Environmental Chemistry and Microbiology
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Module - 3
Lecture - 15
Chemical Kinetics - V

Welcome everyone to our online NPTEL course of Environmental Chemistry and Microbiology. This course will be taught by Professor Sudha Goel and myself, Professor Anjali Pal. We are both from the Department of Civil Engineering, IIT, Kharagpur. We have divided this course into 2 parts. The first part Environmental Chemistry will be covered by me, and the second part, Environmental Microbiology will be taught by Professor Sudha Goel. This is my module 3.

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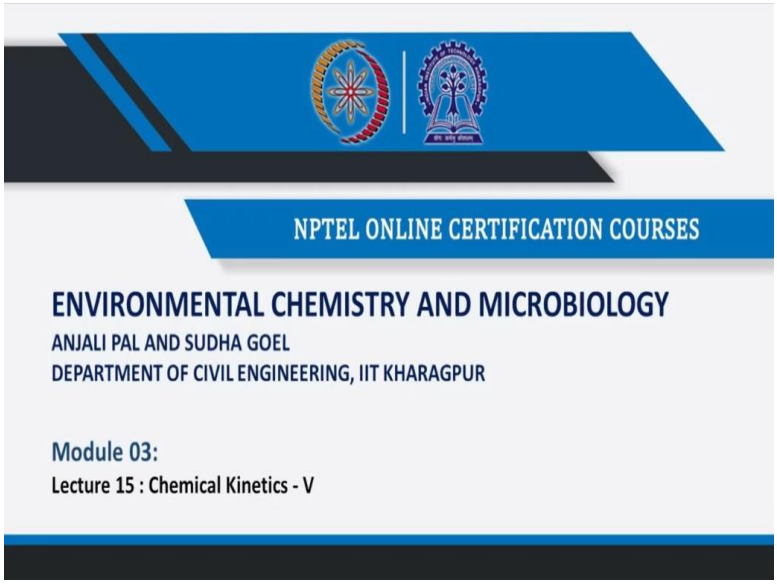

I am discussing the chemical kinetics. This is the fifteenth lecture.

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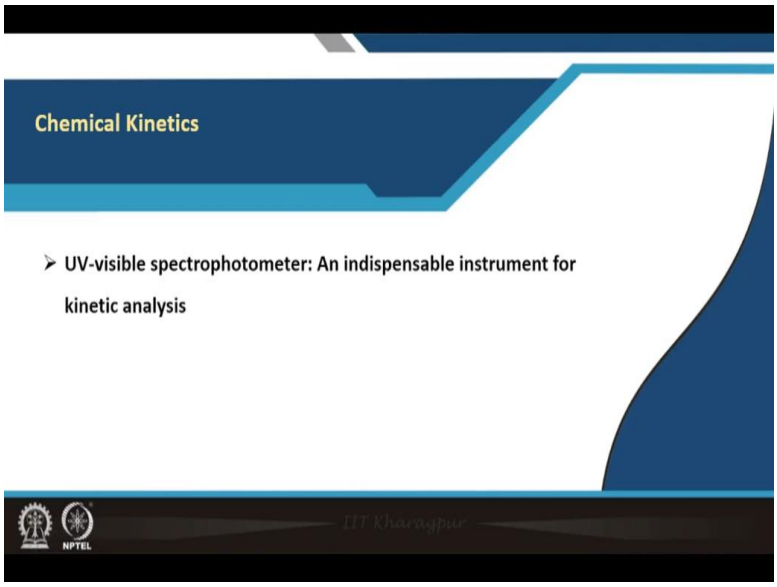

I will show a real demonstration or real application of some method by which you can determine the order of a reaction. In the earlier slides, I have shown you what is the order of a reaction; and how to determine the rate; and what are the different methods that we can apply, like differential rate law, differential, integrated rate law to determine the order of the reaction. Here I will show you how we can determine the order, okay. UV-visible spectrophotometer is a very common and a cheap instrument which is present in every M.Sc or M.tech labs. It is very much useful as I have told you (maybe in eleventh or twelfth lecture) that absorbance values we can use to determine the progress of the reaction, to monitor the reaction. So, here I will explain those things in a simple way, so that you understand.

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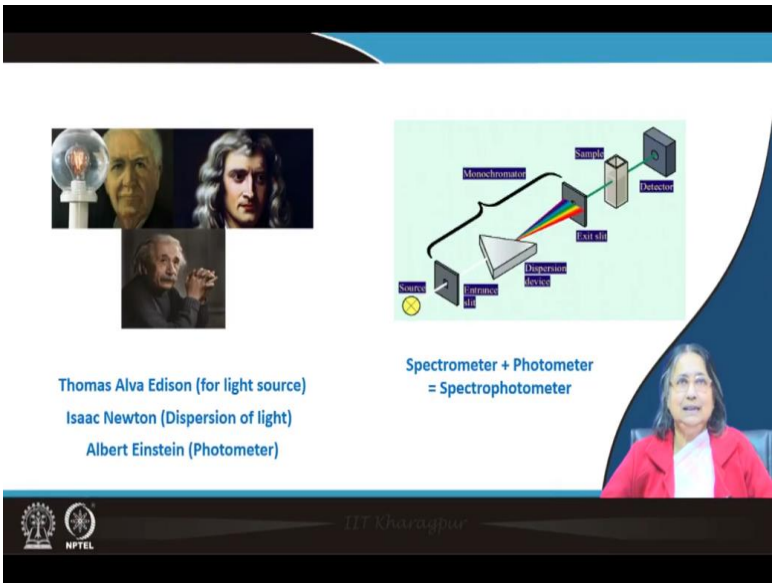

Now, what is the spectrophotometer? Here (in the last slide) you can see that see famous scientists. The first one is Thomas Alva Edison. He invented the electric bulb. Then you can see Sir Isaac Newton, who has discovered the dispersion of light. You know that, when white light is passing through a prism you can see the dispersion. Then, you can see 7 different lights. Next you will find the image of Einstein. You know that Albert Einstein got the Nobel Prize for photoelectric effect. He is most famous for his discovery is $E = mc^2$. But he got the Nobel Prize on that photoelectric effect. So, basically, all 3 scientists' contribution are here in spectrophotometer. What is a spectrophotometer? It is basically spectrometer + photometer. So, for spectrometer, you know that first thing is the light. Light is like leg. A man cannot walk without a leg. Bulb is the source of light. Here actually, for the visible light, tungsten valve is used. On the other hand, for the UV source, hydrogen discharge lamp or deuterium lamp is used. Now, second part is the diffraction grating. That means, the light is dispersed in different wavelengths. So, previously prism was used, but now diffraction grating is used. Now, you see (in the previous slide) different lights are coming. Then it passes through some solution where the light is absorbed and then the photometer is coming. So, photometer is coming to monitor the light like a brain with eye. So, there are 3 parts. One is the leg, i.e., the lamp part, and then the heart, i.e., the spectrometer part, and then photometer part, i.e., the brain with the eye. So, this is the simple way by which I can tell the what is the spectrophotometer.

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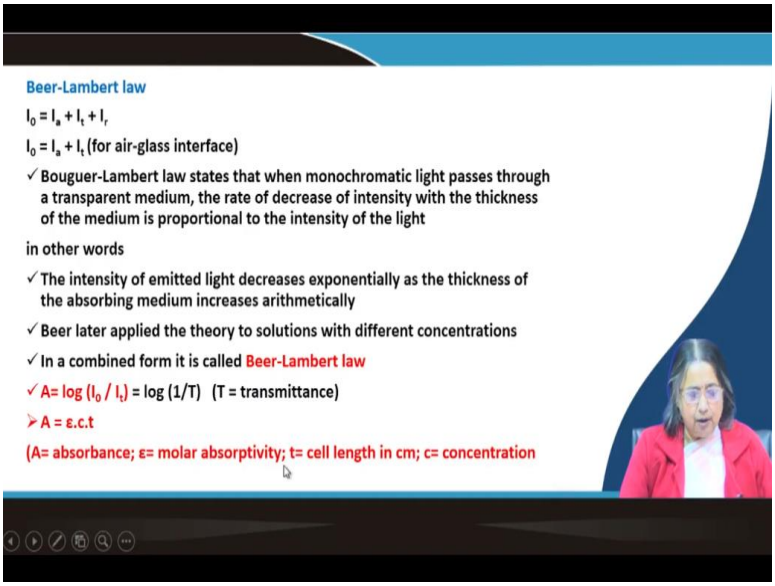

Now, the principle of measurement in a spectrophotometer is governed by Lambert-Beer law. When a light passes through a medium, you know, then 3 things can happen. So, first thing, the absorption can happen. Then, transmission of light and reflection can happen. But if you

think about a very good air-glass interface, then you can neglect reflection (because it is below 5 percent) And then, it is basically the I_0 is a combination of $I_{absorption}$ and $I_{transmission}$. So, what Lambert said (this is actually Lambert-Bouguer law. But it is more famous as Lambert law) that, when monochromatic light passes through a transparent medium the rate of decrease of intensity with the thickness of the medium is proportional to the intensity of light. So, according to Lambert law, it can be said in other words that absorbance (A) which is nothing but log (I_0/I_t), is proportional to t (thickness). Another scientist Beer extended this. Beer later applied the theory to solutions with different concentrations. So, by combination, it is called Beer-Lambert law.

Absorbance (A) is log(I_0/I_t). A is $\varepsilon \times c \times t$. From the Beer-Lambert's law.

$A=\varepsilon \times c \times t$

So, what is c, what is t, and what is epsilon? t is the thickness, c is the concentration and then, epsilon is a constant. It is called molar absorptivity or absorptivity, depending on the how you express the concentration. Previously, the name was extinction coefficient. Now, it is called absorptivity. Now, in the spectrophotometer, we apply this principle. In most of the spectrophotometers, this t is 1. This is the cell length (path length). Path length is thickness of the cell that we use. Now, because it is a linear equation, so absorbance value can be related to concentration, because t is constant. It is a straight-line equation passing through the origin. So, this is called the Beer's law calibration.

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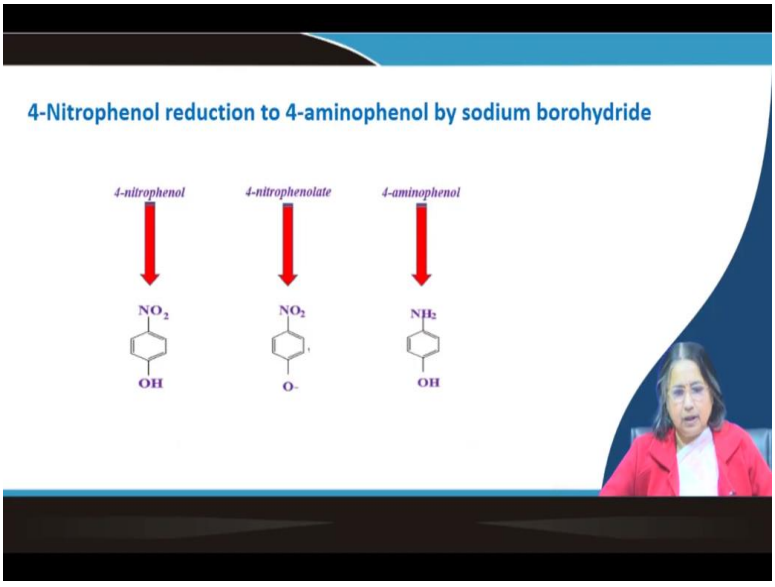

Now, let us take some specific examples. In the last slide a very important reaction (reduction of 4-nitrophenol to 4-aminophenol in sodium borohydride medium) has been shown and it has now become a benchmark reaction. Those who are from organic chemistry background,

they all know that the compound shown at the left side of the last slide is nothing but nitrophenol. With a benzene ring, if there is an OH group, we call it phenol. And in the phenol moiety, there is another NO_2 group attached in the benzene ring. That is why it is called nitrophenol. Now, instead of nitro group, if there is amino group, then it is called aminophenol. The compound shown at the right side of the last slide is aminophenol. You know that phenolic (OH) group is acidic. So, hydrogen can be taken out by alkali. when it is taken out by some alkali, it becomes O^-. Then, instead of phenol, we call it phenolate (O^-). So, it is nitrophenolate. And why the 4 is coming? Because, with respect to phenol group, it is the fourth position. That is why, 4.

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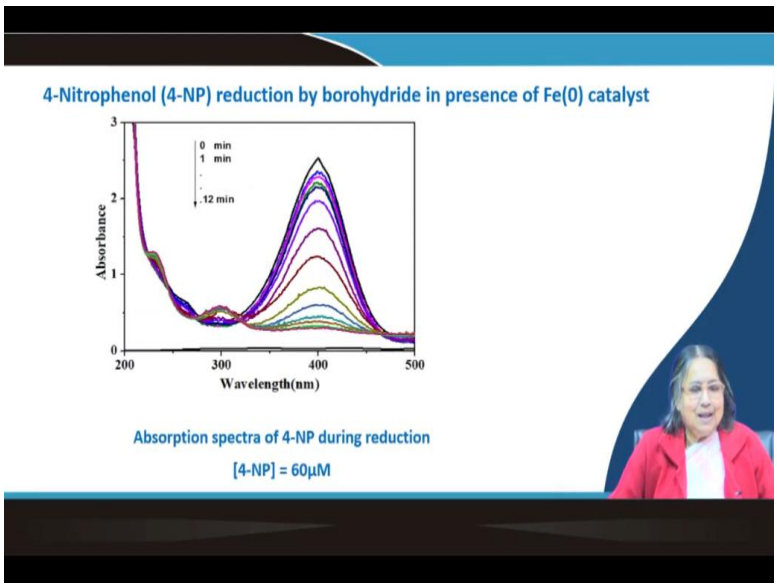

Please refer to the slide no. 3 of this lecture. I showed you the schematic drawing for spectrophotometer. The light is passing through the prism. It is dispersion. Then, it is passing through the medium (i.e., some solution is kept in the cell). How much absorption occurred? Which light is absorbed? All are measured. After that the curve shown in the last slide is obtained. This is called absorption spectrum. Spectrum is singular. If there are many then it is called spectra. What we are doing actually? We are reducing the nitrophenol to aminophenol. Nitro group is coming to amino group. This can be done by hydrogen gas (zinc and HCl produces hydrogen gas). Or we can do it by a strong reducing agent borohydride. Although this reaction is thermodynamically feasible, but it is kinetically very slow. Whether some reaction will happen or not, that will be decided by thermodynamics. And how fast it will go, that will be decided by kinetics. If there is no catalyst, only sodium borohydride, then the reduction is very slow. It may take 24 hours, 48 hours, something like that. But if we put some catalyst, then it becomes faster. That is a separate chapter. I will discuss catalyst in next

module. Anyway, you should know it, otherwise you will not understand. So, this is basically, we are doing nitrophenol reduction to aminophenol, by using the zerovalent iron nanocatalyst. Now, this is the spectrum of nitrophenolate. Why nitrophenolate? It is so because, as soon as you put borohydride, the medium will become alkaline. So, nitrophenol will be automatically converted to phenolate. That is why, you are getting, absorption spectra of nitrophenolate. Now, you have started the reaction by using the catalyst in presence of borohydride which is a reducing agent. By using spectrophotometer, you can get the spectra shown in the last slide starting from 0min to 12min. You are putting absorbance against wavelength. The maximum absorption occurs at 400 nanometers. This is characteristic of the nitrophenolate. Now, you see here, nitrophenolate is reduced to aminophenolate. But absorption for aminophenolate occurs at 293nm. With this position (293nm), we are not very much interested. We are interested at 400 nm. How with time this peak is going down? That is important for our kinetic analysis. So, what we are doing? From the starting of the reaction, we are measuring the absorption spectra. We are getting different absorbance values at 400nm wavelength at different times. We had noted down.

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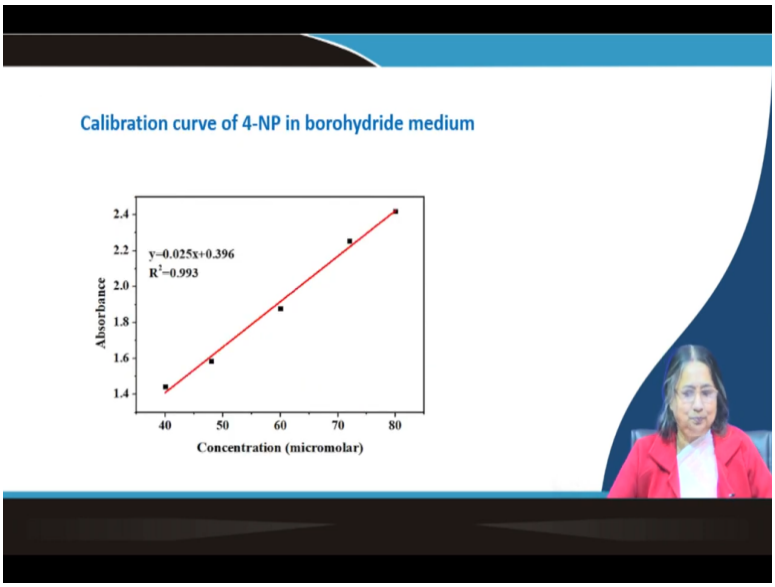

To know the concentration, I told you that we have to do some calibration curve. So, the calibration curve of 4 nitrophenol (actually 4 nitrophenolate in borohydride medium) has been obtained first (as shown in the last slide). We plotted absorbance vs concentration of nitrophenolate. This is a linear plot. This is the Beer's law curve. Now, once you get the Beer's law curve, then we can see here, how it is good from the R^2 value. It is very good (0.99). If we know the absorbance value, we can tell the concentration from this. If we know, the absorbance value we can easily find out the concentration. So, this is required to know the

concentration of the nitrophenolate at different time intervals. Similarly, we got some data at different times of 4 nitrophenolate after we started the reaction. So, it is under chemical kinetics.

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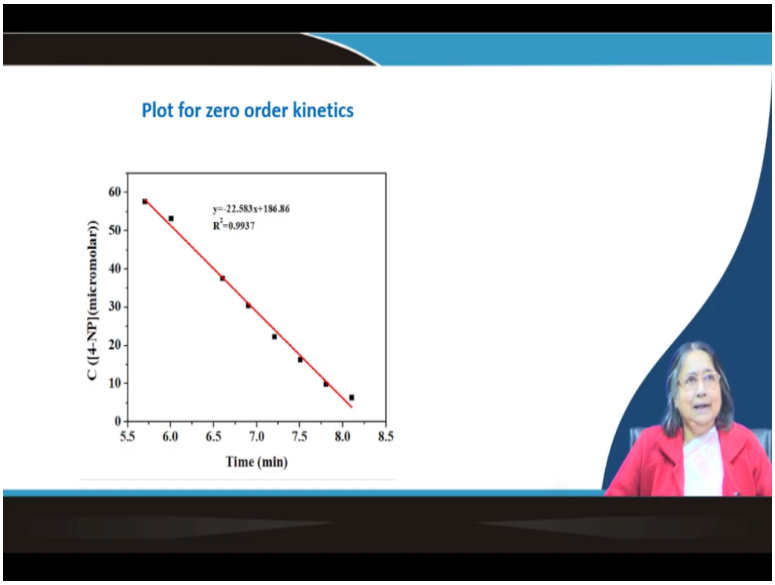

Now, after getting the data, we have made some table. We have converted absorbance values to concentration by using the calibration curve. Now, we are plotting concentration (C) values against different times. Now, I told you, that for zero order kinetics, you should get a straight line, when you plot concentration (C) versus time. So, you can see a very good straight line you get, with the R^2 value 0.99. Now, this is the zero-order curve. Let us see other curves (for first order, second order).

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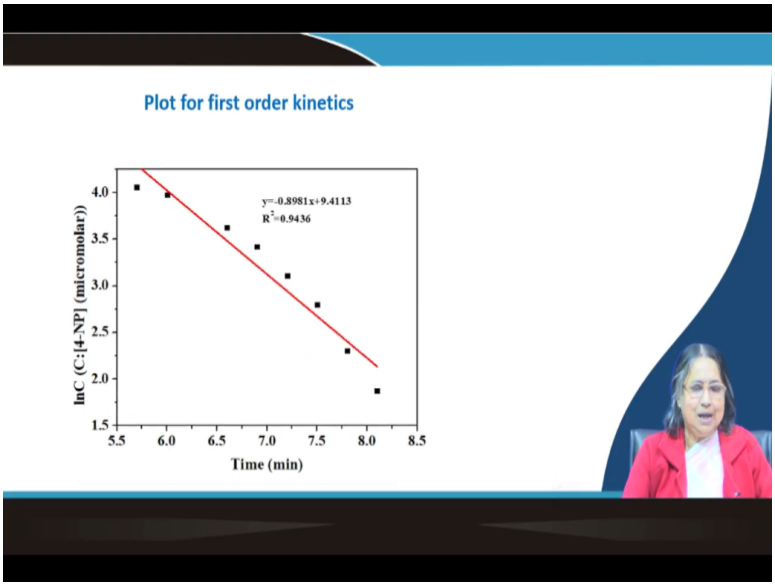

For first order curve, we know that you have to plot ln C versus time. So, for the same data set, we are plotting lnC versus time. So, you can see from the last slide, that it is not a linear curve (R^2=0.94). So, it is not linear. That means, our nitrophenolate reduction is not following first order reaction. Now, let us plot for second order.

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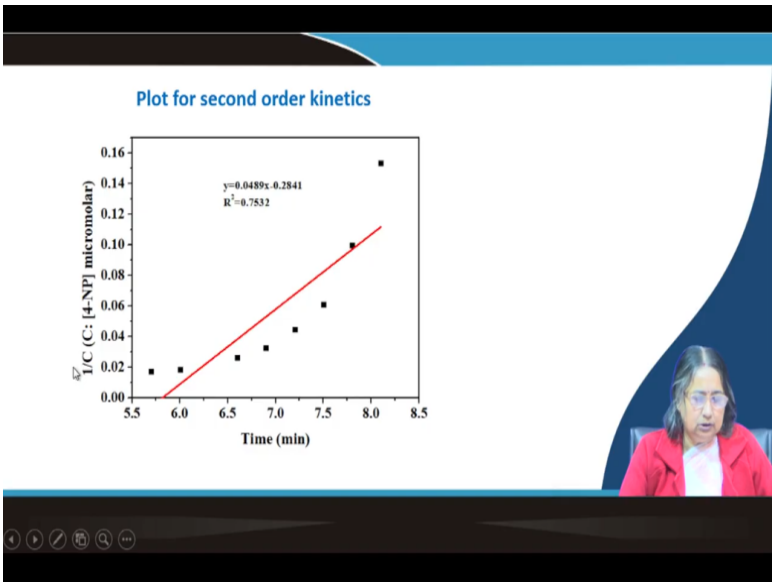

So, in the second order plot, you have to plot 1/C against time. Now, you see in the last slide that it is also not linear. So, second order is also not followed. So, among the 3 (zero order, first order and second order) we see that zero-order is following very good linearity. So, nitrophenolate reduction by borohydride is following zero order reaction. So, this way, you have to first do the experiment. Here, I have used absorbance values to monitor the reaction. But you can use other values like fluorescence you can use; you can use other properties also. You have to get that data first; then you have to need to plot it against time. From different plots you have to see which order it is following. This is the main theme for determining the order. You have seen that; I have used integrated rate law.

For zero order C versus t, should give linear plot. For first order, ln C versus t, should give linear plot and for second order, 1/C versus t, should give the linear plot. So, here we see that, zero order reaction is following. Many surface catalysed reactions give zero order kinetics.

Now, you can tell me, what is the need to know the order? It is because, order is a very important thing for a reaction. Rate is important.

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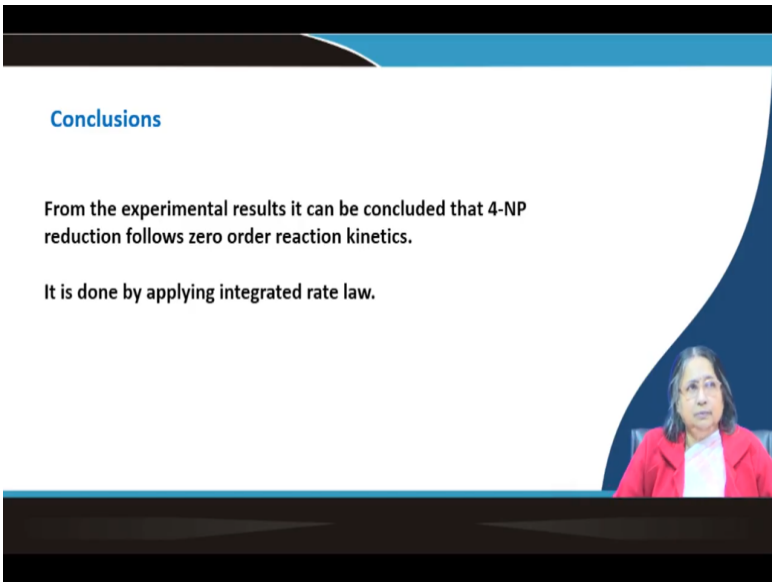

Now, from these lectures in Module 3, we have learnt that the 4 nitrophenol reduction follows the zero-order reaction kinetics and it is done by applying the integrated rate law. And from the lectures under module 3, you know what do you mean by rate of a reaction; order of a reaction; how to determine the order; how to determine the rate; and what are the different methods to do it, what is zero order reaction; what is first order; what is second order; what is pseudo-first order reaction; how does the rate or rate constant depends on the temperature. Finally, I explained how by simple method you can tell the order of a reaction.;

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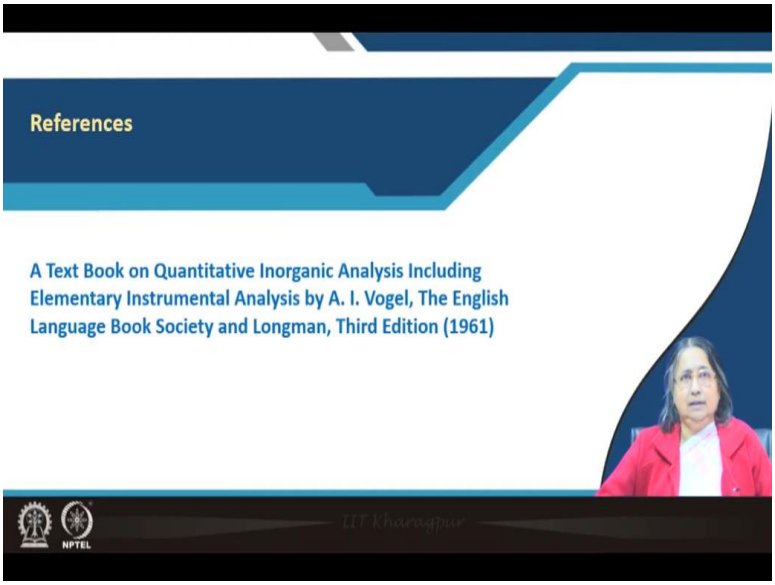

You can read the book written in the last slide by A. I. Vogel to know the spectrophotometer; what is spectrophotometer; what are the different components; and what is Lambert-Beer's law; what is calibration carve etc. Thank you.