Environmental Chemistry and Microbiology

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Lecture - 02
Acids, Bases and Salts- II

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. This is my second lecture and I am covering the acids, bases and salts. Today, I will tell about the pH concept and the strength of acids and bases, the hydrolysis of salts, what is the pH upon hydrolysis of salts will get in the solution.

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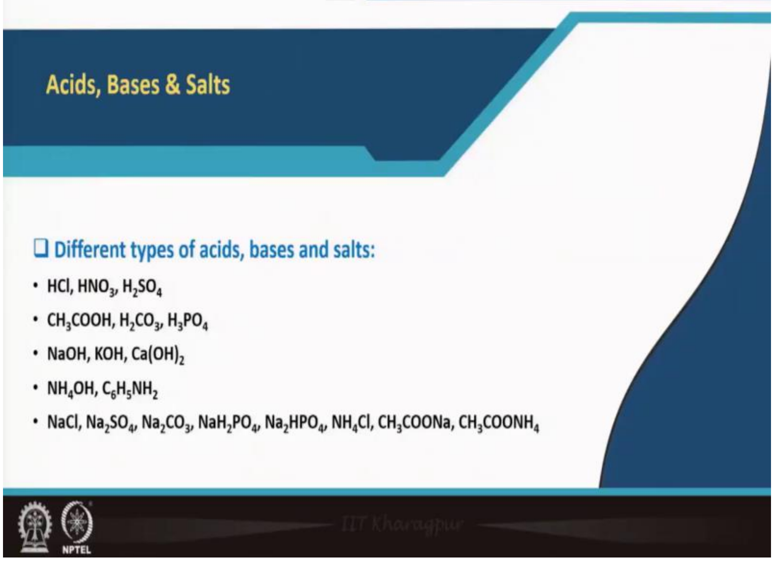

Acids, Bases & Salts

❑ Different types of acids, bases and salts:

- HCl, HNO_3, H_2SO_4
- CH_3COOH, H_2CO_3, H_3PO_4
- $NaOH$, KOH, $Ca(OH)_2$
- NH_4OH, $C_6H_5NH_2$
- $NaCl$, Na_2SO_4, Na_2CO_3, NaH_2PO_4, Na_2HPO_4, NH_4Cl, CH_3COONa, CH_3COONH_4

We all know that there are different types of acids, bases and salts. Some of the acids are shown here: HCl, HNO_3, H_2SO_4, acetic acid, carbonic acid, phosphoric acid and then some bases are also shown: NaOH, KOH, calcium hydroxide, ammonium hydroxide, aniline (organic base). Examples of some common salts are sodium chloride, sodium sulfate, sodium carbonate, sodium dihydrogen phosphate, disodium hydrogen phosphate, ammonium chloride, sodium acetate, ammonium acetate. So, there are different types of acids, bases and salts. Some are weak, some are strong, some are inorganic, some are organic. We will discuss about those.

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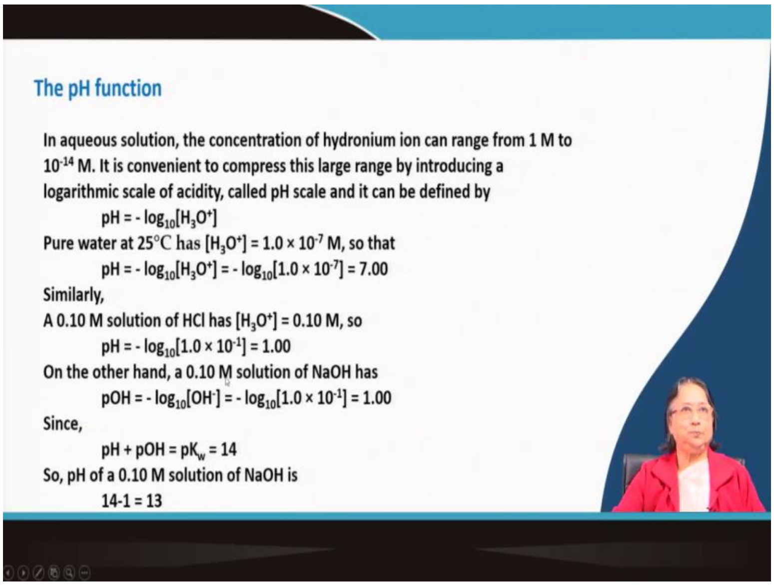

The pH function

In aqueous solution, the concentration of hydronium ion can range from 1 M to 10^{-14} M. It is convenient to compress this large range by introducing a logarithmic scale of acidity, called pH scale and it can be defined by

$$pH = -\log_{10}[H_3O^+]$$

Pure water at 25°C has $[H_3O^+] = 1.0 \times 10^{-7}$ M, so that

$$pH = -\log_{10}[H_3O^+] = -\log_{10}[1.0 \times 10^{-7}] = 7.00$$

Similarly,

A 0.10 M solution of HCl has $[H_3O^+] = 0.10$ M, so

$$pH = -\log_{10}[1.0 \times 10^{-1}] = 1.00$$

On the other hand, a 0.10 M solution of NaOH has

$$pOH = -\log_{10}[OH^-] = -\log_{10}[1.0 \times 10^{-1}] = 1.00$$

Since,

$$pH + pOH = pK_w = 14$$

So, pH of a 0.10 M solution of NaOH is

$$14-1 = 13$$

Before going to acids and bases in the aqueous solution we must know what is the pH? In aqueous solution, the concentration of hydronium ion (I already explained in my first lecture what is hydronium ion) can range from 1 molar to 10^{-14} molar. It is convenient to express this large range by some logarithmic scale and there comes the pH scale. We know that pH is nothing but negative log of hydronium ion concentration (shown in equation (1)).

$$pH=-\log_{10}[H_3O^+]\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(1)$$

Measurement of equilibrium constants in case of pure water is generally conducted at 25^0C. Why the temperature is important? Because, we all know that the equilibrium constant depends on the temperature. And I will show you later on the different values of the equilibrium constant of water dissociation and you will see that how it varies with temperature. Now, at 25^0 C the H_3O^+ concentration for pure water is nothing but 10^{-7} molar and pH therefore is 7 (shown in equation (2)).

$$\begin{aligned} pH&=-\log_{10}[H_3O^+] \\ &=-\log_{10}[1.0\times10^{-7}]=7 \end{aligned}\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(2)$$

Similarly, 0.1 molar solution of HCl has H_3O^+ concentration equal to 0.10 M. So, pH will be given as follows:

$$\begin{aligned} pH&=-\log10[1.0\times10^{-1}] \\ &=1 \end{aligned}\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(3)$$

So, pH is nothing but $-\log_{10}[H^+]$. Similarly, pOH is nothing but $-\log_{10}[OH^-]$. So, 0.1 molar solution of NaOH must have a pOH equal to 1(shown in equation (4)).

$$pOH=-\log_{10}[OH^-]=-\log10[0.1]=1\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(4)$$

Since pH + pOH is nothing but pK_w.

So, pH + pOH = 14.

So, if we can calculate the pH of this NaOH solution (pH of 0.1 molar solution of NaOH) as 14 - 1 i.e. 13.

So, the concept of pH and pOH is very important.

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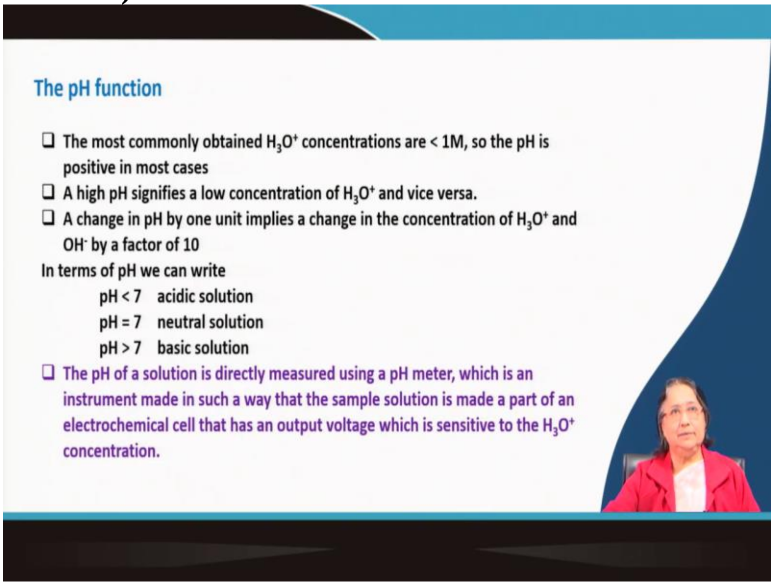

The pH function

❑ The most commonly obtained H_3O^+ concentrations are < 1M, so the pH is positive in most cases

❑ A high pH signifies a low concentration of H_3O^+ and vice versa.

❑ A change in pH by one unit implies a change in the concentration of H_3O^+ and OH^- by a factor of 10

In terms of pH we can write

pH < 7 acidic solution
pH = 7 neutral solution
pH > 7 basic solution

❑ The pH of a solution is directly measured using a pH meter, which is an instrument made in such a way that the sample solution is made a part of an electrochemical cell that has an output voltage which is sensitive to the H_3O^+ concentration.

The pH values usually are between 0 and 14. But in rare cases it may be negative, and the pH can go a little above 14 also. Say for example pH of 2M $HClO_4$ is negative and that of 4M NaOH is slightly above 14. But, in general we can say that pH scale is from 0 to 14 and we know that, change in pH by 1 unit implies a change in the concentration of H_3O^+ and OH^- by a factor of 10.

And, we can easily say that for neutral solution the pH is 7. For acidic solution, the pH is below 7 and for alkaline solution or basic solution the pH is above 7. The pH of a solution is directly measured using a pH meter, which is a very simple and portable instrument. We can also use instrument which is made in such a way that the sample solution is made a part of an electrochemical cell that has an output voltage and is sensitive to the H_3O^+ ion concentration. We all have seen that the pH meter a very simple instrument and to measure the pH is also very easy.

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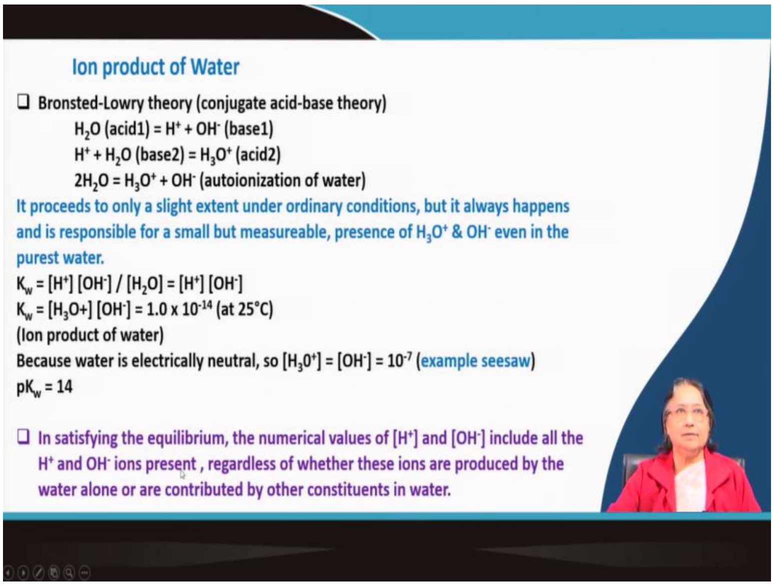

Ion product of Water

☐ Bronsted-Lowry theory (conjugate acid-base theory)

H_2O (acid1) = $H^+ + OH^-$ (base1)

$H^+ + H_2O$ (base2) = H_3O^+ (acid2)

$2H_2O = H_3O^+ + OH^-$ (autoionization of water)

It proceeds to only a slight extent under ordinary conditions, but it always happens and is responsible for a small but measureable, presence of H_3O^+ & OH^- even in the purest water.

$K_w = [H^+][OH^-] / [H_2O] = [H^+][OH^-]$

$K_w = [H_3O+][OH^-] = 1.0 \times 10^{-14}$ (at 25°C)

(Ion product of water)

Because water is electrically neutral, so $[H_30^+] = [OH^-] = 10^{-7}$ (example seesaw)

$pK_w = 14$

☐ In satisfying the equilibrium, the numerical values of $[H^+]$ and $[OH^-]$ include all the H^+ and OH^- ions present , regardless of whether these ions are produced by the water alone or are contributed by other constituents in water.

I have already told in my first lecture, about ion product of water. What is ion product of water? We know from the Bronsted-Lowry theory of conjugate acid-base pair that water can act as an acid when it can give H^+ ion, and the OH^- ion is nothing but its conjugate base. The conjugate acid-base pair is shown in equations (5) & (6):

$$H_2O(\text{acid1})=H^+ +OH^-(\text{base 1}) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

$$H^+ +H_2O(\text{base 2})=H_3O^+(\text{acid 2}) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

Now, combining these 2 equations ((5) & (6)), we can write the equation (equation (7)) which is nothing but the autoionization of water.

$$2H_2O=H_3O^+ +OH^-(\text{autoionization of water}) \ldots\ldots\ldots\ldots(7)$$

This ionization proceeds in slight extent, under ordinary conditions, but it always happens. This is very important to remember. It always happens and it is responsible for a small but measureable presence of hydronium ion and hydroxide ion even in the purest form of water. We will see that it is slightly dissociated and it forms H_3O^+ ion and OH^- ion.

So, K_w which is the equilibrium constant of that reaction can be written as follows:

$$K_w=\frac{[H^+][OH^-]}{[H_2O]}=[H^+][OH^-] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

But, actually we should write

$$K_w=[H_3O^+][OH^-]=1.0\times10^{-14}\ (\text{at } 25^0\text{C}) \ldots\ldots\ldots\ldots\ldots(9)$$

This is most important and K_w is called the ion product of water.

Because water is electrically neutral, that means $[H_3O^+]$ is same as the $[OH^-]$ and this is nothing but 10^{-7} and pK_w is 14.

Now, I will show you seesaw as an example. In satisfying the equilibrium the numerical values of H^+ and OH^- ion concentrations include all the H^+ and OH^- ions present. It is true not only for water, but if something is there in the water, then also we have to remember that the product of $[H^+]$ and $[OH^-]$ will be nothing but 10^{-14} (at 25 °C).

This is very important and when H^+ ion concentrations become higher, OH^- ion concentration must go to a low value. This is just like a seesaw.

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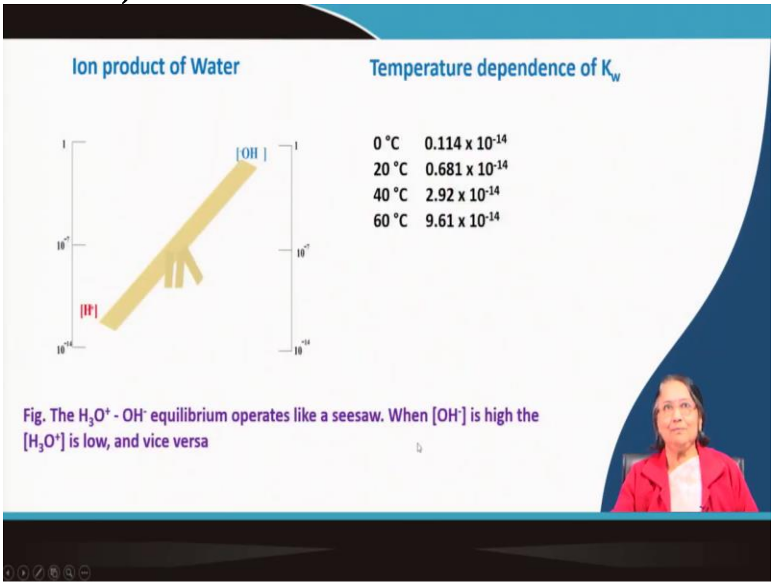

Ion product of Water

Temperature dependence of K_w

0 °C	0.114×10^{-14}
20 °C	0.681×10^{-14}
40 °C	2.92×10^{-14}
60 °C	9.61×10^{-14}

Fig. The H_3O^+ - OH^- equilibrium operates like a seesaw. When $[OH^-]$ is high the $[H_3O^+]$ is low, and vice versa

We know seesaw. We all played seesaw in our childhood days, some person sits at one end and some other person at the other end. So, sometimes one end goes down while the other end goes up and vice versa. The scale of both $[H^+]$ and $[OH^-]$ has been varied between 1 and 10^{-14}. When $[OH^-]$ reached 1, $[H^+]$ must be 10^{-14} and vice versa. And here it is also shown that the values varies at different temperatures.

Say, for example, the value of K_w you see at 0^0C, it is 0.114×10^{-14} whereas, at 20^0C it is 0.681×10^{-14}, and at 60^0C it is 9.61×10^{-14}. So, you can see here the difference in values of K_w at 0^0C and 60^0C is almost 10 fold.

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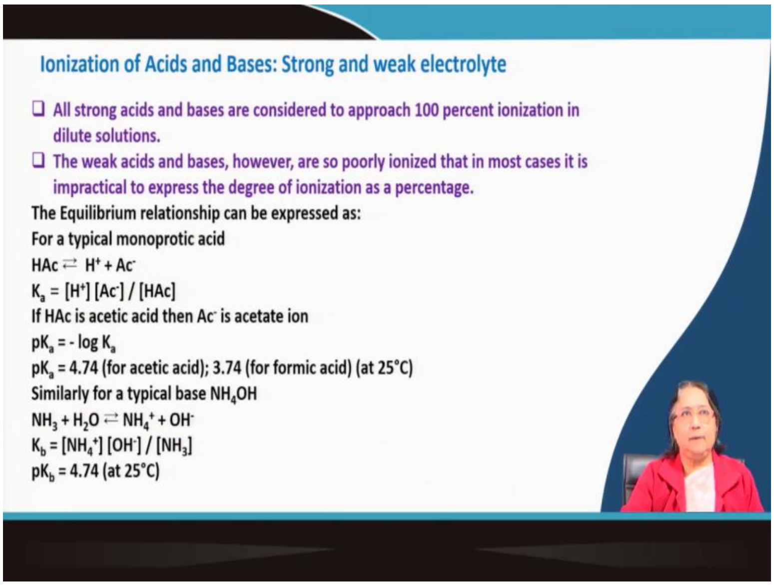

Ionization of Acids and Bases: Strong and weak electrolyte

- ☐ All strong acids and bases are considered to approach 100 percent ionization in dilute solutions.
- ☐ The weak acids and bases, however, are so poorly ionized that in most cases it is impractical to express the degree of ionization as a percentage.

The Equilibrium relationship can be expressed as:
For a typical monoprotic acid
$HAc \rightleftarrows H^+ + Ac^-$
$K_a = [H^+] [Ac^-] / [HAc]$
If HAc is acetic acid then Ac^- is acetate ion
$pK_a = - \log K_a$
$pK_a = 4.74$ (for acetic acid); 3.74 (for formic acid) (at 25°C)
Similarly for a typical base NH_4OH
$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$
$K_b = [NH_4^+] [OH^-] / [NH_3]$
$pK_b = 4.74$ (at 25°C)

Now, let us come to the ionization of acids and bases. If you remember the Arrhenius concept (the electrolytic dissociation theory) he has first observed that when different things are put in solution, then they give different conductance that means, the acid may be strong or it may be weak. This is not only true for acids, but it is true for bases also. So, there are some strong acids and there are some weak acids. Those which are strong, they are called strong electrolyte, which are weak they are called weak electrolyte and depending on the degree of dissociation, the acidity will vary in the solution.

All strong acids and bases are considered to approach 100% ionization in dilute solution. So, strong acids will be 100% dissociated. As for example, HCl: if you put some HCl in water, then HCl will be completely dissociated. But if you put, say for example, small amount of acetic acid in water, then it will not dissociate 100%. It will dissociate only very slightly and hence, it is called weak acid or weak electrolyte. Weak acids and bases however, are so poorly ionized that in most cases it is impractical to express the degree of ionization as a percentage.

Now, here as an example, I have shown a monoprotic acid (equation (10)). Say for example, acetic acid (CH_3COOH) is taken and it is represented as HAc.

$HAc \leftrightharpoons H^+ + Ac^-$....................(10)

As because acetic acid is not 100% dissociated so, we must consider the equilibrium constant, which is usually expressed as K_a (a is due to the acid):

$$K_a = \frac{[H^+][Ac^-]}{[HAc]} \text{......................(11)}$$

Now, here also just like the H^+ ion concentration and pH, here also the K_a value and pK_a value is related in a similar way. What is pK_a? pK_a is nothing but - $\log_{10}$ of K_a. So, if K_a is in terms of 10^{-5}, then pK_a will come in terms of 4 point. The pK_a value for acetic acid is 4.744 and for formic acid it is 3.75 at 25^0C. Therefore, formic acid is stronger than the acetic acid. So, the acid which is stronger will have lower pK_a value.

Similarly, for a typical weak base such as ammonium hydroxide, we can tell that ammonium hydroxide can be dissociated as follows:

$NH_3+H_2O \leftrightharpoons NH_4^++OH^-$...................(12)

The equilibrium constant is denoted as K_b (b for base), and K_b is expressed as follows:

$$K_b=\frac{[NH_4^+][OH^-]}{[NH_3]} \text{...............................(13)}$$

This is very interesting for me that pK_a of acetic acid is 4.74 and pK_b of ammonia is also 4.74.

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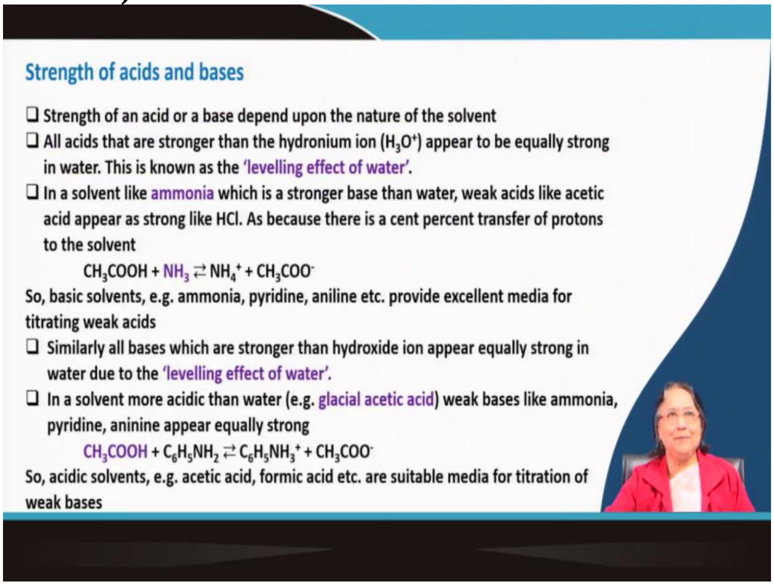

Strength of acids and bases

❑ Strength of an acid or a base depend upon the nature of the solvent

❑ All acids that are stronger than the hydronium ion (H_3O^+) appear to be equally strong in water. This is known as the 'levelling effect of water'.

❑ In a solvent like ammonia which is a stronger base than water, weak acids like acetic acid appear as strong like HCl. As because there is a cent percent transfer of protons to the solvent

$$CH_3COOH + NH_3 \rightleftarrows NH_4^+ + CH_3COO^-$$

So, basic solvents, e.g. ammonia, pyridine, aniline etc. provide excellent media for titrating weak acids

❑ Similarly all bases which are stronger than hydroxide ion appear equally strong in water due to the 'levelling effect of water'.

❑ In a solvent more acidic than water (e.g. glacial acetic acid) weak bases like ammonia, pyridine, aninine appear equally strong

$$CH_3COOH + C_6H_5NH_2 \rightleftarrows C_6H_5NH_3^+ + CH_3COO^-$$

So, acidic solvents, e.g. acetic acid, formic acid etc. are suitable media for titration of weak bases

Now, let us come to the strength of acids and bases:

You know that strength of acids and bases depend upon the nature of the solvent. I already discussed about the Arrhenius concept and the Franklin concept. So, the strength of acid and base will depend on the solvent. How much it is acidic? Whether it is acid or not? Why it is acidic? Everything will be decided by the solvent. All acids that are stronger than the hydronium ion appear to be equally strong in water. This is called levelling effect of water.

So, HCl, HNO_3 and then perchloric acid will be equally strong and this is called the leveling effect in water. It is so because all of them are stronger than the hydronium ion. Everything is leveled up by the water molecule. In a solvent like ammonia which is stronger base than water, weak acids like acetic acid appear as strong as HCl. I have explained that acetic acid is a weak acid because it is a weak electrolyte. It will not dissociate 100%. But instead of water, if you take ammonia as a solvent then in that solvent the acetic acid will act as a strong acid just like HCl in water. It is so because there is a 100% transfer of proton to the solvent. And say for example, if you take acetic acid as a solvent, ammonia will act as a strong base. Not only ammonia, pyridine, aniline etc., will also show same behavior. They are also organic bases. Similarly, all bases which are stronger than the hydroxide ion appear equally strong in the water due to the levelling effect. This is just the opposite levelling effect of water. In a solvent more acidic than water that is glacial acetic acid, weak bases like ammonia or pyridine or aniline will behave as strong bases. So aniline is a weak base. Hence it is not completely dissociated, but if you take acetic acid as a solvent, then it will act as a strong base.

This tells that strength of acids and bases depends on the solvent. I will tell you later part of my lecture, how the titration between different types of acids and bases can be done. What should be the indicator? But here just remember that acidic solvents like acetic acid, formic acid etc. can be a suitable media for titrating weak bases because titration of weak base or weak acid is difficult. This is how you can make weak bases or acid strong, if you can properly select the solvent. This is very interesting.

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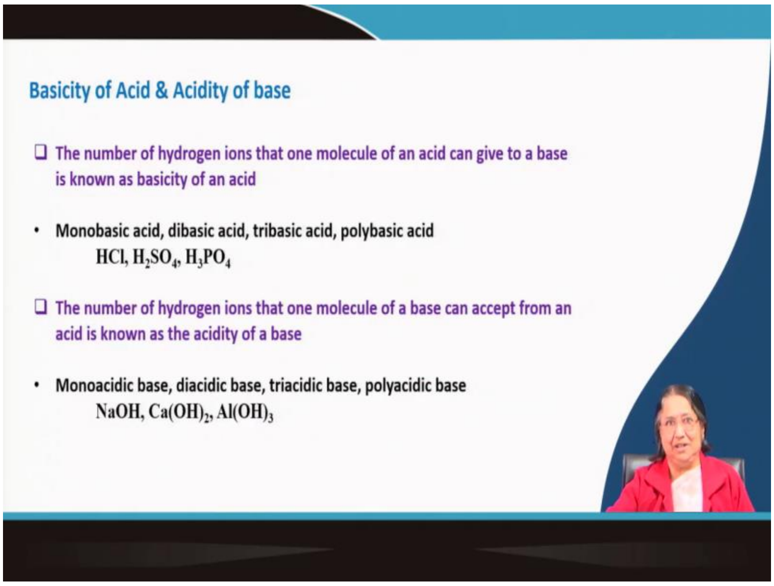

Basicity of Acid & Acidity of base

❑ The number of hydrogen ions that one molecule of an acid can give to a base is known as basicity of an acid

- Monobasic acid, dibasic acid, tribasic acid, polybasic acid
  HCl, H_2SO_4, H_3PO_4

❑ The number of hydrogen ions that one molecule of a base can accept from an acid is known as the acidity of a base

- Monoacidic base, diacidic base, triacidic base, polyacidic base
  $NaOH$, $Ca(OH)_2$, $Al(OH)_3$

Now what is basicity of an acid and acidity of a base? The number of hydrogen atoms that one molecule of an acid can give to a base is known as basicity of an acid. Say for example, H_2SO_4 is a dibasic acid because two protons are there. HCl is a mono basic acid because there is only one hydrogen. In phosphoric acid there are 3 hydrogens, so it is a tribasic acid. Other than the monobasic acid, others (like dibasic acid, tribasic acid etc.) can be said as polybasic acid.

Similarly, the number of hydrogen ions that one molecule of a base can accept from an acid is known as the acidity of a base. Say, for example, NaOH is a monoacidic base, then $Ca(OH)_2$ diacidic base and $Al(OH)_3$ is a triacidic base. So, here also other than monoacidic base (like NaOH), all bases are poly acidic base.

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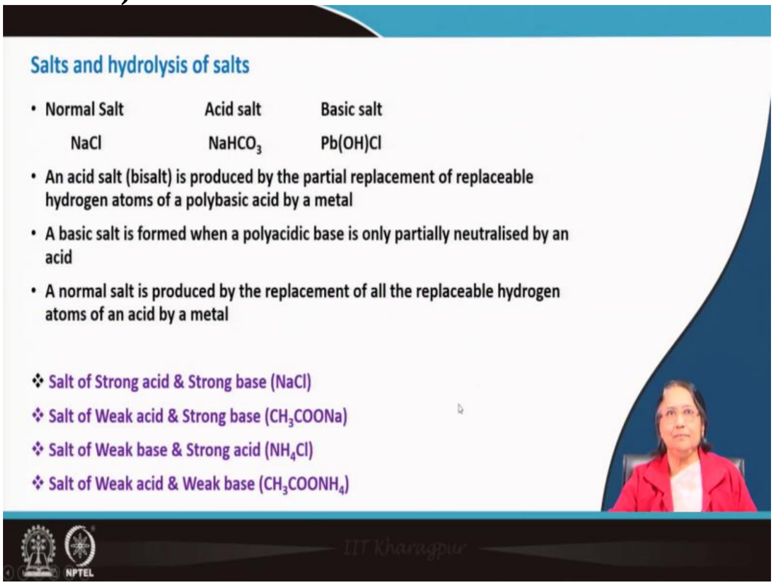

Salts and hydrolysis of salts

Normal Salt	Acid salt	Basic salt
NaCl	$NaHCO_3$	Pb(OH)Cl

- An acid salt (bisalt) is produced by the partial replacement of replaceable hydrogen atoms of a polybasic acid by a metal
- A basic salt is formed when a polyacidic base is only partially neutralised by an acid
- A normal salt is produced by the replacement of all the replaceable hydrogen atoms of an acid by a metal

❖ Salt of Strong acid & Strong base (NaCl)
❖ Salt of Weak acid & Strong base (CH_3COONa)
❖ Salt of Weak base & Strong acid (NH_4Cl)
❖ Salt of Weak acid & Weak base (CH_3COONH_4)

Now, let us come to the hydrolysis of salts:

I have shown you initially that there are many different kinds of salts. How can we classify them? What is the way that we can classify them? Actually, there are 2 types of classification. In one type of classification, we can tell that salts can be divided in three categories: normal salts, acid salts and basic salts. And by definition, we can tell that in NaCl does not have any replaceable hydrogen atom or any replaceable OH group. That is why it is called normal salt.

In $NaHCO_3$ you can see that there is 1 hydrogen which can be replaced by any metal, so, it is an acid salt or bisalt. And in Pb(OH)Cl there is one OH group which can be replaced. So, it is a basic salt. But there is another type of classification we can tell depending on from which acid and which base they are produced. Say for example, some salts can be produced from strong acid and strong base. A good example is sodium chloride. Thus it is a salt of strong acid and strong base. Now, there may be some salts like sodium acetate (CH_3COONa), where you can see that it is produced from acetic acid and sodium hydroxide. So, it is a salt produced from a weak acid acetic acid and a strong base sodium hydroxide. There may be another type. For example, ammonium chloride which is produced from a weak base that is ammonium hydroxide and a strong acid that is HCl.

And lastly, the salt (CH_3COONH_4) which is produced from a weak acid and weak base that is acetic acid and ammonium hydroxide. We all know that ammonium hydroxide is a weak base because it does not dissociate fully and acetic acid is a weak acid because it does not dissociate fully. So, ammonium acetate or ammonium formate are the salts produced from weak acid and a weak base. When these salts will hydrolyze they may give either an acidic character, or a basic character, or neutral character to the water. Now, how we will determine the pH when a salt is dissolved in water that we can see here.

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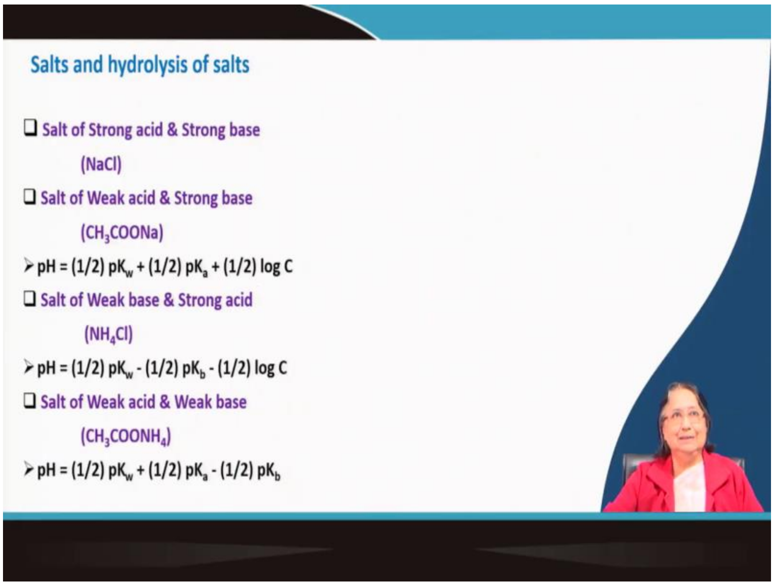

Salts and hydrolysis of salts

☐ Salt of Strong acid & Strong base

(NaCl)

☐ Salt of Weak acid & Strong base

(CH_3COONa)

➢ $pH = (1/2)\ pK_w + (1/2)\ pK_a + (1/2) \log C$

☐ Salt of Weak base & Strong acid

(NH_4Cl)

➢ $pH = (1/2)\ pK_w - (1/2)\ pK_b - (1/2) \log C$

☐ Salt of Weak acid & Weak base

(CH_3COONH_4)

➢ $pH = (1/2)\ pK_w + (1/2)\ pK_a - (1/2)\ pK_b$

All salts will hydrolyze. Some salts can give acidic character, some salts can give basic character that much I told. But what is the formula that we can apply? See here when the salt is coming from strong acid and strong base. For example, NaCl. If you put some NaCl in water what should be the pH? It is neutral pH. But when you dissolve some sodium acetate (which is coming from weak acid and strong base) in water then what will the pH of the solution? When you put some sodium acetate in water then you may think that it will be neutral pH. But it is not. It is not because it is produced from a strong base and a weak acid. So, it will show the basic character in water. And what is the formula that you can use to determine the pH? It is given by the following equation (equation (14)):

$$pH=\frac{1}{2}pK_w+\frac{1}{2}pK_a+\frac{1}{2}\log C \text{ ....(14)}$$

What is C? C is the concentration of the salt and pK_a is equilibrium constant of the weak acid. So, you have to consider the K_a value and the pK_a value of that acid.

Similarly, if it is salt of a weak base and a strong acid (ammonium chloride), you will think that when it will dissolve in water it will give neutral pH, but it is not. It will give some acidic pH to the water. And how can you calculate? This is given by the following equation (equation (15)):

$$pH=\frac{1}{2}pK_w-\frac{1}{2}pK_b-\frac{1}{2}\log C \text{ ....(15)}$$

In the same way, C is the concentration of the salt. Here ammonia is the base. So, pK_b of ammonium hydroxide you have to use here.

And for the salt of weak acid and weak base (example: ammonium acetate) you have to use the following equation:

$$pH=\frac{1}{2}pK_w+\frac{1}{2}pK_a-\frac{1}{2}pK_b \text{.....................................}(16)$$

Here the salt is produced from a weak acid and a weak base. So, both the terms pK_a and pK_b are to be considered here. Now, depending on how much weak, whether it is very weak or it is not that weak, the overall pH will vary. Depending on the base also it will vary. It is so because these two terms are coming. So, depending on the strength of this weak acid and weak base, you have to calculate and you have to see what the pH of the solution is coming.

This is also very interesting to me, because I have seen that if you use the ammonium formate and ammonium acetate, you will see in case of ammonium acetate, the pH is something and in case of ammonium formate it is something else. One is more acidic, other one is less acidic. I will show you how it is coming in other lectures. Thank you.