Course on Analytical Chemistry
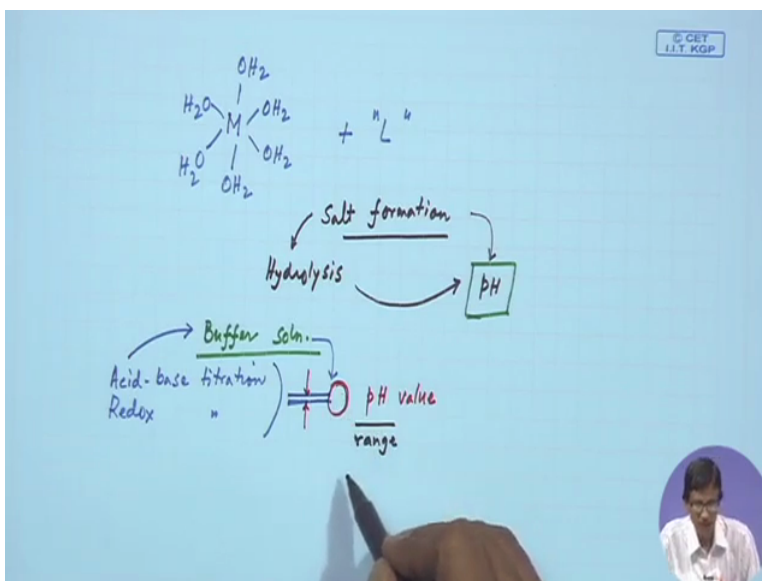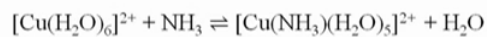**Professor Debashis Ray**
Department of Chemistry
Indian Institute of Technology Kharagpur
Module 4
Lecture No 16
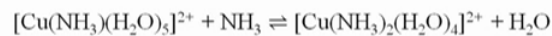**Spectrochemical Methods - I**

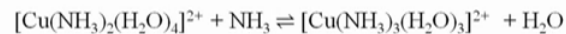(Refer Slide Time: 0:36)

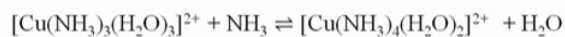(Refer Slide Time: 1:03)

Formation Constants for complex ions

$[Cu(H_2O)_6]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)(H_2O)_5]^{2+} + H_2O$

$$K_1 = \frac{[[Cu(NH_3)(H_2O)_5]^{2+}][H_2O]}{[[Cu(H_2O)_6]^{2+}][NH_3]}$$

$[Cu(NH_3)(H_2O)_5]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_2(H_2O)_4]^{2+} + H_2O$

$$K_2 = \frac{[[Cu(NH_3)_2(H_2O)_4]^{2+}][H_2O]}{[[Cu(NH_3)(H_2O)_5]^{2+}][NH_3]}$$

$[Cu(NH_3)_2(H_2O)_4]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_3(H_2O)_3]^{2+} + H_2O$

$$K_3 = \frac{[[Cu(NH_3)_3(H_2O)_3]^{2+}][H_2O]}{[[Cu(NH_3)_2(H_2O)_4]^{2+}][NH_3]}$$

$[Cu(NH_3)_3(H_2O)_3]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + H_2O$

$$K_4 = \frac{[[Cu(NH_3)_4(H_2O)_2]^{2+}][H_2O]}{[[Cu(NH_3)_3(H_2O)_3]^{2+}][NH_3]}$$
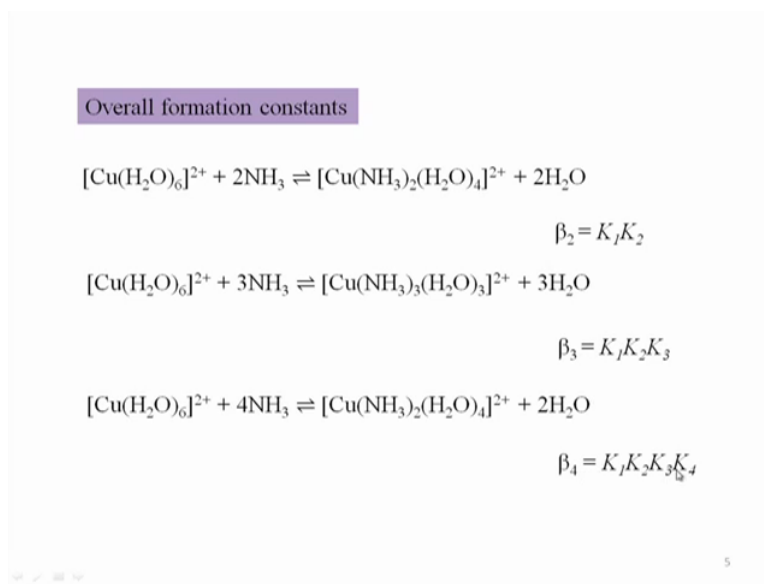
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Hello and welcome to this class when we are discussing about the formation constants of the metal complexes and we see that if we can have more than one ligand systems around the middle center, when we think of the corresponding (())(0:37) that means if we have any metal ion which is bound by 6 water molecules and we allow it to react with some incoming ligand so we can have so many equilibrium constants, so in case of copper so far we have seen that this 2nd K2 value we can get depending upon the individual concentration of the species what is forming over there.

Similarly we can have the 3rd one the K3 value and forth one, so the 4th one we can write in this particular form simply or supposedly that you can have this particular formula in your hand so we should know about that it cannot be stable form of this way that means if you can have the corresponding tetramine complex actually there is forming over there as the detriment copper species so your detriment copper species will be stable one without these 2 water molecules because we are thinking of the replacement of all 6 water molecules but is not actually taking place like this so you have the.

So what you can do for the determination of K4 value is only your formulas is being changed, so your concentration will also be different and you are starting concentration that means when you have this that means if we think that the presence of 3 water molecules and 3 ammonia molecule can be there but when the 4th is coming it will basically take away 3 such water molecules that means these 2 will also go away.

So your water concentration will only be different from this particular part and your ammonia molecule will be there. So but these we are dividing that means the formation constants of these complexes what we are talking about in a step wise manner that means the 1st, 2nd, 3rd, 4the but it is not in actual practice. In actual practice it is (())(2:39) process where the overall reaction we have to follow.

Overall formation constants

$$[Cu(H_2O)_6]^{2+} + 2NH_3 \rightleftharpoons [Cu(NH_3)_2(H_2O)_4]^{2+} + 2H_2O$$

$$\beta_2 = K_1K_2$$

$$[Cu(H_2O)_6]^{2+} + 3NH_3 \rightleftharpoons [Cu(NH_3)_3(H_2O)_3]^{2+} + 3H_2O$$

$$\beta_3 = K_1K_2K_3$$

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_2(H_2O)_4]^{2+} + 2H_2O$$

$$\beta_4 = K_1K_2K_3K_4$$

So what is the overall formation constant? So how we can think of a complete removal of all the water molecule by ammonia around this copper center. So if we get that so if we get that for this particular beta 2 the formation of these by 2 of them then if we can have 3 of them in you have the beta 3, then you can have the 4th one, so when the 4 of them and be there that means K-1, K-2, K-3 and K-4, so the products of all these 4 the individual stability constant can give rise to.

So products of all 4 K value that means the K1 multiplied by K2 multiplied by K3 and K4 will give you a constant what is designated as a 4th step overall 4 step of these will give you a beta 4 of this particular molecule. So these equilibrium concentrations are also very much useful because just now in our previous class what we have seen that the corresponding hydrolysis and the salt formation.

We are talking about the salt formation, so how this salt formation can useful to get you or take you in some point where we have seen in one case is the hydrolysis reaction and how this particular salt formation or its hydrolysis altogether can say are something about its corresponding pH value and if something is forming over there that means some condition is forming for a particular reaction where we see that these particular pH important in terms of not only in the presence of only acid or only base but a salt with acid or a salt with a base. So this pH for the salt formation and the salt in presence of the excess acid or in presence of the excess base can gave rise to a condition which we consider as a buffered solution.

Buffer Solutions

It resists changes in pH when it is diluted or when acids or bases are added to it.

Prepared from a conjugate acid/base pair, such as acetic acid/sodium acetate or ammonium chloride/ammonia.

A solution containing a **weak acid, and its conjugate base,** may be acidic, neutral, or basic --- depends on the positions of **two competitive equilibria**

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \quad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

So how we define this buffered solution that we will see that this is a typical solution and very interesting solution because most of this analytical techniques because in our next class we will be (())(5:08) probably in this particular class also introduced the corresponding spectrochemical methods where we go for different titrimetric method where you can use some instruments for the measurement of some titration reaction.

So this particular condition you have to maintain so before that we should know why we maintain or why we use some buffer solution and is a typical process where the reaction is taking place for an acid base or the corresponding formation of the salt in presence of excess acid or an excess based. So the definition tells us that it resists the pH, that means the pH is not very quickly changing when it is diluted with water and when acid or bases are added to it.

So this basically tells us that a preferred type that means if a preferred type of this particular conjugate acid base pair, such as acetic acid sodium acetate or a corresponding base, ammonia is a base and the corresponding salt so the corresponding salt or the corresponding ammonia which is the conjugate acid of that particular base. So conjugate acid base pair either acid and its corresponding conjugate form or the base of its conjugate form can give rise to a corresponding condition where we get a buffered medium.

So a solution containing a weak acid or its conjugate base, maybe acetic, neutral or basic, so how you think of so, if by definition of this buffered solutions if we consider that depending upon the

nature of the week acid and its conjugate base that means acetic acid and its corresponding salt that means sodium acetate or potassium acetate. How do we know that, that particular solution acetic, neutral or basic, so that will be depending on the position of 2 competitive equilibria.

So just now what we were discussing in our previous class that how the hydrolysis reaction is taking place and how the interaction can take place for his hydrolysis reaction when we consider that typical acid is reacting with water forming a corresponding ions that means your water molecule is functioning as a base taking the H plus from the corresponding acid to give you H3O plus so this corresponding K value is for the concentration individual concentration of H3O plus and A minus divided by the corresponding acid concentration.

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$$A^- + H_2O \rightleftharpoons OH^- + HA \quad K_b = \frac{[OH^-][HA]}{[A^-]} = \frac{K_w}{K_a}$$

If the first equilibrium lies farther to the right than the second, the solution is acidic.
If the second equilibrium is more favorable, the solution is basic.

Relative concentrations of the hydronium and hydroxide ions depend on the magnitudes of K_a and K_b and the ratio between the concentrations of the acid and its conjugate base

Aspirin (2-acetoxybenzoic acid) contains buffers to help prevent stomach irritation from the acidity of the carboxylic acid group aspirin

So the 2nd one so this is basically the corresponding concentration what we just now seen is corresponding (())(8:03) concentration which is termed as Ka that means a stands for acid. Acid is your HA or (())(8:10) which is your acetic acid so the equilibria constant for this K value is such that we are considering the corresponding acid of this concentration of acetic acid. Now if we can have for the corresponding conjugate base that means the acetate ions which is getting a hydrolyzed we have considered that how hydrolysis can take place.

Give rise now the corresponding Kb value and this Kb value we have also considered earlier that this is nothing but your Kw and Ka. So this Ka thing can come into the picture along with your Kw value so these all are related so Kb, Ka and Kw. So we are considering basically 2

equilibrium conditions, the 1st equilibrium is lying somewhere and the 2nd equilibrium, how they are getting changed depending upon the nature of this acid and the corresponding conjugate base. So if the 1st equilibrium lies farther to the right than the 2nd, the solution is acidic.

So this particular equilibrium so what we have seen that the 1st equilibrium lies farther to the right that means the corresponding disassociation of the corresponding acetic acid or any other acid so you have the corresponding acid form and its corresponding ions, the solution would be acidic. The 2nd equilibrium if it is more favorable, the solution will be basic that means if you can have this corresponding acetate ions which is reacting with water forming hydroxide ions, so this is your corresponding strong base so if this equilibrium is favorable you have a corresponding solution which will be basic in nature.

Otherwise if both of them are matching that means this both of the equilibrium are competitive and of comparable magnitude you can have a neutral solution. So we can have the relative concentration of hydronium and hydroxide ions. So one is for the acidic nature and another for the basic nature of the thing condition are dependent on the this K value and previously we have seen that in this case is the Kb value the Ka Kb and the ratio between the concentration of the acid and its conjugate base.

So concentration of the acid and its conjugate base this HA and A minus and the corresponding Ka and Kb value will tell us about the corresponding fate of the buffered medium. So why we require this buffered condition because this buffer solution or the buffer condition is always very much important thing that means this buffered solution when used will afterwards we will see that whenever we go for some acid-base titration or in some redox titration.

We see that we should not allow to change the corresponding pH of the medium to a large extent because we will be doing this particular reaction in a very small pH window where if we add this buffer solution that means whenever we go for the titration using some acid or using some base or one oxidising agent or reducing agent the condition is such that we should not allow to change this particular reactions for its pH to a large extent otherwise we will be in trouble if we just allow this particular window to be big enough. So how this buffer can help in several areas so one such medicine we all know the painkiller Aspirin we know that the 2 acetoxy benzoic acid.

It contains buffer also to prevent the stomach irritation from the acidity of the carboxylic acid group in the Aspirin. So you have this corresponding acetoxy benzoic acid so benzoic acid is basically therefore a (acidic) acidic form so if it is in the buffered medium your acidity can be controlled in your body at the same time.

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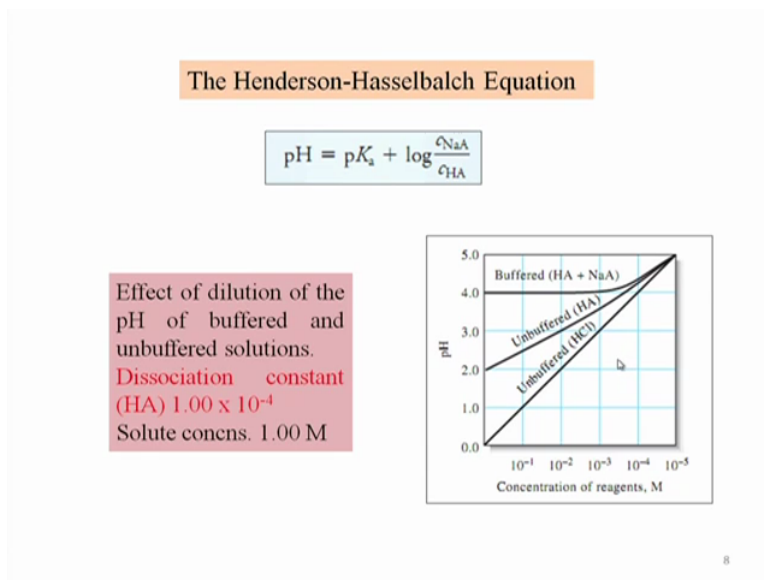
So this 2 things that means your corresponding pH control of the pH and the corresponding medium, how we are forming that can be considered by a simple equation which is known as the Henderson Hasselbalch Equation. Henderson Hasselbalch Equation tells us that how we get a corresponding pH of a buffered medium, so pH of a buffered medium can be obtain if we have a relationship like this from this equation that pH will be related to the pKa value plus the log of the corresponding salt and the acids C NaA divided by C HA, C NaA is acetate ions it will be the concentration of the corresponding sodium acetate and the C Ha will be the corresponding concentration of the acetic acid.

So these 2 equations this this equation is basically useful to see where we consider the corresponding change in pH value with the change in the concentration of the reagents. So when we change the corresponding reagent as your HCL. So if we just change the corresponding concentration from this that means it is 10 to power minus (())(14:07) when you change from say a right-hand side to the left that means your concentration is increasing.

So your pH is also changing say pH5 to pH1 and then to 0 but if you see the corresponding slope is almost is 45° slope of this particular plot of this hydrochloric acid, so as you go as move for the change in the concentration is pH is changing in a very drastic manner, so the pH dependence on the concentration of the hydrochloric acid which is unbuffer that means no buffered condition has been added in terms of the corresponding salt of the hydrochloric acid.

Similarly if you can have some weak acid like HL like your acetic acid, if it is unbuffered also your pH can vary from 2 – 5 again due to the change in the corresponding concentration from 10 to power minus 1 to 10 to the power minus 5, so only in the dilute condition your pH is going to the corresponding PK value which is 4.75 per acetic acid but if we see that a typical buffered medium, so if the buffered medium is C is almost horizontal up to this point of 10 to the power minus 3 (())(15:29) concentration of that particular mixture of acid and salt.

So if it is acetic acid and sodium acetate mixture and if it is buffered we do not consider the corresponding change or the very first change in pH value with the change in the concentration so that is why it is a very good advantage for handling a buffer solutions for this particular reaction or in some other cases that corresponding titrations. So the effect of dilutions for this particular (())(16:02) we can explain in this fashion also the dilutions of the pH of a buffered and unbuffered solutions, if we have a disassociation constant of this weak acid is one into 10 to the power minus 4 molar and the solute concentration of 1 molar. So one molar solute concentration if you consider so due to the dilutions from left to right what we see that for a particular disassociation of this HA and which is unbuffered in one case, how quickly they are changing from left to right following the Henderson Hasselbalch Equation.

Buffers do not maintain pH at any constant value, but changes in pH are relatively small when small amounts of acid or base are added

Buffer capacity – the number of moles of strong acid or strong base that 1 L of the buffer can absorb without changing pH by more than 1.

Acid Rain – Buffer Capacity of Lakes

The principal buffer of natural water is a mixture of **bicarbonate ion and carbonic acid**.

Limestone-rich areas have lakes with relatively high concentrations of dissolved bicarbonate and thus low susceptibility to acidification.

So these buffers basically at some point it is not maintaining a pH at a constant value so what does it mean that we are talking about some window or some space for that corresponding change in the pH value in the buffered medium. This is not that we can fix the pH are a particular value of say 4.5 or 4.8 but we get basically a range so a range of pH value can be there while due to the addition of acid or due to the addition of base particular pH where you will not change drastically. So this do not maintain pH at a constant value by changing pH is relatively small compared to your unbuffered condition this change is relatively small when small amount of acid and bases are added, you can consider the addition of base or addition of acid as the titrant.

So during the addition of those titrants into the reaction medium in conical (())(17:44). Your pH value will not change very much if your medium is a buffered medium and a relative term related to that of your buffered capacity is also defined in terms of the number of moles of strong acid or strong base that one leader of buffer and observe without changing the pH by more than one. So some of these solutions that means a solution of a buffered solution of 1 liter, 1 liter of that buffered can absorb a strong acid or the strong base so that the corresponding value, the number, the digit for the corresponding number of moles of acid or moles of base which can be added to 1 liter of buffered such that your pH cannot change more than one so plus minus 1.

So range that we are basically get for this particular ratio. Second this the Henderson Hasselbalch Equation is in the logarithmic mean value so the range is 1 to 10 so the corresponding pH change

will be plus minus 1 so that particular range in terms of the corresponding moles values of these moles can be considered as your buffered capacity. So this buffered capacity is also a very useful thing or our understanding for the different lakes in terms of acid rain because this is a natural phenomenon we all know that due to the corresponding environmental pollution.

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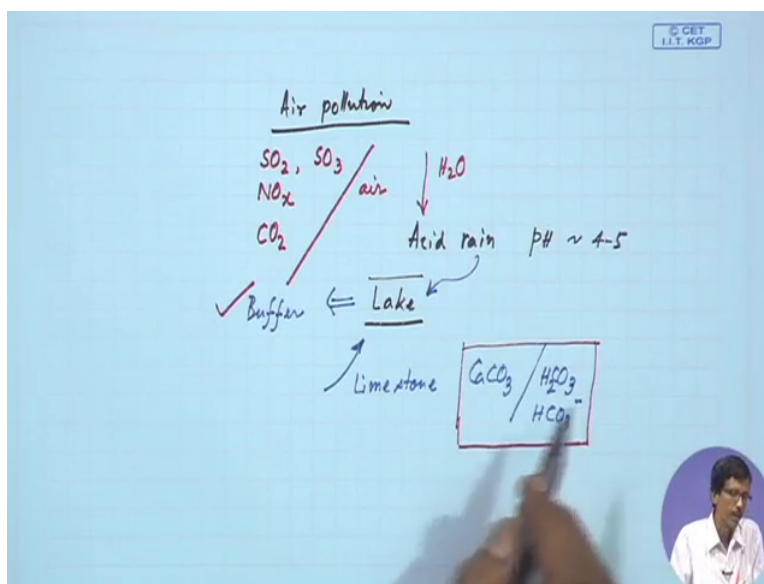
So we know that air pollution is there so this air pollution can give rise to several oxides, oxides of say sulphur which is sulphur dioxide or sulphur trioxide. Then corresponding NOx we called the different nitrogen oxides and obvious the carbon monoxide and carbon dioxide. So if we have all these oxides in air and when rainwater is coming over all these oxides, these all will be converted to the corresponding acids so these we all know that when it is coming through acid we get acid rain. So our soil the surface soil of Earth is getting polluted or in the rainforest we get the typical acid rain and is definitely the pH is in the range of 4 to 5 for this particular acid rain in some cases.

So what happened to that particular acid rain to some lake because if there are several lakes available and where we can have the corresponding rainwater accumulation within this particular lake so what should be the corresponding defense mechanism for this lake for a change in pH because acid is supplied by in terms of the corresponding rain which is coming out into the air pollution and is in dumbed with in the lake and the natural mechanism is such that if we can have a corresponding buffer medium within the lake itself that means if your Lake is forming and is

surrounded by some of this limestone rocks, so lime stone rocks that means calcium carbonate rock is there.

So if we can have calcium carbonate rock and this calcium carbonate in presence of your corresponding acid like carbonic acid H2 C03 or HCO3 minus. So these are the things that means you have the salt and corresponding acids so this is the acid and the salt and this combination of this calcium carbonate and its corresponding acid and his corresponding acid (()) (22:02) can give rise to a corresponding buffered condition.

So this buffered medium can take these acid from the acid rain but it is pH will not change very much because your medium is buffer so that is a natural defense mechanism or the natural process where we see that the different lakes can have a certain amount of buffer capacities because we have corresponding definition of this buffered capacity so how much acid or how much base it can observe but in this particular case is the acid from the (())(22:35) how much it can basically consume due to the formation of this particular deposition from these carbonate rocks.

So the principal buffer of natural water is basically a mixture of bicarbonate ion and the carbonic acid. So the rocks are getting dissolving over there and due to the availability of this acid either from the water itself or some amount of acid from the acid rain, we get the bicarbonate and the iconic acid, so the mixture of this bicarbonate and carbonic acid will be a typical buffered medium. So that we will also see as a very good example understanding this particular buffered media when you talking terms of the corresponding titration of this bicarbonate ion by some assets so that we will see also that how we can go for the responding reaction where we determining the aniline or the unknown analyte concentration falling a titration where the titrants concentration or the titrant value volume will be useful to understand the unknown concentration.

So in this case the corresponding limestone rich area of those lakes, they have dissolved bicarbonate and therefore the bicarbonate ions and the carbonic acid. So they have the corresponding affinity and thus low susceptibility to acidification though rain waters, the acidic rainwaters are dropping or accumulating inside the corresponding lake but the buffer capacity of

that particularly lake will not allow its corresponding pH to change drastically from the corresponding acid rain what we get from there.

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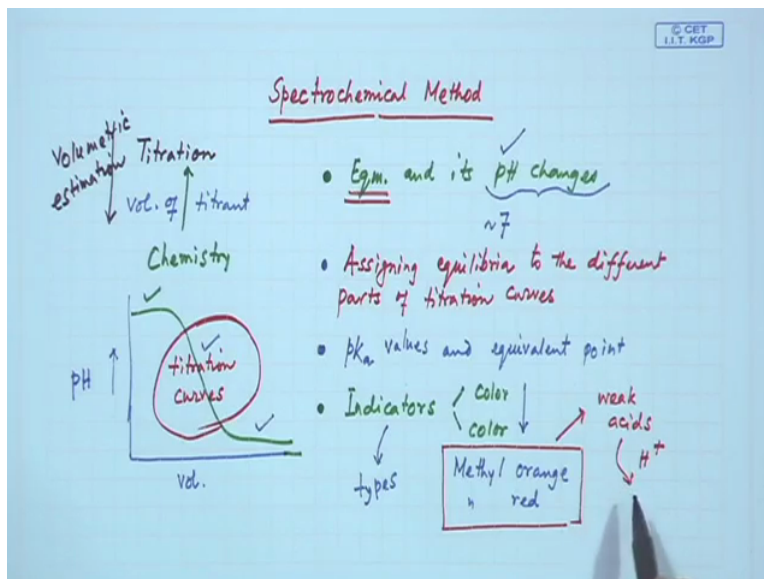
So just this particular part or at this particular point we will be finishing our equilibrium process so next we will be going for the spectrochemical methods. So today we will only just introduce that, that spectrochemical method, how we can use that for our regular titrimetric methods of the titrimetric processes where we consider this spectrochemical methods serially from the titration will introduce you for that titration reaction. How we go for the titration and as we all know that volumetric estimation is nothing but your titration.

Volumetric estimation or the quantitative analysis of any unknown solution is your titration reaction, so the chemistry which is involved in this particular titration, so we must have the corresponding chemistry involved in this titration reaction. What we can follow, so far what we are discussing is the corresponding equilibrium process so this particular equilibrium will also be there and that equilibrium process when we talk in terms of the corresponding acid-base reaction or the hydrolysis of any other salt, we should consider the equilibrium and its pH changes.

So during the titration also will consider a typical equilibrium for this acid-base reaction and how the pH is changing and how to monitor because you have to change the pH, you have to monitor the pH change because at the neutralization point where you consider the corresponding acid-base titration reaction. So at the neutralization point your pH as a very characteristics value, if we

consider that is typically neutralize so pH value should be close to that of our neutral value as we all know it should be pH 7. So this particular thing that means there are several equilibrium processes will also be there.

So if we get this titration and if we see that this volumetric estimation so this volume of some titrants, so some volume of a titrants we are adding and during this particular edition of this titrant your pH is changing involving some of this equilibria and if you consider that this particular plot, if we just simply plot something where in x-axis we just plot the volume used for this titration that means the volume of the titrants we are adding and we are looking at the corresponding pH change so the other axis will be occupied by the change in the pH. So for this plot that whatever plot we will be getting in this fashion that means the volume of the titrant what we are adding and due to this addition of this titrant your pH will be changing so whatever will be getting over here so this plot basically will give us something which is known as your titration curve.

So these are nothing but your titration curves, so how you start wherefrom we are starting that means your pH can be starting from here say up to 10 or 11 or pH is starting from 0 to 1 at this particular point and as you keep on changing the corresponding pH value with regard to the addition volume of some titrant the volume of this titrant addition can be your acid, it can be your base also. So for this particular acid-base titration so you can have not only a single equilibrium but you can have more than one equilibrium.

So assigning the different stages of these titration curves, that means assigning the different equilibria to the different parts of titration curves, this is important, how we assign a particular titration curve. Suppose your titration curve is like this, okay. So how what is happening over here and what is happening over here and what is happening over here. So these are the typical assignments this particular processes what is taking place during the corresponding neutralization reaction.

So how we can assign all these things, then in terms of the corresponding pH because the Henderson Hasselbalch Equation we have seen just now that this has some relationship with the corresponding PK value, the PK value we all know that whenever we are considering the equilibrium of this particular processes this K values are important so KA and KB values are

there so we are considering the corresponding acid disassociation constant so we can have its corresponding PK value. Suppose it is your acetic acid so acetic acid is being titrated with a corresponding solution of sodium hydroxide or potassium hydroxide whose strength is known. So this PK value and the corresponding PK value what will be requiring for a neutralization or the equivalence point, so PK values and equivalent points that means if we get this particular titration curve where you see where is your equivalent point and how this particular PK value can be there depending upon its corresponding change in the pH values.

So related to this fashion what we can find out in terms of the corresponding PK value, we can find out the use of the indicators for this sort of titration. How we have to indicate this that means some indicators will use from the school days we all know that the different indicators we are using for identifying your acid-base reactions so this acid-base reaction is a very simple reaction as we can put some indicator and these indicators can change its color. So color for acid form and color for your basic from will be different and this value we can understand that which particular form is there, so there will be change from one particular color to the other by these indicators. So these indicators what are of these the types, what are these materials?

So types of is indicators and which particular compound again we all know that, the chemist always have this particular advantage for acid-base, for redox, for complexometric titration all we in all these cases you will see that there will be different indicators to be utilized for this titration so for simple acid-base titrations how we can correlate this, we know some name only say methyl orange, methyl red these are the some names of these indicators for typical acid-base reaction.

How and where we can use these indicators, where we can use MR or MO for the titration reaction and interestingly like that of our discussion related to the weak acid or weak based thing that these indicators the acid-base indicators are also some weak acids that means they can itself take a proton or can donate the proton which is getting accepted by this molecules and due to that the structural change can take place and there will be a corresponding change in the corresponding absorptional in the electromagnetic radiation, that is why it can give rise to or it can change its color.
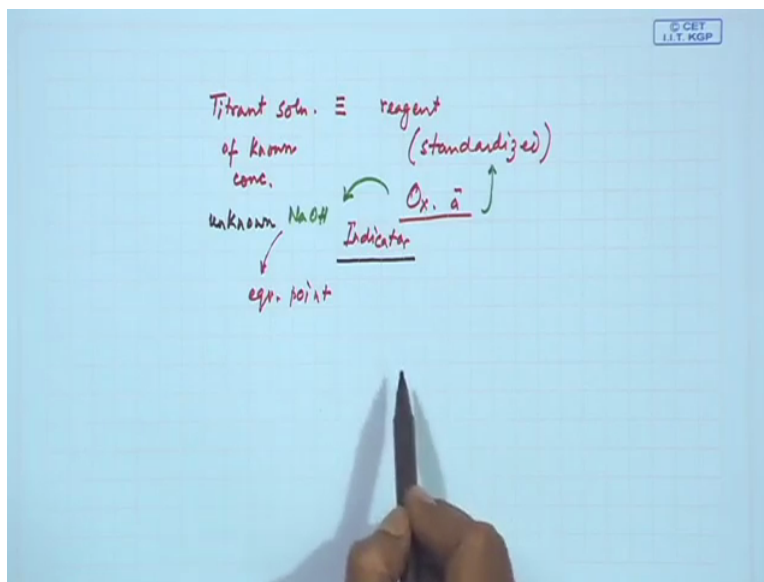
 So what we find over that, that you have a titrant solution and that titrant solution will be utilised then titrant solution of known concentration will be utilised with that of our reagent which can be standardized. So any acid or any base some of these that means we all know at as I told you that oxalic acid which is a very good primary standard show your oxalic acid can be a standard solution and that standard solution can be stable enough and react with the analyte.

So these oxalic acid can be titrated with sodium hydroxide and when we titrate this particular oxalic acid with sodium hydroxide we use some indicator and we titrate this with analyte and with a sufficient rate of the reaction we can reach up to the equivalence point where the corresponding change in the color of this indicator will occur and we can find out the corresponding amount of oxalic acid which is being consumed by this unknown concentration of sodium hydroxide.

So in this particular fashion we will find out the corresponding known concentration or unknown strength of the sodium hydroxide by the use of the corresponding oxalic acid which is a known strength which can be taken in your (())(35:51) for this titration. So before going into the detail of this spectrochemical method where we will be utilising the spectrometers or the color meters for this titration. In our next class we again once again we will discuss even about the different titration, the titration curves and the back titrations, what are things can be useful for this analytical techniques, okay. Thank you very much.