Atomic and Molecular Absorption Spectrometry for Pollution Monitoring

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Lecture – 18
Quantitative analysis – II

Continuing in our quest for how to use a spectrophotometer effectively, we can extend the similar concept of inorganic chemistry where you use to do that titration. Now, can we do a photometric titration to the same accuracy with respect to volumetric analysis? In general, I think many of you are familiar with the acid based titrations and then complex of metric titrations and then there will there are aide metric titrations like that different kinds of titrations are there prepetition titrations and all those things. And many of them you must have studied and practiced also in your practical classes during your college days.

Now, is there something like a photometric titrations also, the answer is yes, we can do photometric titrations using a spectrophotometer. What we can do normally is if we assume that there is a substance A and it reacts with a colour the reagent are the complexes will keep on forming. So, once the complex is formed their colour will not change. So, at the end of the titration, the absorbance will come to a standstill, so that should be the end of titration.

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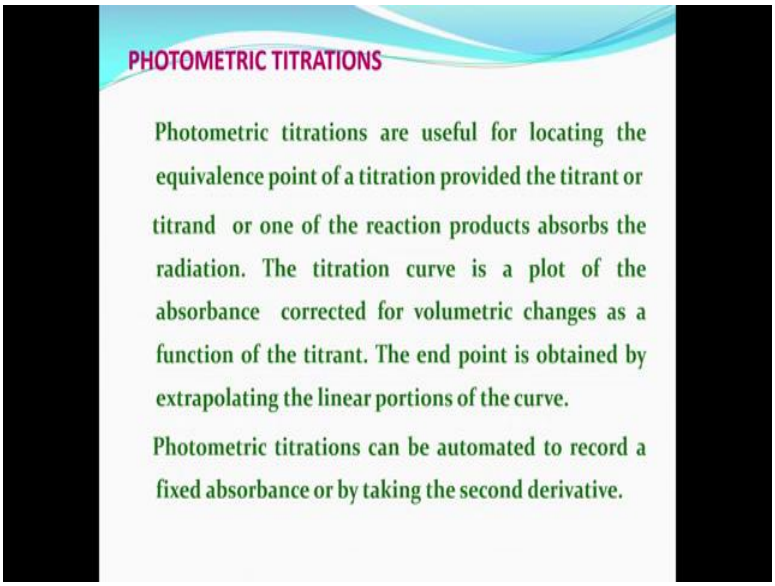

So, basically photometric titrations are useful for locating the equivalence point of a titration provided the titrant or titrand or one of the reaction products absorbs the radiation. This is very important know. In most of these spectrophotometric titrations, either should be colour formation or there should be colour disappearance, if any one of these are not there is not there then there is no case for a photometric titration. Basically, what a titration curve describes, it describes the plot of absorbance corrected for volumetric changes because we are going to add some reagent. So, it is going to increase the volume of the titrant and which should be plot a absorbance should be plotted a versus the total amount of reagent that is concentration of the reagent. The end point normally is obtained by extrapolating the linear portions of the curve, because obviously, it is not possible for rest to a end exactly at a particular point.

So, what we do is we normally extend the linear portions of the curve and the intersection we take it as the end point of a reaction. So, what is so great about this, the answer is the photometric titrations are normally done at ppm levels - parts per million, milligram per litter level. Whereas, now normal titrations what you are familiar with are done in milligram quantities that is one thousand times higher concentrations than spectrophotometric titrations that is the biggest advantage. Then there are other advantages also which we will see later. And sometimes photometric titrations can be automated we can have a readymade recorder. So, even if you shoot the end point, still you should be able to pin point the end point later that is another advantage. Third is you

can record the first derivative, second derivative absorbance also, so that is also very important with respect to the analysis of amino acids.

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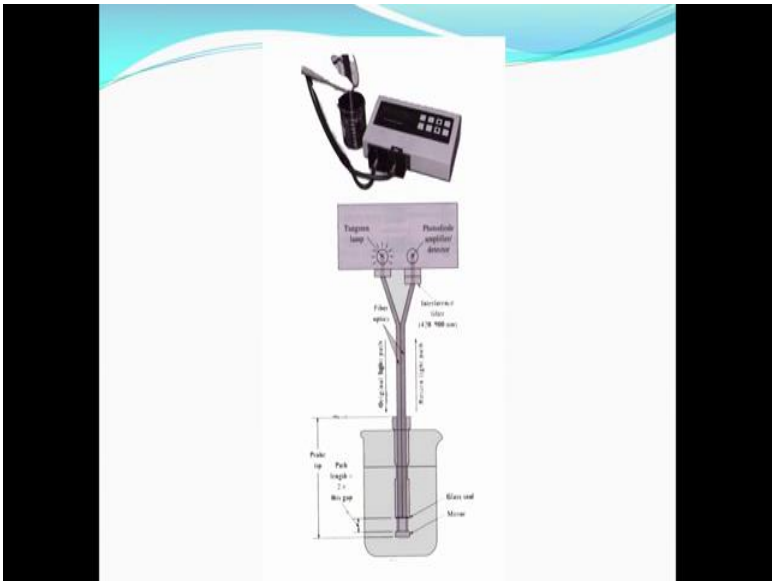

So, look at it. Now, what how does it look a photometric titration operators. This is the picture of photometric titration operators; on the top, I have shown a spectrophotometer and attachment, tungsten lamp here, and a tungsten lamp here, and a photodiode detector here. What happens form the tungsten lamp, the radiation falls through, and then the reaction is taking place, here the path length, and then the absorbed radiation, the height of the sample is the height of the beaker.

So, the radiation will pass through like this reach the mirror or something like that and then again travel through the same distance; that means, path length will be doubled, and then it will reach the detector. So, for a given absorbance for a given solution the path length is always double in this design. It is need not be necessarily in all designs we have some moment of filter and other things also here; if necessary we use them otherwise for a given wave length which should photometric titration should be possible very comfortably one can do the titrations.

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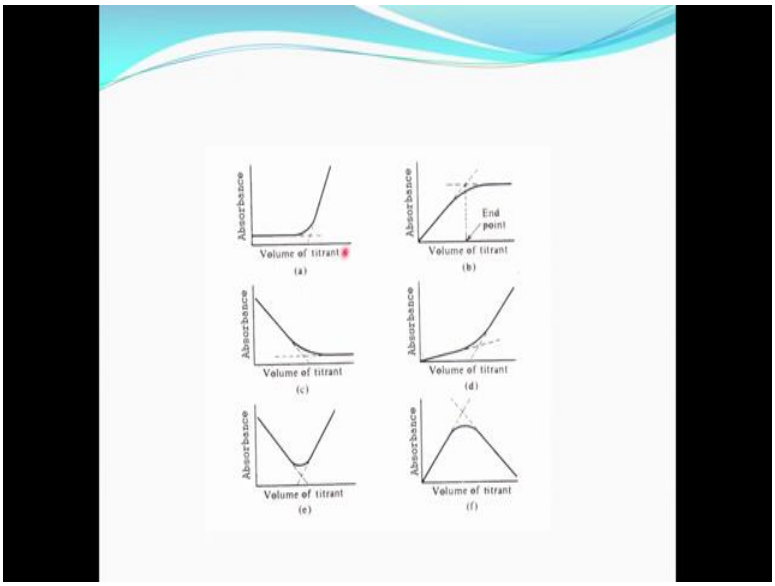

So, here are some of the titration curve typical titration curves, there we plot absorbance versus volume of the reagent titrant. So, in this case, in the first case, where I am pointing the pointer, we can deduce that the absorbance is constant here that means there is no reaction. After sometime when the all the reactant is consumed, there is going to be some sort of a colour complex formation and the colour complex formation keeps on increasing and the titration end point of this would be this obtained by extrapolating the straight line portions of this very simple this thing. So, in this case, we can conclude that the reaction product is coloured and the reactant is not coloured. So, absorbance will remains almost constant. So, until the minimum complication point is reached there will not be much change in the absorbance sometimes what happens is there is certain amount of colour keeps on forming.

So, this is b is another type of reagent, where absorbance keeps on forming. And once all these reagent is all the titrant is used up, the addition of the kilting agent or colouring agent, we will not increase because there is no more metal ion to be reacted. In that case, what happens the absorbance of the substance complex in the titrant will remain constant? So, part b is where the complex keeps on forming, but once one of the components is used up, the absorbance will be become constant. So, the interaction inter section of these two this portion, this portion as well as this portion, this is the inter section point that is where to conclude that these equivalence point has occurred. Once

you get the equivalence point it is very simple n 1 v 1 is equal to n 2 v 2 that kind of reaction you can calculation, you can always go ahead.

Now, look at volume look at the third picture c. Now, here what is happening the absorbance is very high in the beginning itself that means, the titrant is a coloured substance. I keep on adding reagent and the coloured substance keeps on losing the colour decomposes, and then once all the material is used, up the reagent colour, which is colourless will maintain the absorbance constant. So, for highly coloured substance, this is the kind of photometric titration curve, you will be expecting in this case.

Now, look at d here there is certain amount of colour formation, and also there is additional colour because if it was only one type of complex, it would have reached like b, it would have got a curve. Now, here what is happening is I have first equivalence point after that there is one more equivalence point it is forming another complex say m x two if this is m x 1 this could be m x 2 or something like that which is also having same absorbance lambda max. And then it keeps on increasing until you get a end up with a curve like this b. So, I have not drawn this third part. So, you can see that in this case there is a formation of second complex also with the same reagent.

But here you can imagine that the absorbance remains the same that means both complexes are of the same colour. If both complexes are of the same colour, you will end up with a curve something like this. Now, imagine I have two complexes, one is coloured complex, but after reacting with reagent, it is forming one more complex whose lambda by x is different. So, the absorbance keeps on coming down at some point it reaches minimum, and then you will see the formation of some other colour. And if the lambda max of this part of the complex is very near to this, you need not change the wave length.

So, the same wave length will keep on giving you increased absorbance. So, if you get a curve something like this, I would simply conclude that there is complex in formation here the complex is getting used up the metal ion is used get up, but at the same time another complex is formed which is almost of the same colour. Because I am not changing the wavelength and then that complex colour also keeps on increasing. So, this is a very typical reactions of several metal ions which are coloured. For example, if you do any titration with respect to using chromium or manganese, the colour will keep on

coming down and the complex colour will keep on increasing. So, suppose this is orange then is red, you can use the same wavelength to continue that titration, and once you continue finish the titration you will be able to determine the equivalence point in this case.

Now, here what is happening there is increase in the complex, complex is being formed, absorbance is increasing, and then the absorbance is decreasing and then again it is reaching zero. So, there are two complexes are being formed, one is an coloured complex, and another is a non-coloured complex, very simple interpretations. And you may you have to remember that most of these reactions must follow photometric rules where the absorbance can vary only from 0 to 2. So, their solutions have to be extremely dilute and one has to be a little careful in interpreting the absorption, titration and titrant concentrations.

You have to take into account the dilution effect. If you do not take dilution into effect the analysis will definitely be wrong. And of course, it does not make sense if we do the analysis wrong without taking into to dilution even in normal titrations in our day-to-day experiments. What we do is we take the dilution very dilute solution and in the conical flask and concentrated solutions in the burette, so that the actual volume changes if not corrected should be at least negligible, so that is what makes the difference between normal titrations and such titrations.

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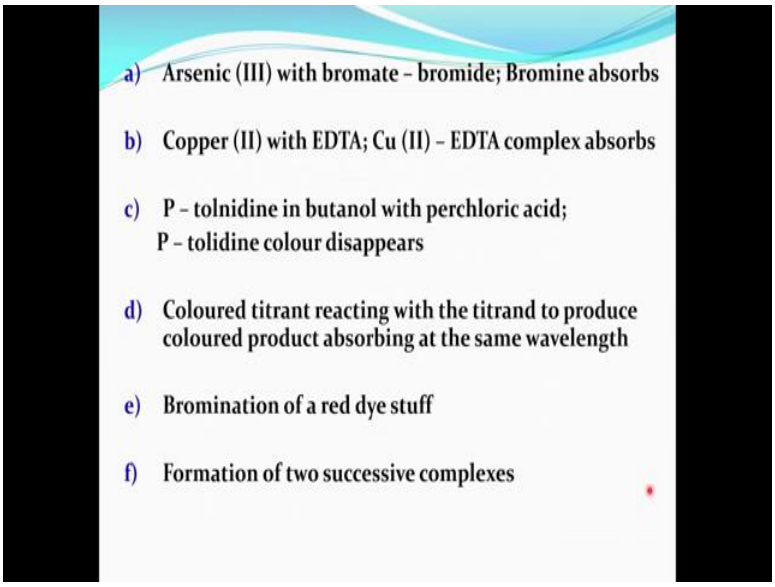

Now, this part a, this one is a, I am giving an example for this curve the example is arsenic three with bromated-bromide. Here what happens initially arsenic is colourless, it will react with bromate and bromide, mixture forming arsenic bromide and arsenic bromide is coloured. So, absorbance keeps on increasing. Now, second one copper with EDTA. So, copper forms two types of single complex with EDTA. Initially copper is colourless, I am saying colourless because it is not necessarily colourless need not be colourless, but the quantity of, but the concentration of copper is so low it will be in ppm level you will not able to see any absorbance here.

So, I am saying it is colourless, but copper EDTA complex is coloured. So, EDTA will keep on giving the increased absorbance until it reaches the equivalence point. After that any addition of EDTA which itself is colourless cannot increase the concentration of the colour or copper absorb cannot increase the absorbance. So, reagent is colourless, but reactant is colourless, but the complex is coloured. So, there will be an increasing curve attaining a constant value.

Now, the third one para tolnidine in butanol with perchloric acid; here para tolnidine is a very simple chemical which is available in almost all the chemical shops it is used for the determination of chloride in swimming pools very normal reagent. So, this is third one para toluidine is coloured and perchloric acid is colourless. So, the colour keeps on coming down and then once all the para toluidine is used up, the concentration of the colour of the reaction mixture remains constant or colourless, so very simple example of such a reaction. Now, look at the fourth one coloured titrant reacting with titrand to produce coloured product absorbing at the same wavelength.

Now, the next one is this one bromination. So, initially the bromine is coloured, the sample is not coloured sample is coloured bromination, it keeps on coming down once the bromination is there completed, the brominating reagent itself is coloured. So, absorbance will keep on increasing. So, this is another type which you have seen. And formation of two successive complexes - the last one, which is very easily understood one is coloured and another is not coloured. So, different types of titrations can be conducted using the photometric titrations.

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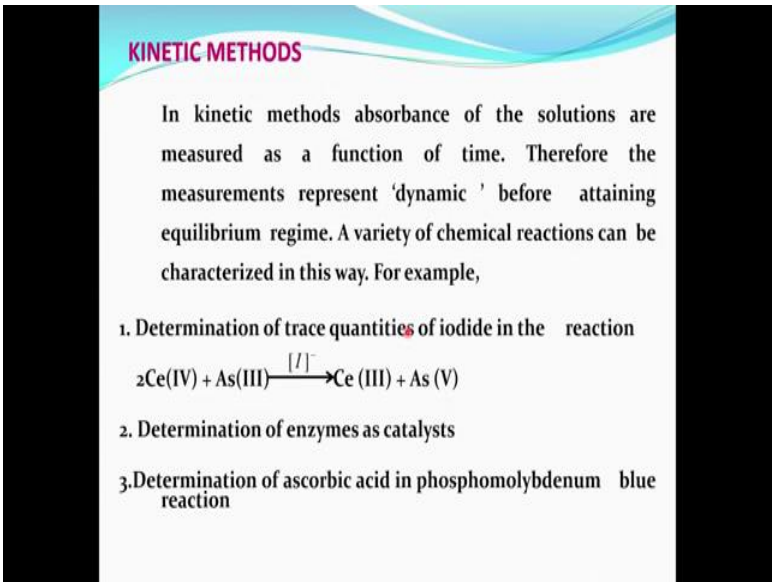

So, advantages of a spectrophotometer using a photometric titration involve the ppm level. Once again, I am retreating - ppm level analysis, no danger of over shooting because any way we are going to over shoot the end point, exact equivalence point cannot be reached manually you have to draw the curve and then extrapolate. And the reactions will be extremely accurate to the point of about 10 rasie to minus 3 or minus 4 molar concentrations. Very few titrimetric titrations titrimetric methods are available for titrimetric determination of compounds and organic things, organic compounds at 10 rasie to minus 3, 10 raise to minus 4 molar concentrations.

Then another aspect we are going to discuss now that is the kinetic methods. In kinetic methods, what is important, the reaction should continue and you would like to know the rate of a chemical reaction. So, the rate of a chemical reaction can be followed, if one of the substances is coloured. So, all you have to do is make the reaction, take out a sample from time to time, and determine the concentration, how much is consumed or how much is produced like that as a function of time. So, then you can plot the chemical rate equation and other things. So, the actual measurements suppose you have a spectrophotometer, and put your reaction mixture in a cell, and just relax, ask the computer to measure absorbance, every five minutes or every one minute. So, it will keep on giving you a number of absorbance readings versus time and that is it basically.

So, we get a dynamic chemical method before attaining equilibrium time. Once equilibrium is attained, there will not be any change in the concentration and which intern means there is no change in the absorbance either. So, a variety of chemical reactions can be characterized by spectrophotometry. In fact, spectrophotometry has become one of the most important techniques to determine the kinetics of a chemical reaction, and there are several examples where you can follow such reactions spectrophotometrically.

Now, here we can see the determination of trace quantities of iodide in this reaction. For example, 2 cerium and cerium will react with arsenic, this is an catalytic reaction. Cerium will get reduce to cerium 3, arsenic will get oxide to arsenic 5, this reaction proceeds in presents of iodide ion. Now, the cerium is slightly yellow coloured, arsenic is not coloured, but iodide cerium 3 is not coloured I think, cerium 4 is coloured cerium three is not coloured, and iodide ion is not coloured. So, by following the change in the spectra photo absorbance of cerium 3, you can determine the kinetics of the chemical reaction.

Similarly, there are other examples several enzymes as catalysts catalysts. So, such reactions can be followed by photometric titrations. Then there are determinations of ascorbic acid in phosphomolybdenum, blue method reaction, all these things are quite simple basically, but you should know the chemistry of the thing I will not able to teach you all the chemistry that is required in this course. But in general, what is expected of you is to know the chemistry then what you are learning here is the instrumentation and applications potential of the applications etcetera and that is what I am trying to highlight here.

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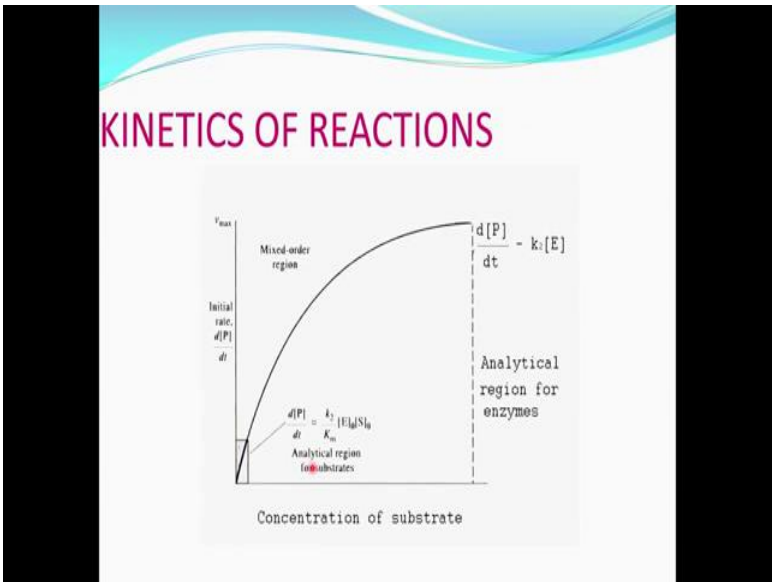

Now, this is how you are chemical reaction will look like the if you plot initial rate change of the d P by dt concentration change, and then this is the concentration of the substance, you will end up with the curve like this. So, d P by dt minus k 2 E. So, there is one k 2 by K m general reaction I have written a general reaction here and this is a mixed order it is not a single order, it is not first order or second order, but in mixed order reaction. So, very simple examples for enzymes, this kind of curves are available in the data section of several data bases and you can look up the methods for such reactions.

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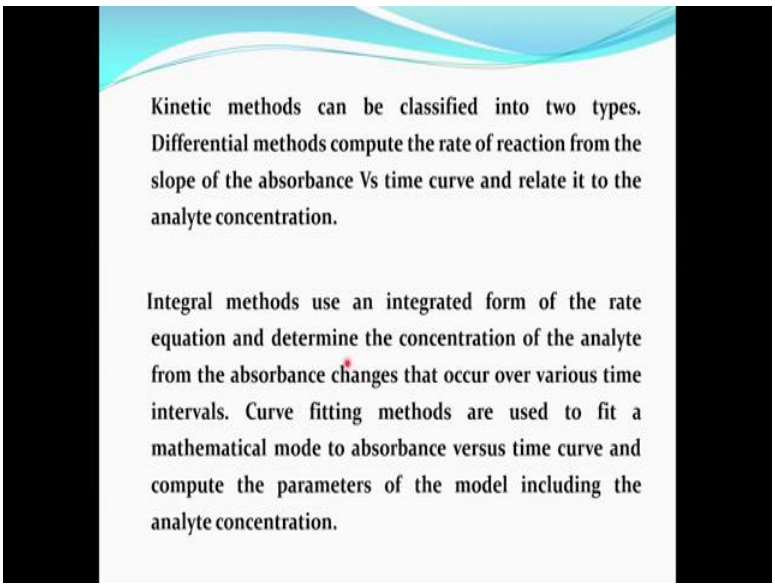

So, kinetic methods can be basically classified into two types. One is the differential method that computes the rate of chemical reaction from the slop of the absorbance versus time. And relate it to the analyte concentration that is one thing. Integration methods are also there; in integration method, what we use is the integrated form of the rate equation and determines the concentration of the analyte from the absorbance changes that occur over various time intervals.

Of course, we need to use curve fitting methods to fit a mathematical model for first order reaction, second order reaction, third order reaction or fraction order reaction all these things are quite possible. But what is important is we are measuring the absorbance versus time curve and other parameters can be computed from the model including the analyte concentration that is what important in chemical kinetic methods.

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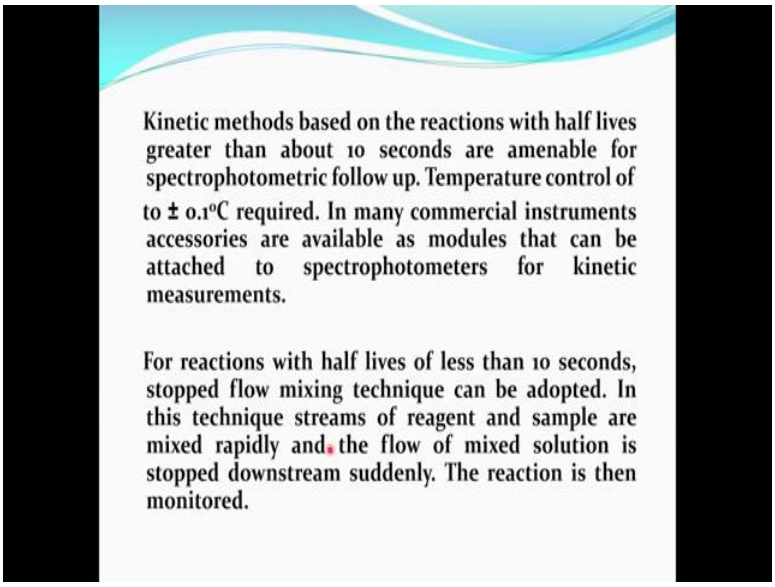

So, kinetic methods based on the reactions with half-lives greater than about ten seconds such reactions are classified as fast reactions; so there also there also amenable for spectrophotometric follow up. So, temperature control is very important in such cases because we know that any chemical reaction is temperature dependent. So, it is very, very important for us to maintain the reaction mixture temperatures up to plus or minus 0.1 degree centigrade. So, you have to have a jacket, jacket at reactor in which the samples are put, and there should not be any heat changes in the reactor. So, the whole thing must be jacketed with cold water circulating, many reactions are exothermic and

some reactions are endothermic. So, all such fast reactions exothermic and endothermic reactions must be very carefully selected and studied using temperature control.

Then several commercial instruments are nowadays available. As you know the one can they are dedicated kinetic measurement instruments. So, there are they will give you an optional switch in the machine weather you want to make absorbance measurements transmittance measurements and then concentration or kinetic methods. So, there are automatically program we take over the kinetic methods then it will ask to you up to at that time you able to you should measure the absorbance. So, you have to feed in all that data whenever you want to use a kinetic method develop a kinetic method and try to determine; what is the order of the reaction.

So, for reactions with half-lives of less than 10 seconds, again what we can do is we take the reaction mixture and cool it immediately there is stop flow reaction means you can bring it to immediately room temperature or cool it immediately or you can mix these stop the flow. And stop flow mixing technique is very effective especially in with half-lives of the reaction, if it is less than 10 seconds. So, this technique in this technique what happens is reagent and sample are mixed rapidly, and the flow of the mixed solution is stopped downstream suddenly. So, the reaction is then monitored.

So, you remember all these things are meant for the fast reactions kinetics. And if it is very slow reaction, there is no problem at all we can determine the every 5 minutes, 10 minutes if you want to measure the absorbance and determine the concentration there is absolutely nothing that can stop you from doing so for thousands of thousands chemical reactions.

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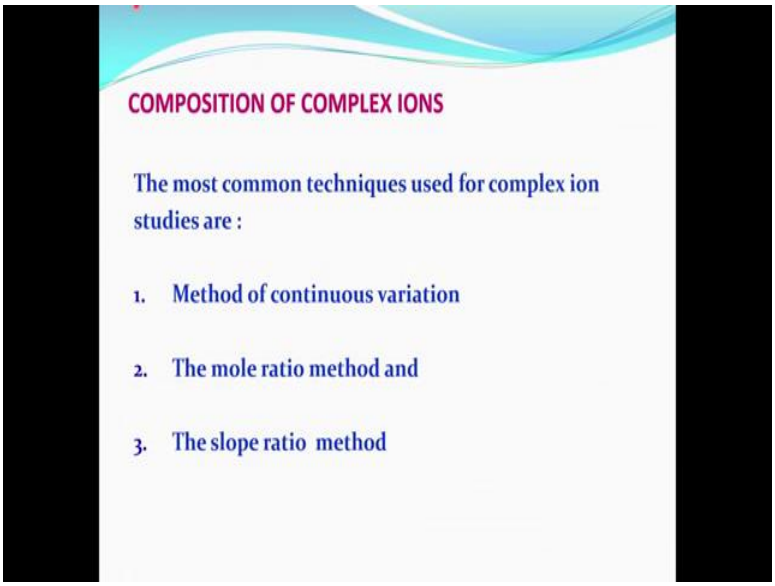

So, another aspect that is composition of a complex, quite often we want to determine, we want to know how what is the composition of a chemical substance. In chemistry subject, we define elements, and then compounds and then mixtures like that. Similarly, any chemical reaction that under goes a transformation using a complex reagent is known as we know it is known as complex reaction. So, basically complex reactions are carried out using high molecular with reagents and these include ethylene, diamante acid and nitro triassic acid and several organic reagents, and several other there is a vast literature of coordinate chemistry, where complex reactions are carried out. And one of the aims of a complex reaction important aspect of a complex reaction is to find out what is the combining ratio of the complex reagent and the element.

Now, this complexing reagent can always be determined by titration and other the classic techniques are there, you can do the titrations you can do the diametric analysis and all that, but spectrophotometrically again it is a very beautiful technique to determine the combining ratio of the reagent and the metal ion. And there are approximately three to four several methods or, but three are most popular and these include the method of continues variation, and another is mole ratio method and the slop ratio method. Technically, they look very intricate, but in actual practice, most of these things are quite simple. For example, we can take a look at one of the methods of method continues variation, it is not something new because we have already seen the curve of the type in the photometric titrations.

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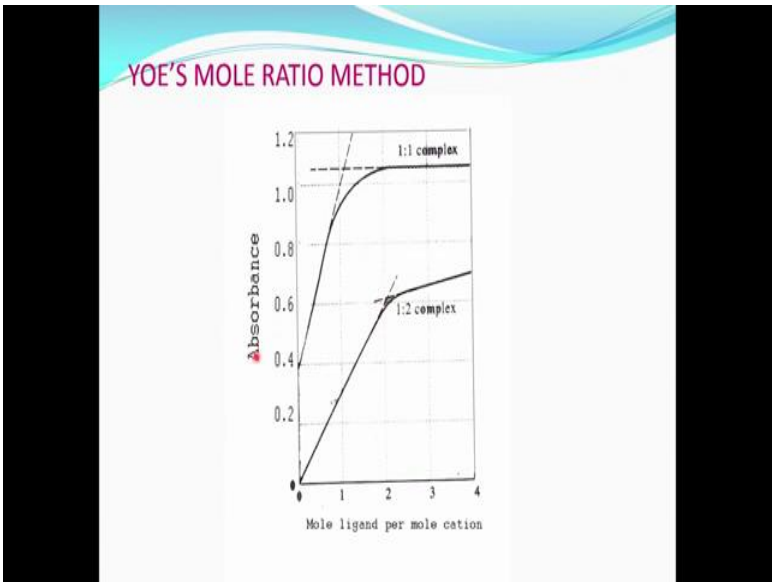

So, method of continuous variation is very simple. This is the mole ratio method, and continuous variation method is essentially the same. This is Yoe's mole ratio method, but method of continuous variation, I have not shown you in this figure, but maybe I will give you an assignment regarding continues mole ratio. Basically it is nothing much, you take three two reagents of the same molarity, one is your reactant and the complexing agent, and you keep on mixing until the composition absorbance of the complex reaches constant, it will be something like this, this curve b.

So, if the molarities of the reagent and the complex are same you will end up with curve something like this and where the implication point occurs it is that you can determine the volume, and this volume is known reactant volume is known. So, if the molarities are same, you can determine whether it is one to one, or one is to two complex excreta. And then we will look at the other two methods that is composition of a complex that is Yoe's mole ratio method.

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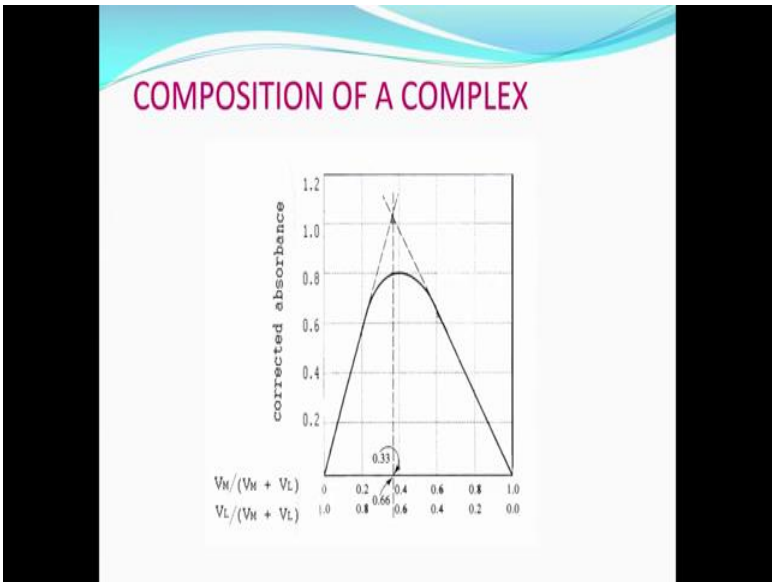

The jobs this is the jobs method. So, this will continue our studies in the next class.

Thank you very much. Have a nice day.