCl to 1 liter of the solution. What should be the pH? It is easy because 1 ml solution has been diluted to 1 liter. So, volume is increased 1000 times and the concentration will decrease 1000 times. So, now it will be

$pH=-\log_{10}(10^{-3})=3$................................(3)

But, if we add same volume, same concentration of that HCl, in 1 liter of solution D. Then should we see any change or we should not see any change? That is the question. In case of solution C, we see change. Initially it was 7 but now it is 3 (huge change!) But what will happen in case of D. I told you that ammonium acetate solution it has the pH say x. Now, with that after addition of 1 ml 1 molar HCl, what would be the pH? That is the question.

Now, a solution of known pH which resists change in pH when a little acid or alkali is added or when the solution is diluted is known as buffer solution. So, buffer solution is a solution, which will resist the change of pH. When you add HCl, it is expected that the pH will change. But if you use buffer and if you add some HCl or NaOH to that buffer solution, the pH will not change. This is called buffer action and the solution is called buffer solution. Here in this case, the solution D which is ammonium acetate, it is a buffer solution. So, when you add 1 ml 1 molar HCl to this solution, pH will not change much. Very slight change may happen but not like solution C. It is called buffer action. This has enormous application in Analytical Chemistry, Environmental Chemistry, and in many process engineering.

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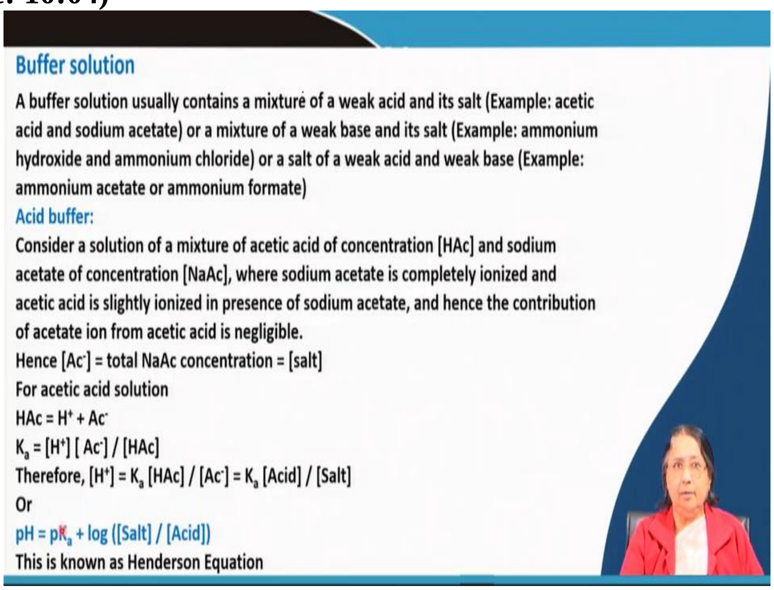

So, we have to know how it acts. And what is the mechanism of buffer action?

If we see the composition, then we will see that buffer solution may be of 2 types: acid buffer and alkaline buffer. If it is acidic buffer, then it is a mixture of weak acid and its salt. Example: acetic acid and sodium acetate. So, it is a mixture of two things, one is the weak acid and the other is its salt.

So, if weak acid is acetic acid then the other thing should be its salt i.e., the sodium acetate and if it is an alkaline buffer, then it should be a weak base and its salt. Example: ammonium hydroxide and ammonium chloride or it can be a salt of weak acid and weak base. Just in the previous slide we have seen ammonium acetate may act as a buffer. Ammonium acetate is nothing but a salt of weak acid and weak base. So, it is also a buffer. Now, if I consider the acid buffer, then consider a solution of a mixture of acetic acid of concentration [HAc] and sodium acetate of concentration [NaAc]. We write concentration in square bracket.

We know that salt is completely ionized. It may be a salt of strong acid and weak base, or it may be a salt of a weak acid and strong base. So, sodium acetate will be completely ionized and acetic acid which is a weak acid will be partially ionized. Then we can see what happens.

Hence, the acetate ion that is present in the medium (the mixture of acetic acid and sodium acetate) is the total sodium acetate concentration. Because the dissociation of acetic acid is very less compared to the dissociation of sodium acetate (sodium acetate fully dissociated), so, most contribution is coming from the sodium acetate.

And we can write:

$[Ac^-]$=total NAc conentration =[salt].....................................(4)

As acetic acid is a weak acid, so we must consider its equilibrium constant. It is defined as:

$$HAc = H^+ + Ac^-$$

$$K_a = \frac{[H^+][Ac^-]}{[HAc]}$$

$$\text{Therefore,}[H^+] = \frac{K_a[HAc]}{[Ac^-]}$$

$$pH = pK_a + \log\left(\frac{[salt]}{[acid]}\right) \text{ ....(5)}$$

This is known as the Henderson equation (equation (5)).

This is a very important expression for a buffer solution.

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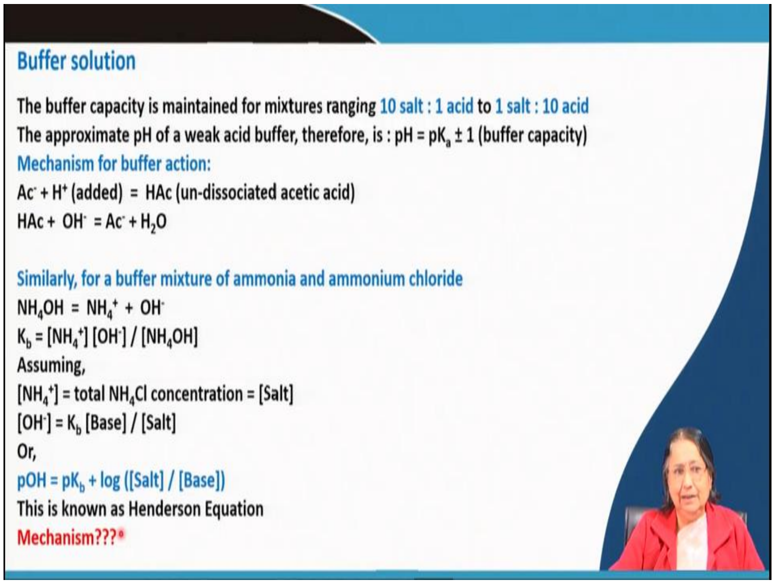

Now, let us come to the buffer capacity. I told you that buffer action will be applicable in some range. It is not the whole range of pH. It will not act in that way. Not only that the buffer only can resist that change when little amount of acid or alkali is added. It is not like that, in 1 liter of buffer solution if you add 100 milliliter of strong acid solution then the pH will be unchanged. If you add small amount of acid or small amount of base to that buffer solution or to a solution which contains buffer, then the change of pH will be not there (means it will resist the change). This is very important. So, buffer capacity is very important. Buffer capacity is maintained in some range. What is the range? We have seen in the last slide that

$$pH = pK_a + \log\left(\frac{[salt]}{[acid]}\right)$$

The proportion $\frac{[salt]}{[acid]}$ is very important.

So, the buffer capacity is maintained for mixtures ranging 10:1 ([salt] : [acid]) or 1:10 ([salt] : [acid]). That means, the range of pH is nothing but

$$pH = pK_a \pm 1 \text{.......................(6)}$$

This is called buffer capacity. Say for example, acetic acid, if we think about acetic acid, I already told you that for acetic acid pK_a is 4.74.

So, pH range is equal to 4.74 ± 1. So, the buffer action will be there in the range of 3.74 to 5.74. It is not right the whole range of pH it will be valid. Now, why it is happening? How it is resisting the pH? This is also very interesting and important i.e, mechanism of buffer action. I have already told you that in the acetic acid / sodium acetate buffer acetate ion is there. So, when you add the H^+ ion, it will immediately combine with acetate ion to form the un-dissociated HAc molecule. If you add little amount of alkali then it will react with the HAc to form acetate ion and water. In this way, even with the addition of H^+ or OH^-, the pH of the medium remains almost constant. Very small change you will observe which is not significant.

Similarly, for an alkaline buffer mixture, I have taken the simple example ammonia and ammonium chloride. We can tell that ammonium hydroxide will be weakly dissociated. It is weakly basic solution. So, it will be dissociated in ammonium ion and OH^-. So, we have to consider K_b. In this case K_b is given by:

$$K_b=\frac{[NH_4^+][[OH^-]}{[NH_4OH]} \text{..............................(7)}$$

Assuming,

$$[NH_4^+]=\text{total } NH_4Cl \text{ concentration}=[salt] \text{......................(8)}$$

$$[OH^-]=K_b\frac{[base]}{[salt]}$$

$$\text{or, } pOH=pK_b+\log(\frac{[salt]}{[base]}) \text{....................................(9)}$$

This is also Henderson equation and the mechanism will also be in the same way as it has been explained in case of acidic buffer. If you add H^+ then what will happen and if you add OH^- in small amount, then what will happen? This will be very similar to the case of acidic buffer.

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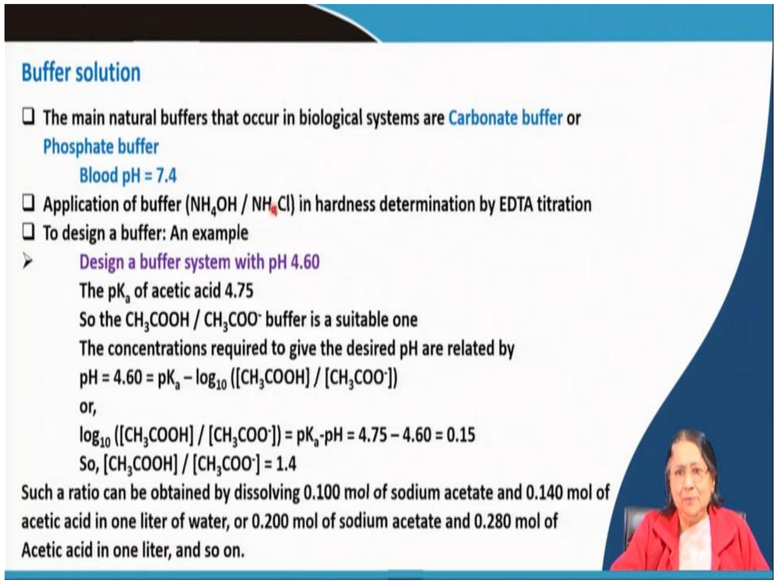

In biological systems, for example in human body, there is also some buffer. You know in our body system many reactions are occirring (enzymatic reactions). They need controlled pH. In our body, the controlled pH is very much necessary. Here, we do not have any ammonium chloride ammonium hydroxide or we do not have acetic acid and sodium acetate. In the biological systems, the buffers are mostly carbonate buffer or phosphate buffer.

You know that the pH of blood is 7.4 (approximately). Now, one application of buffer (NH_4OH/NH_4Cl) solution is the maintenance of pH of water at 9-10, during hardness determination by EDTA titration. If the pH is not maintained, then the reaction will not be complete in the determination of hardness (i.e., calcium ion concentration and magnesium ion concentration, multivalent cation concentration by EDTA).

Now, how to design a buffer? This is very important. Say, for example you have been given a task to prepare a buffer of pH 4.6. Now, there are so many buffers. We can choose different acids. We can choose different bases. We can choose different salts also. How we can decide? Which one you will use for your purpose?

First of all, we have to decide which acid we will take for this purpose. Since its pH is 4.6 (<7) so it is acidic buffer. Now from the pK_a values (at 25^0C) of several acids listed we can easily find out. We know the pK_a of acetic acid 4.74. The buffer capacity is 4.74±1. So if pH is to be maintained at 4.6 then we can use acetic acid / sodium acetate buffer. Now, we have to decide acid and salt ratio (from Henderson equation). We can easily find out the ratio as follows:

$$pH=4.6=pK_a-\log_{10}(\frac{[CH_3COOH]}{[CH_3COO^-]})$$

$$or, \log_{10}(\frac{[CH_3COOH]}{[CH_3COO^-]}) = 4.75 - 4.6 = 0.15$$

$$\frac{[CH_3COOH]}{[CH_3COO^-]} = 1.4$$

So, we can choose various concentrations keeping the ratio constant. For example, we can take 0.100 mole of sodium acetate and 0.140 mole acetic acid in 1liter of water, or we can 0.200 mole of sodium acetate and 0.280 mole acetic acid in 1liter of water

I think you have understood this part. First you have to see which buffer you have to take (which combination) and then you have to decide what is the concentrations that you have to take for the salt and the acid? Thank you for listening to today's lecture. I hope you have understood. Thank you.