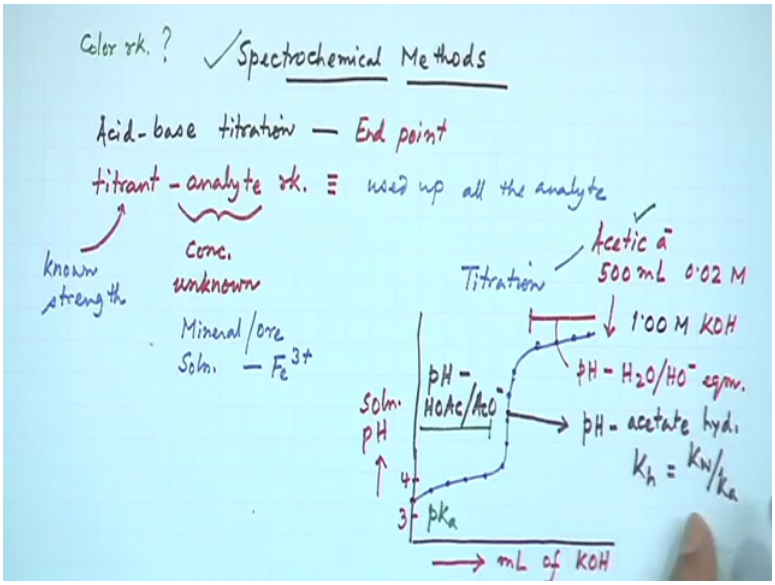
Course on Analytical Chemistry
Professor Debashis Ray
Department of Chemistry
Indian Institute of Technology Kharagpur
Module 4
Lecture No 17
Spectrochemical Methods - I

(Refer Slide Time: 0:27)



Good evening and welcome to this class where we are talking about the spectrochemical methods and our basic intention was that how we can use a spectrometer or a spectrophotometer to monitor a particular acid-base reaction. Say the first example what we can think of is a typical acid-base titration reaction and in other way also we can consider this particular reaction as a titrant analyte reaction.

So we have to use a particular solution of known and strengthen say titrant volume where we will utilise the analyte or the identify the concentration of the analyte in any unknowns sample it can be a solid sample or it can be a solution or it can be gaseous sample solubilized in some solvent where we can go for this sort of reaction where you all know when a particular base solution or a particular acid solution is completely neutralised we get the typical endpoint of that particular reaction.

So this is your unknown so our analyte is unknown so whatever analyte we have where you see that and analyte can be a solid sample from the very beginning what we are talking about, it can be a mineral or it can be a ore sample or it can be a simple solution of any other metal ion say Fe3 plus, so when you go for this particular reaction that means you have a unknown

analyte concentration and that unknown analyte concentration should be consumed by the titrant whose strength is known so known strength of the titrant will be utilised and our basic intention is that you have to use up all the analyte present in this unknown solutions.

So you have to used up all the analyte concentration, so we will take some example of say typical titration, so a titration of say acid-base titration so if we take one such example where we can consider that titration of a acetic acid solution say, so we are just going for acetic acid solution and certain volume we have to take say 50 ml say 500 ml can consume of say 0.02 molar concentration and we want to titrate it with that of a solution of KOH that means potassium hydroxide solution and that potassium hydroxide solution of higher strength, so how we can get a plot where we see the corresponding change in the age values that means in this particular acid-base titration reaction, how we can monitor the corresponding change in the solution pH values.

Since we are going for an acid-base titration reaction where we are starting from acetic acid solution of certain strength so will we at the very lower level of this strength that means between 3 and 4 the pH value will be between 3 and 4 and will start from that particular point this titration and on this axis will be adding the milliliter of that particular KOH solution what we are talking about, so this is say 1.00 molar KOH solution, so milliliter of KOH. So how the thing will change therefore that A will get a typical plot like this so we will just go like this then we will have a sharp increase in the value and then we will just see something.

So these are the points during the titration so once you add certain milliliter of that KOH solution and we can monitor the pH change. So if this can be the change, how we can utilise this particular reaction to go for a spectrochemical analysis because all we know is that for a typical spectrochemical reaction where we should be utilising some color reactions but wherefrom we get the coloration from this because you are acetic acid solution is a colorless solution your KOH also is a colorless solution.

Only thing what we are seeing is the only change in the pH so in this particular range your pH will be dictated or govern by the corresponding PKa value of the acetic acid. So this PKa value of the acetic acid will tell how far we can go during the addition of this KOH values. So once we go this sharp rise so this particular range securely within 1, 2 or 3 anal of the solution, your pH is jumping say 6 to say up to 8 or 10.

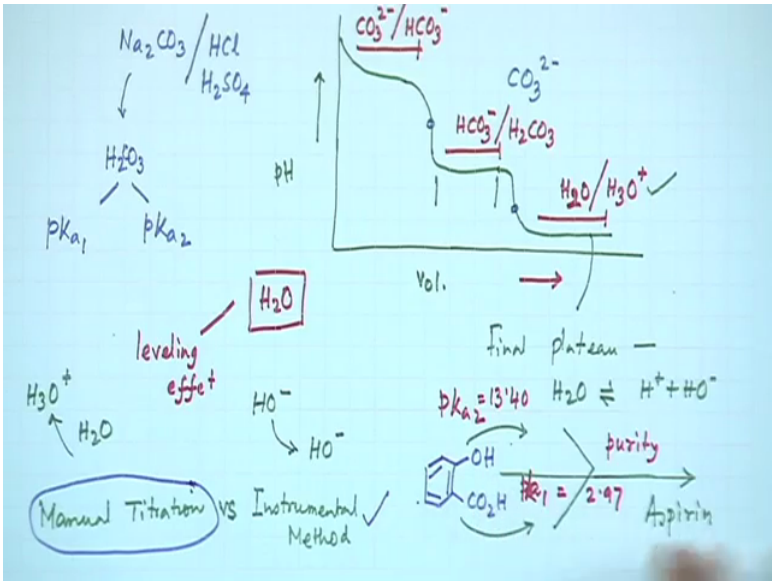
So at this point basically or this particular range when it is going away, so this particular range this horizontal part, this particular horizontal part is basically given by the corresponding pH of a chemical equilibrium what we have discussed so far and we are talking about between the acetic acid and the acetate ion equilibrium, okay so is HOAc and acetate ion equilibrium so we know the PK value of the acidic as a we know the corresponding concentration all these acetic acid and the acetate ion because after addition of this KOH we will be producing certain concentration of these acidic ion in the solution.

So but this particular line so this can be your change in the pH where the changing the pH values can take place where this acetate ion what is forming over there and the hydrolysis of this acetate ion will dictate or will control all give us the corresponding pH value for this particular reaction. So pH will be given by the acetate hydrolysis reaction and will be given by the KOH as we all know which is nothing but your Kw by Ka value. So this particular value will tell us this one then once we reach over here so the vertical line we are finishing we are completing the vertical line in again we are approaching to some horizontal part of the graph.

So this horizontal part is then we have a very slight change or a very small change in the pH value after the addition of this KOH. So milliliter addition of this KOH beyond the endpoint of this titration, will be dictated by simple this pH also will be described by your water hydroxide ion equilibrium. So at the end basically when you are forming this water from the reaction of your base and the acid we all know they are forming salt plus acid salt plus water, so this water will be there and have certain amount of hydroxide due to this addition so this this range of pH will be governed by this particular equilibrium.

So what we see basically from all these examples that whatever thing we are doing we are talking in terms of certain chemical equilibrium and then the control of the corresponding pH which is again related to the PKa values by the Henderson Hasselbalch equation that we have seen so far and ultimately we are talking of something in this particular range where is a sharp change or is a jump in the corresponding pH value, so how we can monitor this particular jump in this pH value that we will see with the help of a direct titration or with the help of some spectrophotometer.

(Refer Slide Time: 10:40)



But if we can have certain combination that if we want to titrate a sodium carbonate solution with some acid say hydrochloric acid or sulphuric acid. So there if we see that we start from a very high pH value because this can be a very useful example where we can monitor not only the pH that means the pH metric titration we will see but also it can be controlled or it can be utilised by the corresponding potentiometric titration, so there has you see we start from your sodium carbonate solution which has a very high pH value and since we have 2 step of this protonation reaction so we will get plot like this with respect to the volume of acid added and the change in the corresponding pH, how the change in the pH so pH in this particular case either you go this way you can go down from here, so as you move this so how the pH is changing from this particular case.

So there also you have corresponding horizontal ranges as well as the vertical points so 2 search vertical points are there where we can see for this particular one where the corresponding acid is your carbonic acid H2CO3 and it can have 2 PK values so we consider them as PKa1 and PKa2 so these particular things will then therefore how to dictate these two values which is an important thing therefore so when we go for this determination or the titration of say carbonate ion. So this particular titration is a very useful one and we can consider a corresponding titration for any such diprotic acid like this particular carbonic acid or any other organic acid that will stay the example.

So during this process so one search equilibrium process with there for the horizontal one so this horizontal position and these 3 horizontal positions will be there and this will be controlled by the corresponding equilibrium concentration of carbonate ion and the

bicarbonate ion. So equilibrium between carbonate and bicarbonate will dictate the corresponding change in the pH value in this horizontal position then the pH in this particular range will also be governed by bicarbonate ion in the next step to your free carbonic acid and lastly like that of our H2O and H3O plus because ultimately whatever acid we are adding then the volume of acid addition will you the corresponding H3O plus. So these determinations are very easy to do and all these things but ultimately what you are getting for all these reactions.

Your water play some important role, so water can show some leveling effect we call and that leveling effect is known as that if we have an acid and that acid strength is higher than that of our water. So any acid which is more acidic than your H3O plus species will donate the proton to water, so if you have the acid so if it is higher than that of your H3O plus, so any acid whose acidity is higher than that of your H3O plus will donate the proton to water so it will be donated to water giving rise to all these H3O plus.

Similarly any base is more basic than HO minus the hydroxide ion which is derived from the water will take off the corresponding proton from the water molecules, so it will form more and more hydroxide ion the water molecules so water can function water can play the dual role of accepting the proton and donating the proton to the system so that is why all the time whether we are going for the acetic acid titration with KOH or we can do for some titration where we can see that water can be protonated by the addition of the acid during your carbonate titration, so will be forming more and more the hydronium ion.

So these particular things so when we go for these 2 changes and basically the final plateau, the plateau over here the 1 the 2nd plateau is here and the third plateau is here so this plateau is the final plateau in this particular case so the final one is governed by the corresponding equilibrium of your water so is H plus HO minus. That is why you see that is particular thing that means it can pick up or you can give due consideration of the corresponding H plus and the hydroxide ion so if you have a strong asset compared to your water it can donate that proton to this water molecule and if you have a strong hydroxide ion-based base which is stronger than the hydroxide which can be liberated from your water molecule.

We see that we can extract this particular proton from water also so that basically sometime we will see that how this leveling effect can control the corresponding titration reaction. So one such example in this regard we can see is the corresponding diprotic material which is your salicylic acid so one such example is how are salicylic acid where with that of the (())

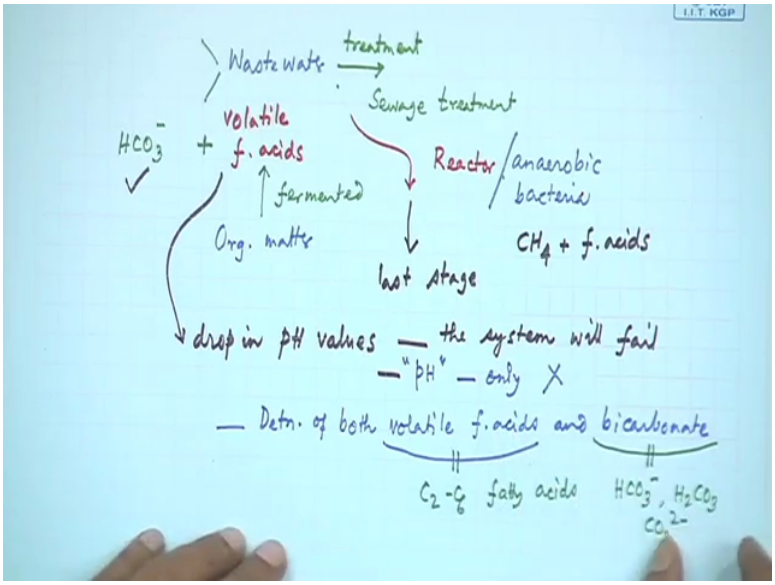
(17:34) your attachment for 2 groups one is the phenol function another is the carboxylic acid function so definitely their PK values are different so this is more acidic compared to your phenol unit and how to check or how to compare how to determine the corresponding purity of this particular species because we all know is a very good ingredient for preparation of aspirin molecule.

So aspirin molecule is nothing but if you go for the acidization of the salicylic acid is the corresponding acetylation of this hydroxyl function of this Salicylic acid will give you the corresponding aspirin. So if we consider that this is stronger so if you have a Pka1 is equal to 2.97 and this PKa2 like that of our carbonic acid we have 1 pk1 another pk2, so this is 2.97 and this is 13.40. So to determine the unknown concentration of salicylic acid for the preparation of aspirin we should know corresponding purity of the (())(19:03) salicylic acid what is available for the conversion of this particular molecule, this salicylic acid to aspirin.

So what we see since this carboxylic acid part is giving rise to a PK value of 2.97 so we can monitor this particular group consumption with that of your sodium hydroxide or potassium hydroxide solution, so we will titrate for this function only this carboxylic acid function we can titrate that means we will go or only neutralisation of this carboxylic acid and not like that both the 2 ends of this we can monitor, so this would the determination of this amount of carboxylic acid found for a sample of salicylic acid will tell us the corresponding purity of this salicylic acid or the preparation of aspirin.

So this is typical manual titration using burette pipette conical flask but if we can substitute particular thing that means always we see that there will be a competition between this manual titration so what we can have a manual titration versus that of our instrumental methods. So in this class of this spectrochemical method we just slowly moving towards the methods what we can use for instrumental methods of analysis but still this particular one this manual titration is still a very good methodology where we can titrate the amount of this unknown samples starting from your acetic acid, this sodium carbonate solution or carbonic acid or salicylic acid, these are some typical examples. So how we can utilise this for real life application where we can go for analysis of wastewater during the corresponding pollution of air sample.

(Refer Slide Time: 21:40)



So we all know that industry is producing for any industrial process we can we basically produce certain amount of wastewater depending upon the corresponding treatment what we do for the corresponding industrial process. So if we see that some of our this wastewater so this wastewater can be treated that mean treatment of wastewater is required before we just throw away this particular wastewater to some natural source outside the river bed or ocean all these things.

So the titrations and be used together that means if we can have for a sewage treatment so the sewage water you can have, so the sewage treatment so for a particular sewage treatment what we get that sewage treatment we can too where large amount of the fatty acids are there which are volatile so if the sample or if the sewages is containing some volatile fatty acids and this volatile fatty acid is basically allowing or taken in a particular reactant. So this particular reactants can be given to a reactor so what are those reactants, reactants are nothing but some bacteria degradation we can do so anaerobic bacteria we can use.

Why we are using this anaerobic bacteria? Because anaerobically we can degrade the whatever organic matter is there that means if we can have this organic matter that means the industry which is involved for doing this particular industrial process they are handling some amount of organic matter and these of organic manners when they are fermented, they produce large amount of bicarbonate ion in the form of carbon dioxide if the medium is alkaline we all know that alkaline medium can consume carbon dioxide giving bicarbonate anion, so how of determine these 2 things together so in a continuous process of doing all these things that means if you go for the degradation of this organic stuff we what we can do

that in this medium you can have both carbonic acid anion that means the bicarbonate anion and the corresponding volatile fatty acids and these fatty acids can built up in the medium.

So when you treat it so during the last stage of this fermentation process and anaerobic bacterial degradation what we see that at the end basically will be looking for the production of methane and fatty acids. So these fatty acids can also be titrated we all so far we have seen that the neutralisation reaction can be utilised for the titration of volatile fatty acids and when this fatty acids are getting degraded we produce certain amount of this bicarbonate anion.

So when we have this particular thing that means when more amount of this volatile fatty acids are producing in the medium instead of this particular bicarbonate anion because this bicarbonate anion production is giving rise to a buffered medium, so that buffered medium can be consumed if we consume more and more of this carbonate buffered medium by the elimination of this volatile amino acids so during this process of degradation what we can do that if there is a huge draw in a pH values you to the production of large amount of this volatile fatty acids the system will collapse.

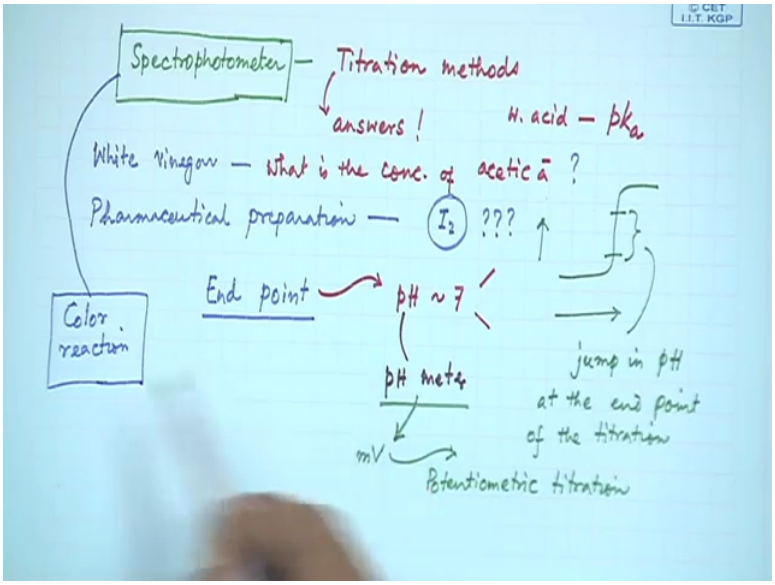
So this particular that means the volatile fatty acids formation of this volatile large amount of this volatile fatty acids formation will grow for drop in pH values and as a result this particular reaction in the reactor will fail. The system will therefore fail so what to do? Only we can go for detection of this particular pH, so this particular only pH determination that means if just simply look the only pH determination of this medium will not help us that there is certain the degradation due to the corresponding change in the pH of the medium or certain amount of this volatile fatty acids is forming over there so only pH determination will not help us a lot, instead what we can do we can determining in this particular case that is why it is a very useful use of the typical titration reaction that we can go for the determination of both this particular volatile fatty acids.

So determination of both volatile fatty acids and bicarbonate is needed so that is why this particular one is only pH metric will not help us so we have to go for the corresponding determination of this volatile fatty acids. What we see that this particular treatment there is a last stage is sewage treatment, so at one end we should go for the corresponding, we should have certain procedure when we can go for this particular volatile fatty acids determination as well as bicarbonate determination and as we have seen that these 2 things we can very easily handle so this volatile fatty acids suppose it is from C2 to C6 fatty acids so fatty acid is

containing 2 carbon to 6 carbon centers so this as well as the bicarbonate so we can have we can have this as HCO3 minus or H2CO3 or CO3 2 minus.

So total quantity of this carbonate species the bicarbonate species and the fatty acids we can determining buy this titrimetric method so sometimes this simple pH determination will not help us much we should have certain amount of other things to do so that we can have a very good idea about the quantity of those individual species which are forming in this particular medium.

(Refer Slide Time: 30:06)



So when we use this particular methodology we can use the spectrophotometers and in this particular case when we go all the spectrophotometers will be seeking answers for different titration results or the different titration methods. So if we can have some titration and that titration we can do by spectrophotometer, what we can get that we can get some answers we must have some answers for some questions. So what are those questions? That means a particular thing what we can answer is that if we have some weak acid and that weak acid how we can level that particular week acid for a particular PK value, that answer how we can give that means weak acid is your acetic acid.

However titration can give you a result for the corresponding strength of the weak acid or the PK value of that particular weak acid using the Henderson Hasselbalch equation that at which particular pH range it can remain as in the acidic from or in the basic form and how these 2 forms that means there are 2 corresponding equilibrium concentration of the free acid as well

as its corresponding anion can control the corresponding overall pH value of the medium that we will see.

So if for real life example if we can have like that of our white vinegar we know that white vinegar if we can have and the question in our hand is that what is the corresponding concentration what is the concentration of acetic acid in that particular vinegar solution. So that we can use so if we have a commercially available white vinegar in hand we can determine the corresponding concentration of this particular sample then we can have some pharmaceuticals so pharmacists or the pharmaceutical industry will also be interested to know for any pharmaceutical preparation.

To check its purity and during the preparation ultimately the yield of that particular preparation that example we have seen just now regarding the preparation of aspirin from salicylic acid. Suppose if you can have certain other pharmaceutical preparation where some iodine is present, so not that the simple acids like salicylic acid so we have 2 use this particular ingredient in the pharmaceutical preparation by some titrimetric method.

So what we see from the titration plot or the titration curve that we must have some endpoint and that endpoint we have to detect because at the neutralisation point what we see if we have a strong acid strong base tradition the pH, the final pH at the neutralisation point will be close to 7 as we all know because whatever salt is forming so that salt will not interfere the corresponding pH value for our titration like hydrochloric acid CHL with that of our sodium hydroxide, so these we all know that out the pH is changing but when we are handling 2 colorless solution your acid is colorless your base is also colorless so handling these 2 solutions how we can detect that particular change.

So when we say that there is a change, the sharp change like this so as we change as we go from this is the volume axis and this is the TH axis so when there is a sharp change and we just only focus our attention over here. So at this particular range how we can detect this particular change, the simplest possible answer is that (())(35:14) if we can have a corresponding instrument which can detect the change in the pH during the volume of addition of some responding titrant because this is your titrant this is your analyed volume. So pH can be monitored very nicely with the use of a pH meter.

We all know that the hydrogen and concentration in presence of the hydrogen gas and all these things is the electrochemical thing can happen and we can have a glass sorry the glass

electrode type of thing and that glass electrode type of thing and determine the corresponding pH of that particular medium. So this particular pH meter can measure the corresponding jump in the pH at the endpoint so this particular pH this jump so this is nothing but your jump in pH, so we have to detect that particular jump in the pH value at the endpoint of the titration.

So how another alternative method we can use without using a pH meter because this pH meter can be switched for the corresponding millivolt also that give rise to our potentiometric titration which is nothing but potentiometric titration, so a very small instrument like that of our pH meter we have to handle to monitor this pH for a simple acid-based titration but what indirectly we can do how to detect this particular change whether we can go for this and our basic choices is for utilisation of the spectrophotometer.

So once we are talking about the spectrophotometer we should be thinking something for any reaction or any change in the corresponding color so who will be looking for some color reaction and whether this particular color reaction can be helpful to detect the endpoint of any titration reaction that color can be measured by a typical spectrophotometer so that we will see in our next class, okay. Thank you very much.