Environmental Chemistry and Microbiology
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Lecture-05
Topics: Acids Bases and Salts –V

Welcome everyone to our online NPTEL course of Environmental Chemistry and Microbiology. I am Professor Anjali Pal from Civil Engineering Department of IIT Kharagpur. I will be covering the Environmental Chemistry part and this is my 5th lecture on acids, bases and salts. In this lecture I will cover the determination of acidity and alkalinity which often we do in our laboratories and it is very important for environmental engineers to know the acidity and alkalinity for a particular sample. I will discuss that in this lecture.

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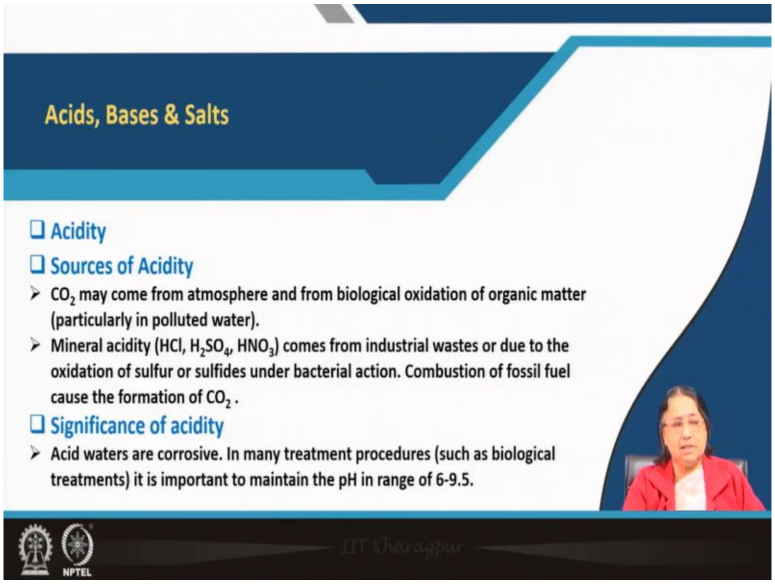

Acids, Bases & Salts

☐ Acidity

☐ Sources of Acidity

➤ CO_2 may come from atmosphere and from biological oxidation of organic matter (particularly in polluted water).

➤ Mineral acidity (HCl, H_2SO_4, HNO_3) comes from industrial wastes or due to the oxidation of sulfur or sulfides under bacterial action. Combustion of fossil fuel cause the formation of CO_2 .

☐ Significance of acidity

➤ Acid waters are corrosive. In many treatment procedures (such as biological treatments) it is important to maintain the pH in range of 6-9.5.

Acidity: We know that acidity may come from different sources and it may be mainly of two types (in environmental purpose). One is the strong acidity like mineral acidity and the other is the carbon dioxide acidity that is coming from the atmosphere and from biological oxidation of organic matter particularly in the polluted water.

Mineral acidity is nothing but the acidity coming from the strong acids like HCl, H_2SO_4, HNO_3. It may come from industrial wastes due to oxidation of sulfur or sulfides under bacterial action or it may come from combustion of fossil fuels (due to the formation of carbon dioxide).

Now what is the significance of acidity? Acid waters are corrosive and also in many treatment procedures such as biological treatments we have to maintain the pH in some range (say for example pH 6 to 9.5). So, we have to monitor the acidity very often and time to time.

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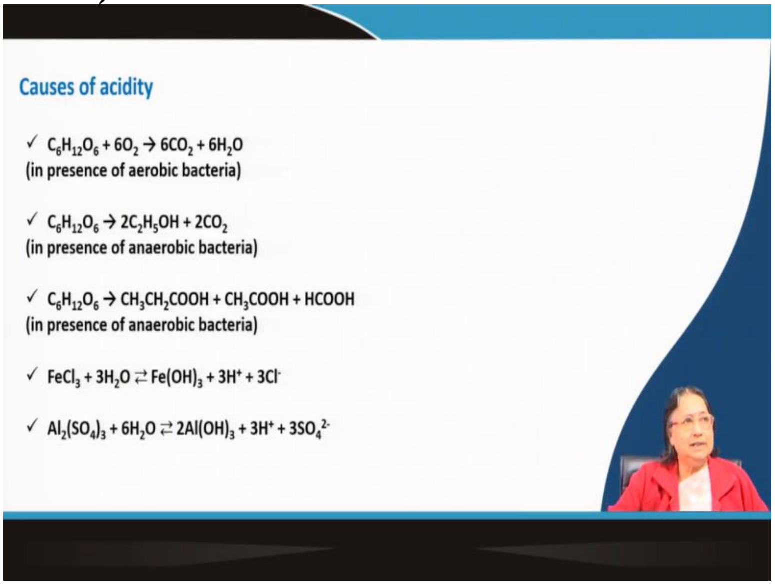

Causes of acidity

- ✓ $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$
(in presence of aerobic bacteria)
- ✓ $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$
(in presence of anaerobic bacteria)
- ✓ $C_6H_{12}O_6 \rightarrow CH_3CH_2COOH + CH_3COOH + HCOOH$
(in presence of anaerobic bacteria)
- ✓ $FeCl_3 + 3H_2O \rightleftarrows Fe(OH)_3 + 3H^+ + 3Cl^-$
- ✓ $Al_2(SO_4)_3 + 6H_2O \rightleftarrows 2Al(OH)_3 + 3H^+ + 3SO_4^{2-}$

It is very important to know the acidity. Now the causes of acidity are shown as follows:

Say for example, there is an organic compound like glucose. When it is oxidized (BOD reaction) it produces carbon dioxide (in presence of aerobic bacteria) which is one type of acidity or in presence of anaerobic bacteria also some type of reaction may occur for organic compounds. Equations in presence of aerobic and anaerobic bacteria are shown as follows:

$C_6H_{12}O_6+6O_2 \rightarrow 6CO_2+6H_2O$ ....(1)

(in presence of aerobic bacteria)

$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 6CO_2$ ....(2)

(in presence of anaerobic bacteria)

$C_6H_{12}O_6 \rightarrow CH_3CH_2COOH + CH_3COOH + HCOOH$ ....(3)

(in presence of anaerobic bacteria)

In case of anaerobic bacteria, we can see that carbon dioxide may be generated. Otherwise, under anaerobic condition (in presence of some bacteria) the same molecule can be converted to weak acids such as acetic acid, propionic acid or formic acid. So, these are also weak acids.

Hydrolysis of some salts also produce mineral acids; for example ferric chloride ($FeCl_3$), aluminium sulphate ($Al_2(SO_4)_3$) etc.

$FeCl_3+3H_2O \leftrightharpoons Fe(OH)_3+3H^++3Cl^-$.......................(4)

$Al_2(SO_4)_3+6H_2O \leftrightharpoons 2Al(OH)_3+3H^++3SO_4^{2-}$................(5)

In equation (4), $Fe(OH)_3$ is a weak base and that is why it is insoluble. On the other hand, the produced HCl will be completely dissociated. So, the solution will be acidic. Similarly, in case of equation (5), H_2SO_4 is produced which gives acidity. So, acidity maybe of different types and we have to know the types of acidity and how much it is present? We also need to know the effects of different kinds of acidity. All these fall under Environmental Chemistry.

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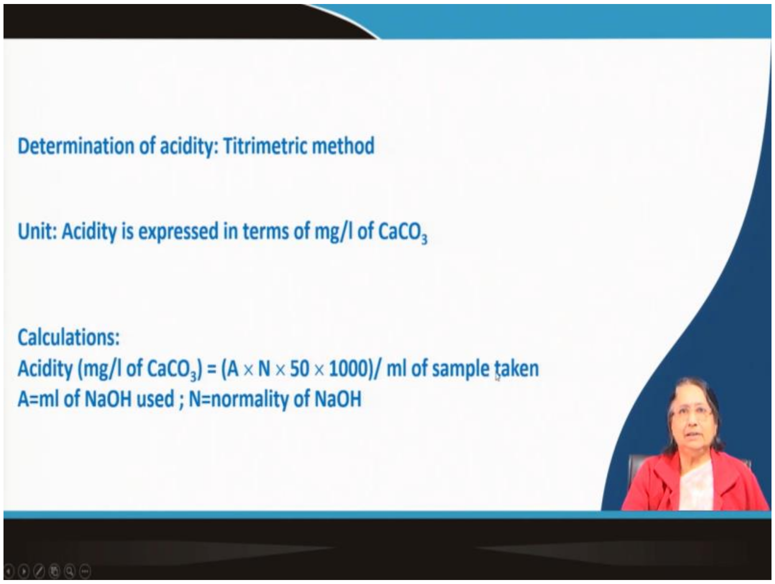

Determination of acidity: Titrimetric method

Unit: Acidity is expressed in terms of mg/l of $CaCO_3$

Calculations:
Acidity (mg/l of $CaCO_3$) = $(A \times N \times 50 \times 1000)$/ ml of sample taken
A=ml of NaOH used ; N=normality of NaOH

Now, let us come to the determination of acidity. We know that we generally use, in the laboratory, titrimetric methods using some burette, pipette and properly chosen indicators. We got idea about the indicators in the previous lecture. The choice of indicator is very important. So here we will see the application of properly chosen indicators.

Say, for example you have a sample which contains acidity. You have to know how much is the carbon dioxide acidity and how much is the mineral acidity. How will you do it? First you take some definite volume of sample. Say for example 100 milliliter of your sample in a conical flask and in the burette, you take some standard alkali solution.

Now first you add a few drops of methyl orange indicator in the solution in the conical flask that you have taken. Now if it is acidic solution then the methyl orange will give the pinkish red color. I told you that methyl orange gives pinkish red color in acid. So, it will be pinkish red color and then you start your titration with addition of alkali (standard alkali solution from the burette).

Now at the equivalence point i.e. neutralization point, the color will be changing and the color of the indicator will be changing from pinkish red to yellow. Now at this point what is neutralized? At this point only mineral acid is neutralized because methyl orange changes its color in the range of pH 3.7 to 4.3. Now you throw the sample and then you take another lot of sample in the conical flask and then this time you add phenolphthalein indicator. Now, you know that it is colorless in acid and pink in alkaline medium. So, you will see it is colorless and then you start your titration by adding alkali solution from the burette. You are adding the sodium hydroxide solution. Now at the end point it will become pink because we know phenolphthalein gives pink color in alkaline medium. Now you can say that acidity is neutralized. At this point what is neutralized? At this point both mineral acid as well as carbon dioxide is neutralized. So, phenolphthalein gives you total acidity and when you add methyl orange as the indicator you get only mineral acidity and then if you subtract the mineral acidity from the total acidity then you will get the carbon dioxide acidity. It is very simple.

So, you see that two most common indicators are phenolphthalein and methyl orange. By using these two indicators you can easily determine the two types of acidity in your water sample and also you can determine the carbon dioxide acidity. But as I told you that methyl orange is a little typical indicator so you need a few trials to understand how the color change is happening and actually what is the neutralization point.

Now, comes the unit. How will you express the acidity? Should we express in the acidity in terms of pH? Should we express in terms of normality? Actually, it is a universally accepted that acidity (environmental point of view) is expressed in terms of milligram per liter of calcium carbonate. We should express acidity, alkalinity and hardness in terms of milligrams per liter of calcium carbonate.

Then how is the calculation? So, for acidity, first you have to determine normality using the formula: $V_1\ S_1 = V_2\ S_2$. Here S_1 is in normality term. Then once you know the normality then you have to convert it in terms of milligram per liter of calcium carbonate and this is very easy to do by using the following formula.

$$\text{Acidity (mg/l of } CaCO_3) = \frac{(A \times N \times 50 \times 1000)}{\text{ml of sample taken}} \quad \text{..........................(6)}$$

A=ml of acid used
N=normality of acid

So why 50 is coming? Because 50 is the equivalent weight of calcium carbonate. The molecular weight of calcium carbonate is 100 and the calcium has valency 2 and only one calcium is there. That is why you have to divide the molecular weight by 2. So, it is the equivalent weight of calcium carbonate and why the 1000 is coming? 1000 is coming because you have to express in terms of milligram. So, it is very simple formula.

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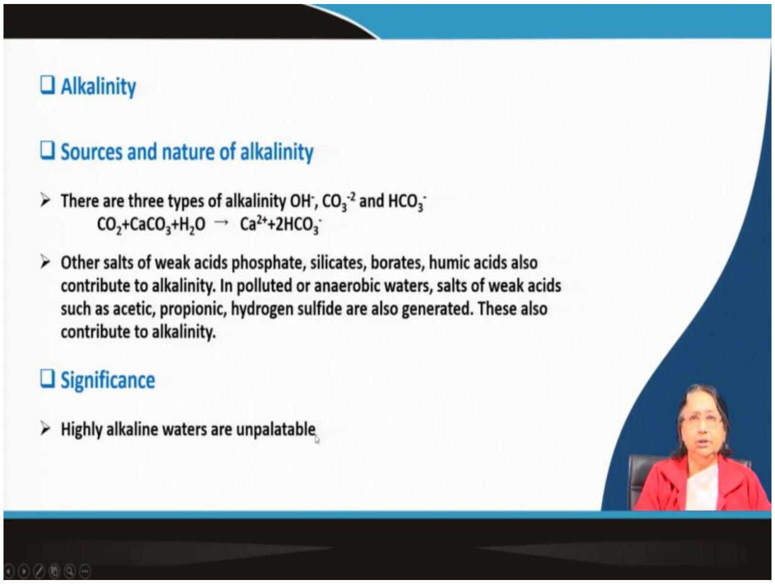

☐ Alkalinity

☐ Sources and nature of alkalinity

- There are three types of alkalinity OH^-, CO_3^{-2} and HCO_3^-
  $CO_2+CaCO_3+H_2O \rightarrow Ca^{2+}+2HCO_3^-$
- Other salts of weak acids phosphate, silicates, borates, humic acids also contribute to alkalinity. In polluted or anaerobic waters, salts of weak acids such as acetic, propionic, hydrogen sulfide are also generated. These also contribute to alkalinity.

☐ Significance

- Highly alkaline waters are unpalatable

Now comes the alkalinity: Similarly, alkalinity determination is also very important. Now what is the sources and nature of alkalinity. There are three types of alkalinity. What are the three types? OH^- ion, carbonate ion and bicarbonate ion can give alkalinity. How the bicarbonate is formed? You know that carbonate bearing rocks when react with carbon dioxide in presence of water they can give bicarbonate.

We know that bicarbonate imparts hardness. Anyway, here we are talking about alkalinity. So how the alkalinity is coming? Some salts like phosphate, silicate etc. can contribute to alkalinity. If we think about sodium phosphate, it is a salt but it is a salt made up of strong base and weak acid. So, sodium phosphate when dissolved, then it is giving alkalinity. Similarly, silicate and borates, salts of humic acid will give alkalinity in water. And in polluted water, salts of weak acids such as acetic acid (sodium acetate, sodium propionate, sodium sulfide) will generate alkalinity. So, all these contribute to alkalinity and highly alkaline waters are unpalatable. Also, we know we cannot tolerate excessive acidity or alkalinity. It has some tolerable limit.

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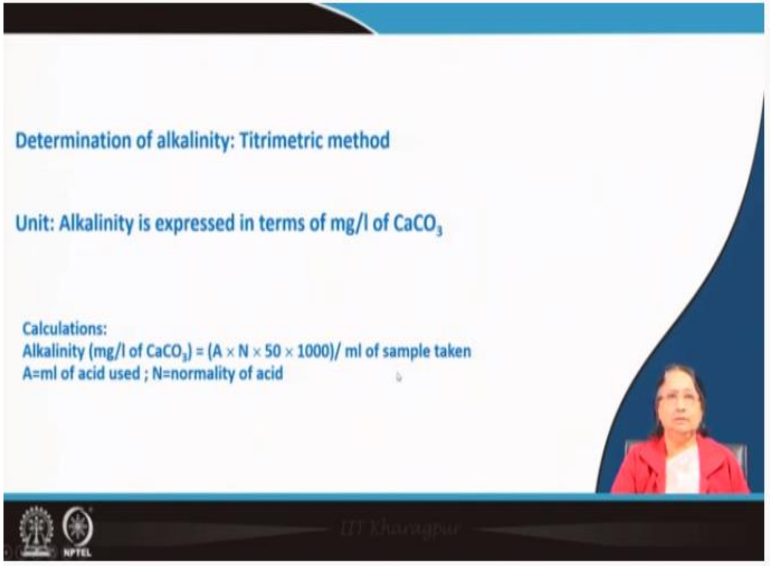

Determination of alkalinity: Titrimetric method

Unit: Alkalinity is expressed in terms of mg/l of $CaCO_3$

Calculations:
Alkalinity (mg/l of $CaCO_3$) = $(A \times N \times 50 \times 1000)$/ ml of sample taken
A=ml of acid used ; N=normality of acid

Now, determination of alkalinity by titration is even more interesting than the determination of acidity and how it will be determined? Although the indicators are the same but the titration is very interesting. As I told you there are three types of alkalinity (OH^-, carbonate and bicarbonate). You have to remember one thing here, that that OH^- and bicarbonate cannot stay together. Why? This is because OH^- immediately reacts with bicarbonate to form water and carbonate. So, these two things cannot stay together. This you have to keep in mind. Now say for example I have a water sample and I want to know the type of alkalinity present, and the concentration. What I will do? I will take say 100 milliliter of the sample in a conical flask. Then first I will add a few drops of phenolphthalein indicator there.

When I add a few drops of phenolphthalein indicator if it is alkaline then it may give a pink color. Then I will start the titration by taking the acid in the burette. So, I will add the standard acid solution in the conical flask. Now what is the color of the indicator here? Because I have started with alkaline solution so it may be pink. If it is pink then I will start addition of acid. So, at the neutralization point it will be colorless. Now what is neutralized here? There are different types of alkalinity. Here actually OH^- is neutralized and carbonate is half neutralized. Bicarbonate is not yet neutralized. Now what is the color here? It is colorless because we have already reached the neutralization point.

So, in this case you do not have to throw the solution. You continue your titration and only thing you have to note down the volume of acid you have added. Now you add methyl orange indicator. So, what is the color of the water? It will show yellow color in alkaline medium.

And then you add acid from the burette and continue the titration. At the neutralization point you will get the color of methyl orange pinkish red i.e., the color in acid. At this point what is neutralized? At this point actually if there is bicarbonate that will be neutralized and the remaining half of the carbonate will be neutralized. You will get the whole amount of bicarbonate and the remaining portion of the carbonate neutralized here.

So, from the volume that you have added you can calculate the concentration of alkalinity. Here first you have added phenolphthalein and you have noted down the volume of the acid required and second from there you have continued the titration and then you have noted down the final endpoint. You can easily calculate how much is the OH^-, how much is the carbonate and how much is the bicarbonate easily.

But one thing you have to remember that OH^- cannot stay together with bicarbonate. If you remember this then you can easily calculate the different types of alkalinity that is present in your water sample. This is very simple but very useful titrimetric method. Now as I told you that for alkalinity also we should not use the normality or the pH but we have to use the milligram per liter of calcium carbonate (in the same way that we did for acidity calculation).

So, first you do the $V_1S_1 = V_2 S_2$ and you get the normality. Then to convert the normality you can multiply it with 50 to get this in terms of calcium carbonate. So, the formula is

$$\text{Alkalinity (mg/l of } CaCO_3) = \frac{(A \times N \times 50 \times 1000)}{\text{ml of sample taken}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

A=ml of acid used
N=normality of acid

So, these two simple titrations we use in our laboratory to find out the acidity and alkalinity. Only burette pipette and the conical flask is required and only two very common indicators phenolphthalein and methyl orange.

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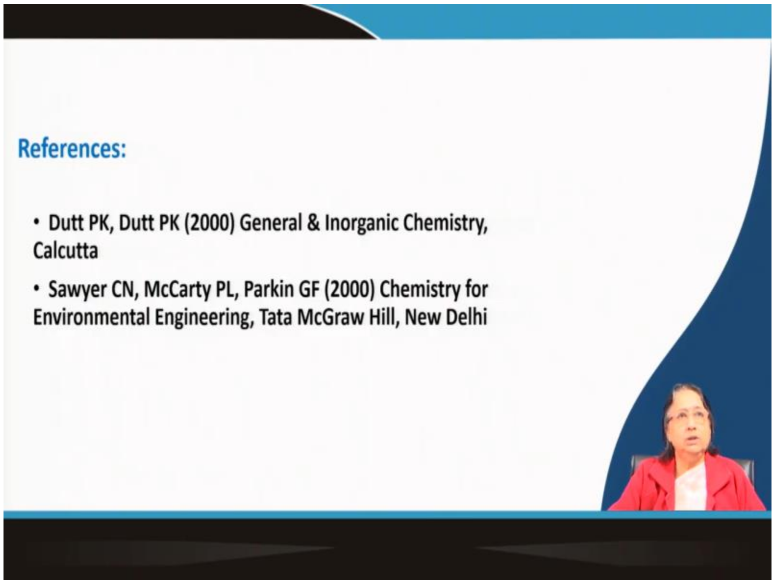

References:

- Dutt PK, Dutt PK (2000) General & Inorganic Chemistry, Calcutta
- Sawyer CN, McCarty PL, Parkin GF (2000) Chemistry for Environmental Engineering, Tata McGraw Hill, New Delhi

Now references:

For entire 5 lectures on acids, bases and salts, you can read from PK Dutt and PK Dutt 2000. It is a common textbook “General and Inorganic Chemistry”. The other book is by Sawyer, McCarty and Parkin. This is “Chemistry for Environmental Engineering”. This is also not costly book. You can easily buy it for environmental engineering course. Thank you.