Environmental Chemistry and Microbiology

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Lecture - 4
Acids, Bases and Salts - IV

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 4th lecture on acids, bases and salts.

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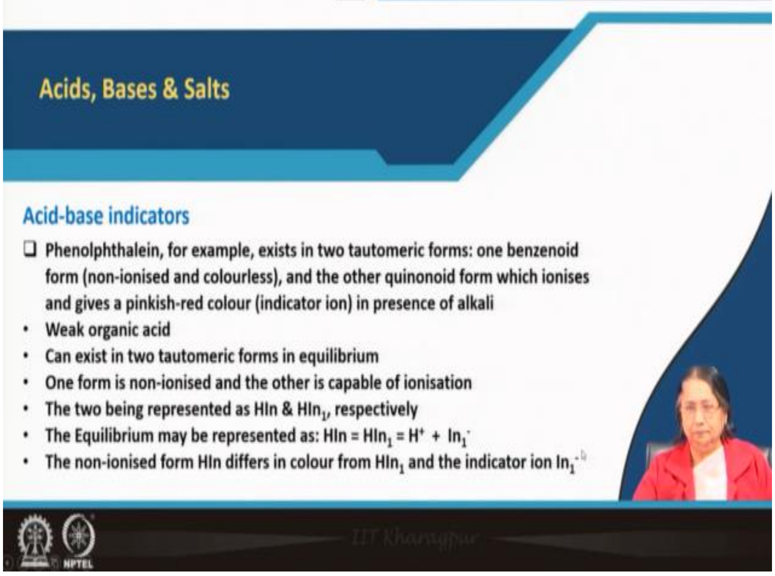

Acids, Bases & Salts

Acid-base indicators

☐ Phenolphthalein, for example, exists in two tautomeric forms: one benzenoid form (non-ionised and colourless), and the other quinonoid form which ionises and gives a pinkish-red colour (indicator ion) in presence of alkali

- Weak organic acid
- Can exist in two tautomeric forms in equilibrium
- One form is non-ionised and the other is capable of ionisation
- The two being represented as HIn & HIn_1, respectively
- The Equilibrium may be represented as: $HIn = HIn_1 = H^+ + In_1^-$
- The non-ionised form HIn differs in colour from HIn_1 and the indicator ion In_1^-

Today in my lecture, I will tell you about the indicators. We all know that indicators are very important in titrations and we know that there are different kinds of indicators, and depending on what type of titration we are doing we have to choose the indicator. Say, for example, there are acid base indicators, which we use for acid base titrations, there are some metal ion indicators which you will use for metal ion determination (as for example, for hardness determination). There are some redox indicators which we use for redox titrations and there are some adsorption indicators also, which we use for other purposes. Now, because we are talking about the acids, bases and salts, I will tell you about the acid base indicators. We all know about the two indicators: one is the phenolphthalein indicator and the other is the methyl orange indicator. We all use these two indicators even from our school days. We are habituated in using these two indicators for our acid base titrations.

How it is happening? Why they are changing the color during our titration? When it is acidic, it shows one color and when it is basic it is giving another color. That I will tell you today.

Now I am starting with the indicator phenolphthalein. Before knowing this phenolphthalein, we must see its chemical structure and we must know what is tautomer? We know isomer. Isomer means two different molecules having the same chemical formula but having different structures. Tautomer is a special type of isomer.

Indicators are weak organic acids. We have already seen that organic acids such as acetic acid, formic acid are weak. We also now know that carboxylic acid group is the main functional group in the organic acid which is a weak acid. I will tell you what is the characteristic of the tautomers? They can exist in equilibrium. They are the different forms of the same molecule and one form is non ionized form (this non ionized form is showing one color), another is capable of ionization (this form is giving another color). The equilibrium may be represented as follows:

$HIn = HIn_1 = H^+ + In_1^-$ ....(1)

Now, if we represent the non ionized form as HIn and ionizable form as HIn_1, then we can tell that it is the equilibrium between HIn and HIn_1. HIn_1 immediately dissociates because it is ionizable form. So, it can be dissociated into H^+ ion and In_1^- ion. These the characteristics of phenolphthalein. The non-ionized form HIn differs in color from HIn_1 (In_1^- is the indicator ion). The structures of HIn, HIn_1 and In_1^- are shown below in the slide.

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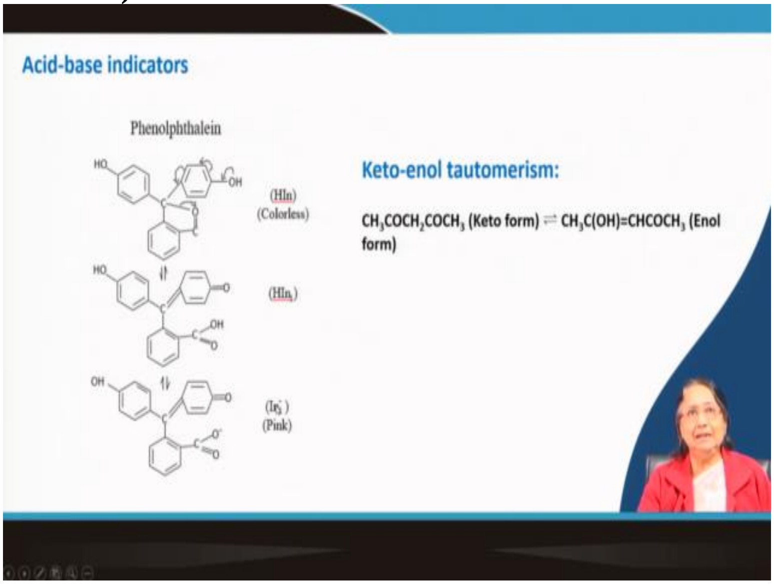

Acid-base indicators

Phenolphthalein

Keto-enol tautomerism:

$CH_3COCH_2COCH_3$ (Keto form) ⇌ $CH_3C(OH){=}CHCOCH_3$ (Enol form)

Now, here comes the structure of the phenolphthalein. I must tell you what is tautomer. I have told you that tautomer is an isomer. We can easily illustrate from the following equation:

$CH_3COCH_2COCH_3$ (keto form)⇋$CH_3C(OH){=}CHCOCH_3$ (Enol form).......................(2)

The first form ($CH_3COCH_2COCH_3$) is nothing but acetyl acetone and it has two ketone groups. CO means C=O here. Two carbonyl groups are separated by one CH_2 group. In the enol form you can see that C=O has become COH and the double bond is formed here between two carbon. That is why it is called enol. Enol means en and ol. En means double bond and ol means alcohol. So, this is called keto enol tautomerism.

Here actually, in the keto form one hydrogen from CH_2 group gets detached and get connected to the oxygen of C=O. Therefore, OH is formed and double bond is created between two carbon atoms. This is the characteristic of the tautomerism. So, one atom or one group can change its place giving two different forms and they are in equilibrium.

Similar type of phenomenon also occurs in case of two tautomers of phenolphthalein (HIn and HIn_1). Now, chromophore is important in case of color development. If there are alternate double and single bond, then color develops. That way HIn has no color.

Now, if you increase the pH that means, under alkaline condition, you know that In_1^- is generated, hydrogen is taken away by the alkali. So, this form shows pink color.

Say for example, I take some acid solution (for example HCl solution) and we put a few drops of phenolphthalein. Then what will be the color? It will be colorless. Now, if I start adding some NaOH into the solution slowly and when the neutralization point will come, that means the pH will be around 7 or maybe more than that, then we will see that the color now has become pink. Why it is pink? It is so because phenolphthalein has changed its structure. So, this is the mechanism. In acid solution, it will have the structure of HIn and when you add alkali slowly, it will be converted into HIn_1 and In_1^-. So, for same compound, there are two different structures and they are the tautomers. It is colorless in acidic condition and pink in the alkaline condition.

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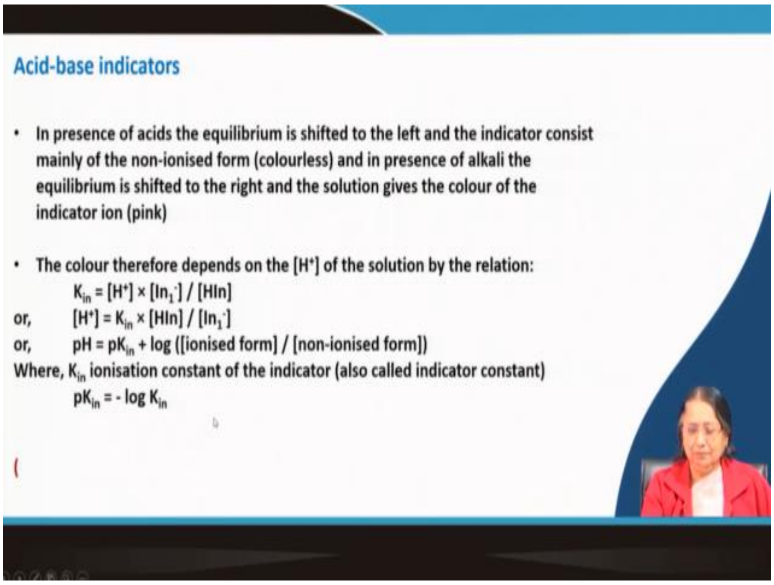

Acid-base indicators

- In presence of acids the equilibrium is shifted to the left and the indicator consist mainly of the non-ionised form (colourless) and in presence of alkali the equilibrium is shifted to the right and the solution gives the colour of the indicator ion (pink)
- The colour therefore depends on the $[H^+]$ of the solution by the relation:

$K_{in} = [H^+] \times [In_1^-] / [HIn]$

or, $[H^+] = K_{in} \times [HIn] / [In_1^-]$

or, $pH = pK_{in} + \log([\text{ionised form}] / [\text{non-ionised form}])$

Where, K_{in} ionisation constant of the indicator (also called indicator constant)

$pK_{in} = -\log K_{in}$

(

So, phenolphthalein is an acid base indicator and in presence of acids the equilibrium is shifted to the left and the indicator consists mainly of the non ionized form (colorless form) and in presence of alkali the equilibrium is shifted to the right and the solution gives the color of the indicator (i.e., pink color).

The phenomenon occurring here is very similar to that occurring with acetic acid (discussed in the previous lectures). Let us indicate the ionisation constant of the indicator by K_{in} and develop the following relationships.

$$K_{in}=\frac{[H^+][In_1^-]}{[HIn]}$$

$$\text{or,} [H^+]=K_{in}\times\frac{[HIn]}{[In_1^-]}$$

$$\text{or, } pH=pK_{in}+\log\left(\frac{[\text{ionised form}]}{[\text{non-ionised form}]}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Now, it is very similar to the equilibrium of the acetic acid in water medium.

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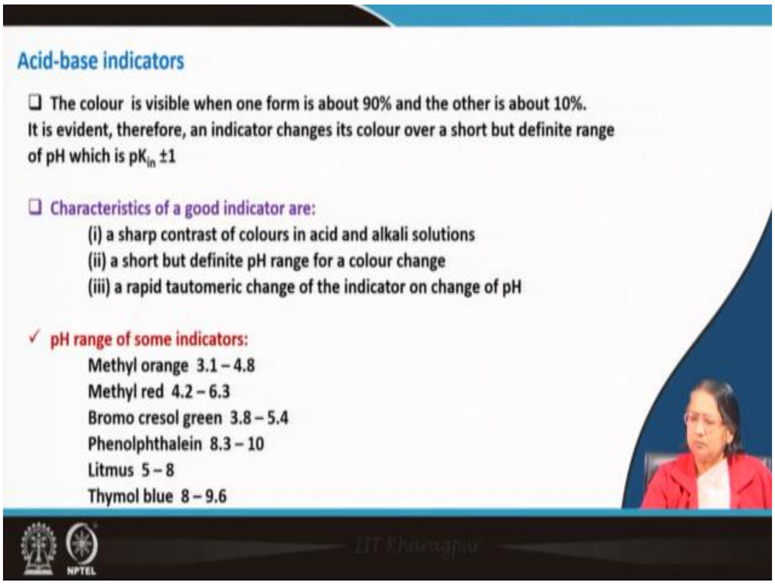

Acid-base indicators

- ❑ The colour is visible when one form is about 90% and the other is about 10%. It is evident, therefore, an indicator changes its colour over a short but definite range of pH which is $pK_{in} \pm 1$
- ❑ Characteristics of a good indicator are:
  - (i) a sharp contrast of colours in acid and alkali solutions
  - (ii) a short but definite pH range for a colour change
  - (iii) a rapid tautomeric change of the indicator on change of pH
- ✓ pH range of some indicators:
  - Methyl orange 3.1 – 4.8
  - Methyl red 4.2 – 6.3
  - Bromo cresol green 3.8 – 5.4
  - Phenolphthalein 8.3 – 10
  - Litmus 5 – 8
  - Thymol blue 8 – 9.6

Now, let us come to the acid base indicators. When we will see colorless and when we will see the colored form? As it is the mixture of two forms, so, one color will be predominating when one form is about 90% and the other form is about 10%. It will also show color at 95% and 5%. But at least it should be 90%. Say, for example, if both the forms are present in 50-50 ratio then you will not visualize the color. It is evident that, an indicator changes its color over a short but definite range of pH which is $pK_{in} \pm 1$.

It is very important to choose the indicator. There are so many different kinds of indicators. You are the one to choose the indicator for a particular titration. Say for example, there are so many indicators like methyl orange, methyl red, bromo cresol green, phenolphthalein, litmus, thymol blue etc. These are very common. Other than these, there are many other indicators and each indicator has its characteristic pH range where it changes its color ($pK_{in} \pm 1$).

For, example, the range of pH for methyl orange is 3.1-4.8. It is 4.2-6.3 for methyl red. So, there are different ranges where it changes the color. For phenolphthalein the range is 8.3-10. Now, what should be the characteristic of a good indicator? First of all, there should be a sharp contrast of color in acid and alkaline solution. I like phenolphthalein very much. It is because you see the contrast (in acid it is colorless, in alkali it is pink). So, you will see the color change very drastic in the neutralization point. But for methyl orange you know that in alkali it is yellow and in acid it is pinkish red. So, if you use methyl orange for acid base titration, you have to be very careful. It needs some trial also. You need some experience to use this indicator.

It is so because the change from yellow to pinkish red or pinkish red to yellow is not sharp change like phenolphthalein. You will see that it is changing the color slowly and you have to be very careful about it. A rapid tautomeric change of the indicator on change of pH means conversion of one form to another form.

The second important characteristic regarding selection of indicator is that it should reach equilibrium fast.

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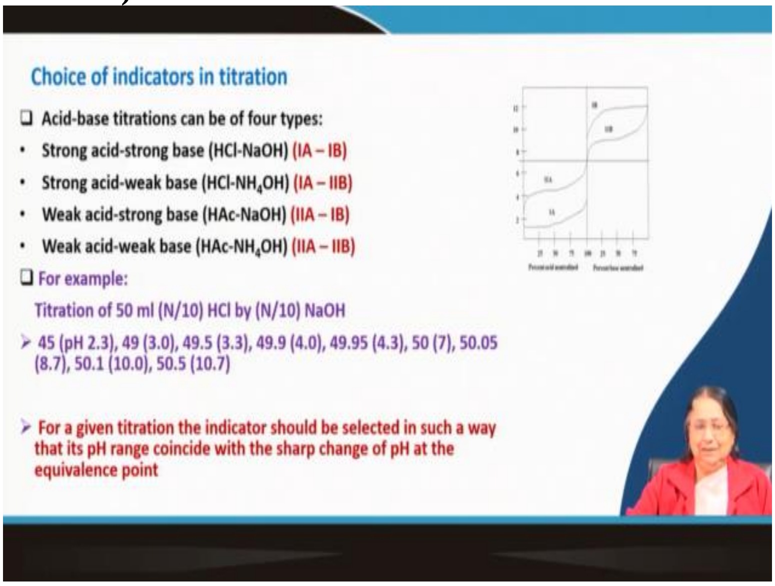

Choice of indicators in titration

☐ Acid-base titrations can be of four types:

- Strong acid-strong base (HCl-NaOH) (IA – IB)
- Strong acid-weak base (HCl-NH_4OH) (IA – IIB)
- Weak acid-strong base (HAc-NaOH) (IIA – IB)
- Weak acid-weak base (HAc-NH_4OH) (IIA – IIB)

☐ For example:

Titration of 50 ml (N/10) HCl by (N/10) NaOH

➢ 45 (pH 2.3), 49 (3.0), 49.5 (3.3), 49.9 (4.0), 49.95 (4.3), 50 (7), 50.05 (8.7), 50.1 (10.0), 50.5 (10.7)

➢ For a given titration the indicator should be selected in such a way that its pH range coincide with the sharp change of pH at the equivalence point

Now, how to choose an indicator? There are different kinds of titrations. Say, for example, for acid base titration, you know, they may be of four different types. For example, it may be a strong acid versus strong base. It may be strong acid versus weak base. It may be weak acid versus strong base. It may be weak acid versus weak base.

In case of strong acid versus strong base it may be HCl versus NaOH. In case of strong acid versus weak base it maybe HCl versus ammonium hydroxide. In case of weak acid versus strong base it maybe acetic acid versus NaOH. In case of weak acid versus weak base it may be acidic acid versus ammonium hydroxide. So, there are different kinds. Then how will you choose the indicator for these titrations?

We shall represent here an example of titration between 50ml of N/10 HCl and NaOH. 50 ml acid solution is taken in a conical flask and NaOH solution is taken in burette. Theoretically, pH 7 should be reached upon addition of 50 ml of N/10 NaOH solution. But we will show here pH at different amount of NaOH added.

Volume of NaOH (ml) added	**pH**
45	2.3
49	3.0
49.5	3.3
49.9	4.0
49.95	4.3
50	7
50.05	8.7
50.1	10.0
50.5	10.7

It is well understood from the table as well as from the slide of previous page that, upon addition of 50 ml N/10 NaOH to 50 ml N/10 HCl, pH 7 is reached. However, at 49.95 ml it is 4.3 and at 50.05 ml it is 8.7. Due to just two drops addition, it is changing so much that means there is a huge jump, and this has been shown by the curve 1A - 1B (shown in slide in previous page).

For strong acid strong base titration any indicator may be suitable. The curve is represented by IA-IB. But for strong acid weak base (represented by IA-IIB) and weak acid strong base (represented by IIA-IB) the range is low. So, some indicators may fit but not all. However, for weak acid weak base (represented by IIA-IIB) the range is very narrow and almost no indicator fit in this range.

So, it is your job to choose. There are so many options, depending on which titration you are doing, you have to select the proper indicator otherwise you cannot do the titration. This is very important for indicator selection. You have to think a lot. But obviously, it is the acid base titration. It is not other type of titration.

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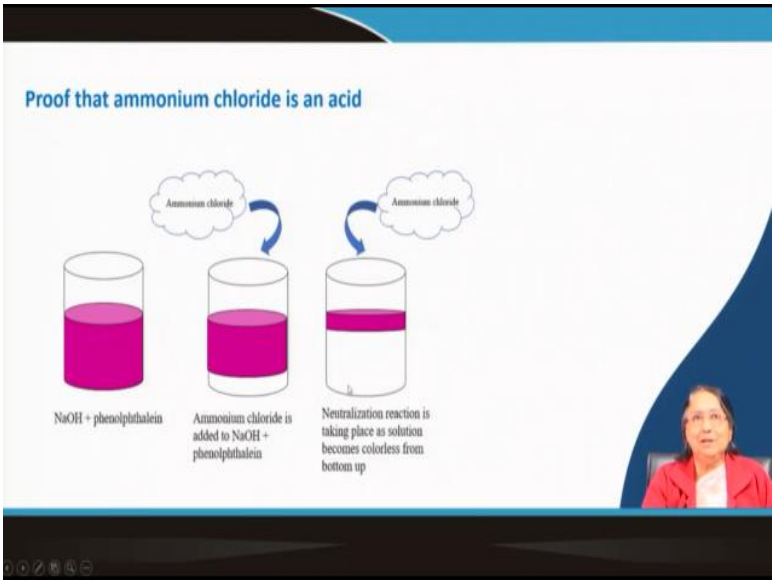

Proof that ammonium chloride is an acid

NaOH + phenolphthalein

Ammonium chloride is added to NaOH + phenolphthalein

Neutralization reaction is taking place as solution becomes colorless from bottom up

Now here one interesting slide I have given to show you the color of phenolphthalein. In the first beaker, NaOH solution is mixed with phenolphthalein, so it is very dark pink color. Depending on the volume phenolphthalein you added, you may get either very dark pink color or light pink color. Here quite a few drops of phenolphthalein have been added that is why it is dark color. Now you are adding ammonium chloride.

So, what will you see? It is a salt. You may think that, the colour will remain the same. But ammonium chloride is a salt of weak base and strong acid (ammonium hydroxide and HCl). As it is a salt of weak base and strong acid that means it will behave like an acid. So, when you are adding you can see that, it is being neutralized slowly. Ultimately you see the phenolphthalein is becoming colorless. That means it is showing the colour neutralization. And then ultimately, you will see that final solution (I have not shown) will be colorless. Obviously, that is because of the hydrolysis of ammonium chloride. When it is hydrolyzed, then it will produce ammonium hydroxide and HCl. HCl is stronger. So ultimately it will neutralize the solution. This is a very interesting experiment that you can also do. Thank you so much.