Environmental Chemistry and Microbiology
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Module - 3
Lecture - 11
Chemical Kinetics - I

Welcome everyone to our online NPTEL course, Environmental Chemistry and Microbiology. This course will be taught by Professor Sudha Goel and myself, Professor Anjali Pal. We are both from the Civil Engineering Department, 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. Now, this is my third module.

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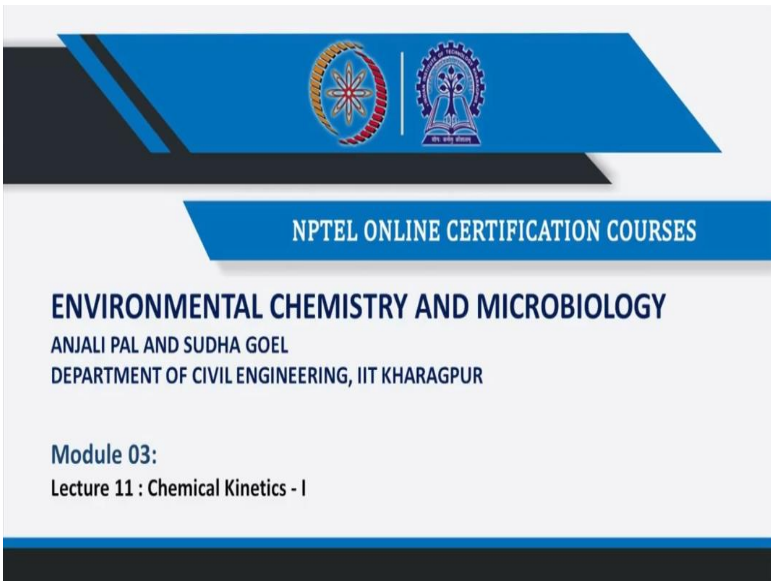

I have already covered acids, bases and salts in my module 1 and chemical equilibrium in module 2. Now, in Module 3, I will discuss about chemical kinetics. This is my eleventh lecture.

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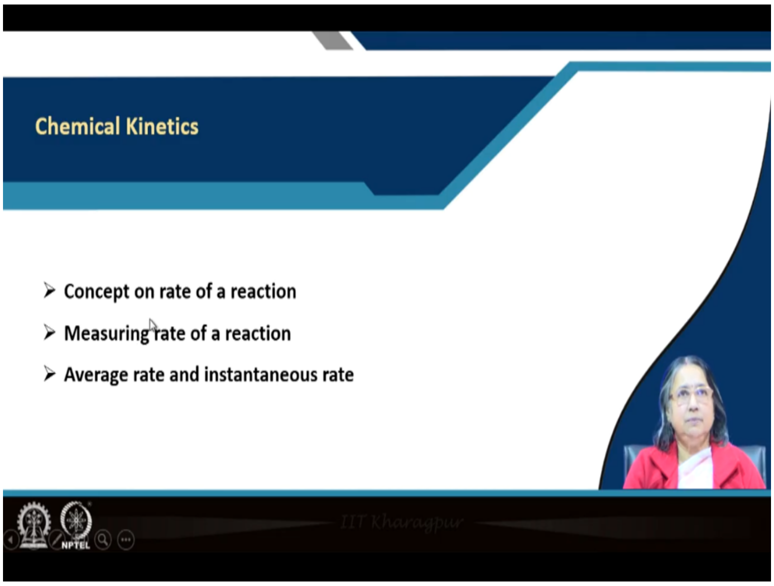

In this lecture, I will cover the following topics: concept on rate of reaction, measuring rate of a reaction, average rate and instantaneous rate.

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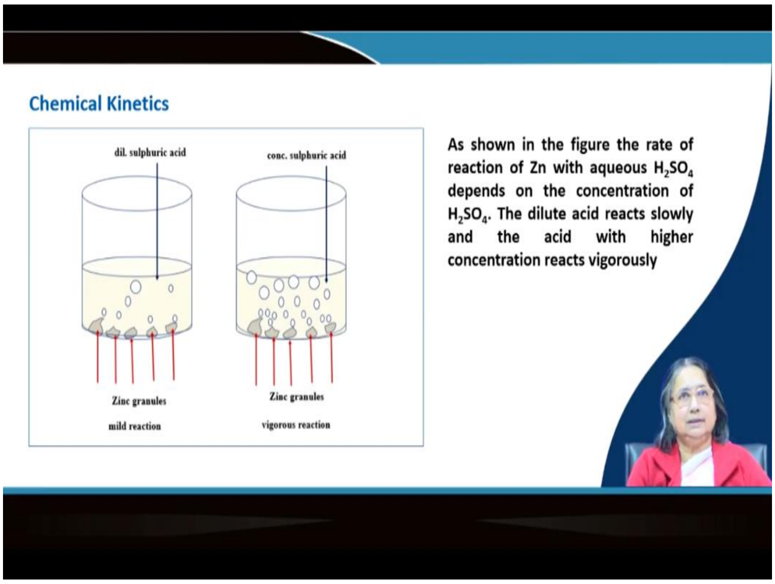

Now, what is a reaction? Say, for example, A and B react to give C and D. Then we will call A and B as the reactant and C and D as the products. Now, if you refer to the slide just above, you will see that there are two vessels. In both the vessels, you see that there are zinc granules. In the first vessel, dilute sulphuric acid is added and in the second vessel, concentrated sulphuric acid is added. Now, what you will see? You will see that, in the first vessel where you have added dilute sulphuric acid, the reaction involves evolution of hydrogen gas and it will form the bubbles. In case of dilute sulphuric acid, you can see that the bubbles are coming out in a very slow process, but in case of concentrated sulphuric acid it is coming very vigorously. That means, in one case the reaction is going on slowly and in other case it is occurring vigorously. So, this is the topic chemical kinetics, under which we will see, why some reaction is slow and why some reaction is fast.

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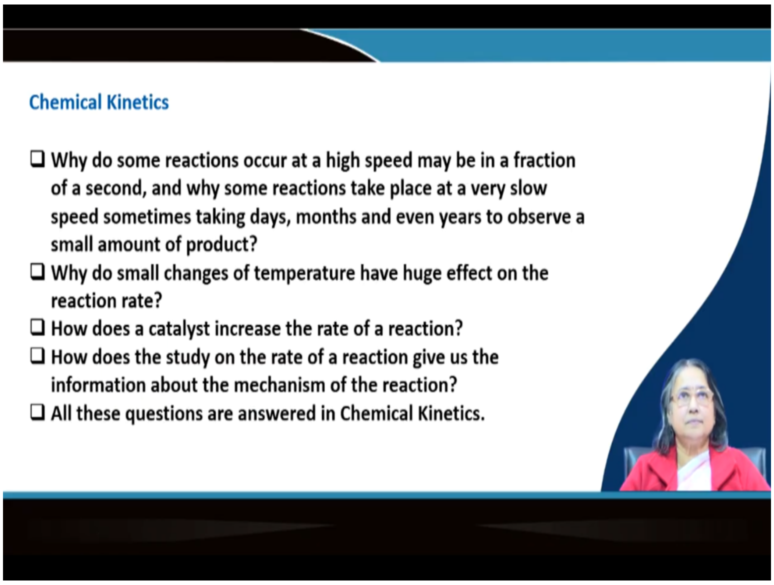

Why do some reactions occur at a high speed (maybe in a fraction of a second)? There are some reactions which you cannot even monitor by using simple instruments. It is so quick. On the other hand, why some reaction take place at a very slow speed? Sometimes it can take days, it can take months, and even it can take years. Say, for example you know that half-life of some radioactive elements are even some million years. So, their radioactive decay is very slow process.

Why do some small changes of temperature can have huge effect on the reaction rate? How does a catalyst increase the rate of reaction? If you mix hydrogen and oxygen, then they will produce water. But this is a spontaneous process, but it will not happen unless you put some spark or you can add some catalyst.

So, catalyst is very important to make a reaction very fast. How does the study on the rate of a reaction give us the information about the mechanism of the reaction? All these questions are answered in chemical kinetics. So, these are the scopes of chemical kinetics.

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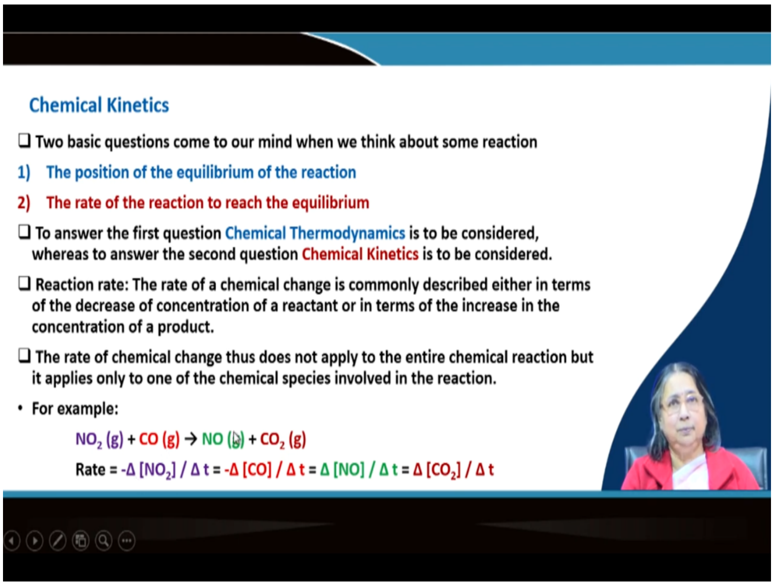

When we see a reaction, two basic questions come to our mind. The first thing is that, the position of the equilibrium of the reaction. What does it mean? How far the reaction will go. This is already covered in the chemical equilibrium. And the second question is the rate of the reaction. When we talk about chemical equilibrium, then we never talk about the speed of the reaction. Whether it will be fast or slow, that will be handled in the chemical kinetics. To answer the first question chemical thermodynamics is important. And to answer the second question, chemical kinetics is important. Now, what is reaction rate. The rate of a chemical change commonly described either in terms of the decrease of the concentration of the reactant or in terms of the increase in the concentration of a product. That means, when a reaction goes on, the reactant concentration decreases and the product concentration increases. The rate of the chemical change thus does not apply to the entire chemical reaction but it applies only to one of the chemical species involved in the reaction.

Let us see the following reaction (1):

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$……………………….(1)

You see here, NO_2 is reacting with carbon monoxide. It is a gas phase reaction to produce nitric oxide and carbon dioxide. We can describe the rate in terms of either reactants, maybe either NO_2, or in terms of CO; or in terms of the products like, either in terms of NO or CO_2 as follows:

$$\text{Rate} = -\frac{\Delta[NO_2]}{\Delta t} = -\frac{\Delta[CO]}{\Delta t} = \frac{\Delta[NO]}{\Delta t} = \frac{\Delta[CO_2]}{\Delta t} \quad \text{…………………..(2)}$$

But only thing we will have to remember that, if we express in terms of the reactants, negative signs should be there, because the concentration is decreasing with time and if we describe in terms of the product, then there will be no negative sign, but it will be positive sign.

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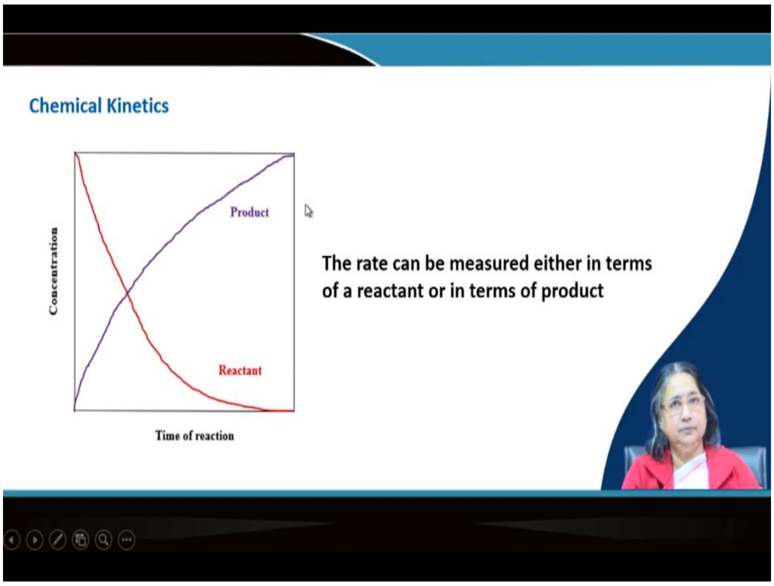

Now, if you see the curve in the last slide, you can easily understand that, curve corresponding to reactants is decreasing and curve corresponding to product is increasing with respect to the time of reaction. So, the rate can be measured either in terms of the reactant or in terms of the product.

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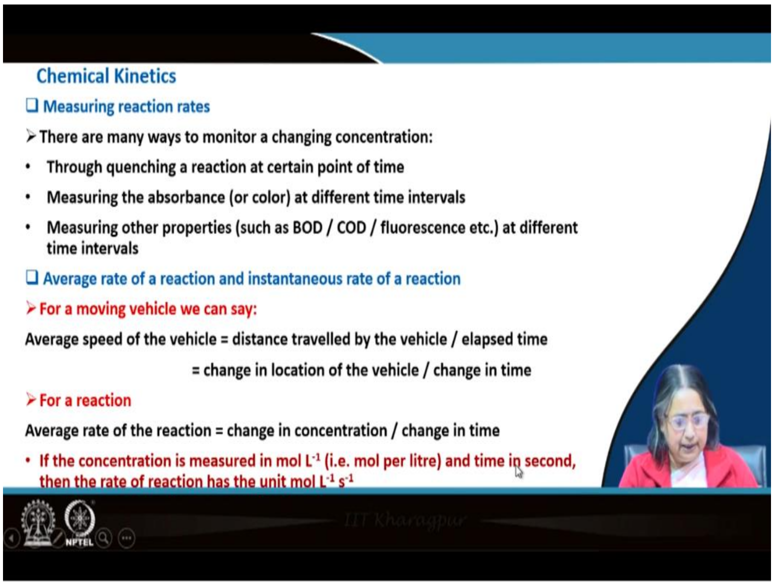

Now, let us see how to measure the reaction rate. Say for example, some reaction is going on. At a particular time, we want to know the concentration. Then, what we should do?

There are several methods. Say for example, quenching method. Say for example, you are monitoring a chemical reaction. At a particular time, you want to see the concentration of a either reactant or product. Then you can take some aliquot from the reaction's reacting solution and then, you can quench the reaction by putting it either in, at a cold temperature or you can dilute it in enormous amount of solvent. Then what will happen? Then the rate of the reaction will slow down. That, then you can have little time to measure the concentration of the reactant or the product. There are also some instruments, which can continuously monitor some properties of some substance, either reactant or product. You can control it, under certain condition. You can regulate the instrument and program the instrument to have some properties, say such as absorbance, fluorescence, etc. So, from time to time, the instrument itself will measure the property and give you the rate equation or the curve.

There are many different ways by which you can measure the reaction rate. For example, you can measure the Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), and other properties, such as conductance or whatever may be. The property should be related with either the product or the reactant. Then only you can measure them accordingly, in different times or time intervals.

Now, what is the average rate of a reaction and instantaneous rate of a reaction? Say for example, I am traveling by a car, So, if I start from Kharagpur and if I want to go to Kolkata, my speed will not be constant throughout my journey time. So, at different places the speed will vary. Then how we can determine? You can determine in terms of average speed. Say for example, in first 1 hour (from the initial time period), if I see what distance I have covered; then average speed will be the distance traveled by the vehicle divided by the elapsed time. So, that is the average speed. So, this is for a vehicle. But what about the reaction? How you can see the rate of a reaction? Here also, average rate may come into picture. Say for example, you take two different times. You determine the concentration at the initial time and then at the final time. You can measure the difference in concentration. You can also easily measure the time that has passed. So, you can easily find out the rate. This is the average rate. If you know the concentrations in moles per litre and the time in seconds, then, it will be like, the rate of reaction has the unit moles per litre per second.

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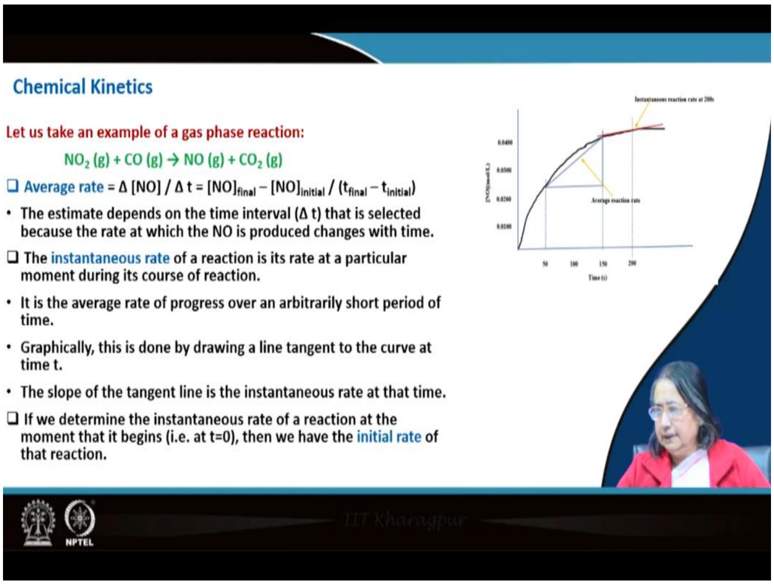

Now, this is the average speed or average rate. It is easy to understand, but then what is the instantaneous rate? That is very important for kinetics. Now, taking same example ((1)):

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$……………………(1)

We can express average rate, in terms of NO. It can be done by measuring difference in NO concentration and the time difference and then dividing difference in concentration by the time difference. It can be mathematically expressed as shown in (2):

$$\text{Rate} = -\frac{\Delta[NO_2]}{\Delta t} = -\frac{\Delta[CO]}{\Delta t} = \frac{\Delta[NO]}{\Delta t} = \frac{\Delta[CO_2]}{\Delta t}$$

$$\text{Rate} = -\frac{1}{2}\times\frac{\Delta[NO_2]}{\Delta t} = -\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\times\frac{\Delta[NO_2]}{\Delta t} \quad \text{…………………..(2)}$$

$$\text{Rate} = -\frac{1}{a}\times\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

There is no problem for finding out average rate when Δt is large. Now, instantaneous rate comes into picture when this Δt is becoming very small. So, an instantaneous rate is the rate of a reaction at a particular moment during the course of the reaction. So, the determination of instantaneous rate is difficult.

Now, follow the graph in the previous slide. Here in this example, you are measuring the concentration of NO. It is one of the products. So, the concentration will increase. So, the curve will be increasing as shown in the figure. So, if you want to determine the average speed between this 50 second and 150 second, you have to consider the time difference i.e., 100 second. You have to also consider the difference in concentration. Difference in concentration divided by difference in time will give the average rate of reaction or speed of reaction.

Now let us see how to determine the instantaneous rate of reaction. Say for example, at the point at 200 second, you want to know the instantaneous rate or instantaneous speed, then what you will do? You have to draw a tangent at this point. And then, you may have to extrapolate it. Say for example, up to 150 second on one side and then up to say 250 second on the other side of the required point. And then follow the same procedure like that of finding average rate of reaction. So, this is very easy. In the beginning, if you calculate the instantaneous rate, then we will call it the initial rate of that reaction.

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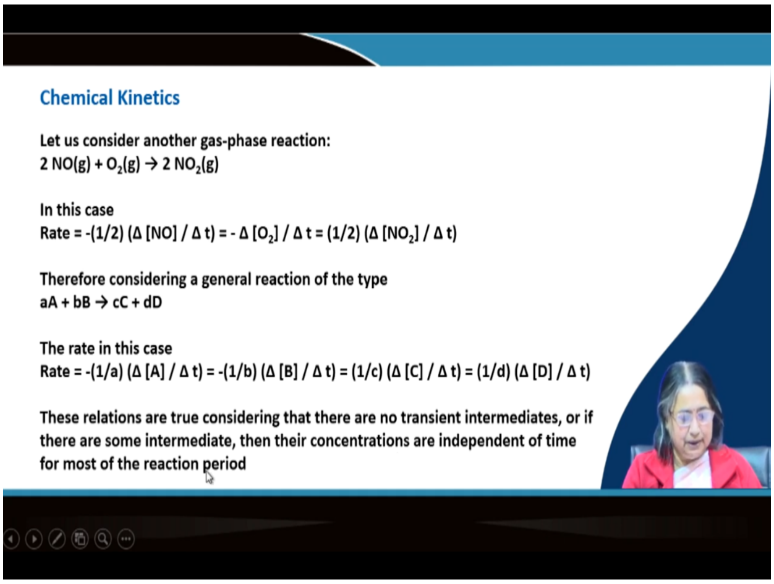

Now, let us consider another reaction ((3)) where stoichiometry of the reactants and products are not 1.

$2NO(g) + O_2(g) \rightarrow 2NO_2\ (g)$……………….(3)

In this case the rate of the reaction is defined as:

$$\text{Rate}= -\frac{1}{2}\times\frac{\Delta[NO_2]}{\Delta t} = -\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\times\frac{\Delta[NO_2]}{\Delta t} \ldots\ldots\ldots\ldots\ldots\ldots..(4)$$

Now, let us generalize it:

$aA + bB \rightarrow cC + dD$…………………..(5)

So, rate is expressed as:

$$\text{Rate}= -\frac{1}{a}\times\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t} \ldots\ldots\ldots\ldots\ldots\ldots(6)$$

But the important thing is that, these relations are true considering that there are no transient intermediates or if there are some intermediates, then their concentrations are independent at least for some time or most of the time period for the reaction. Otherwise this relation will not hold good.

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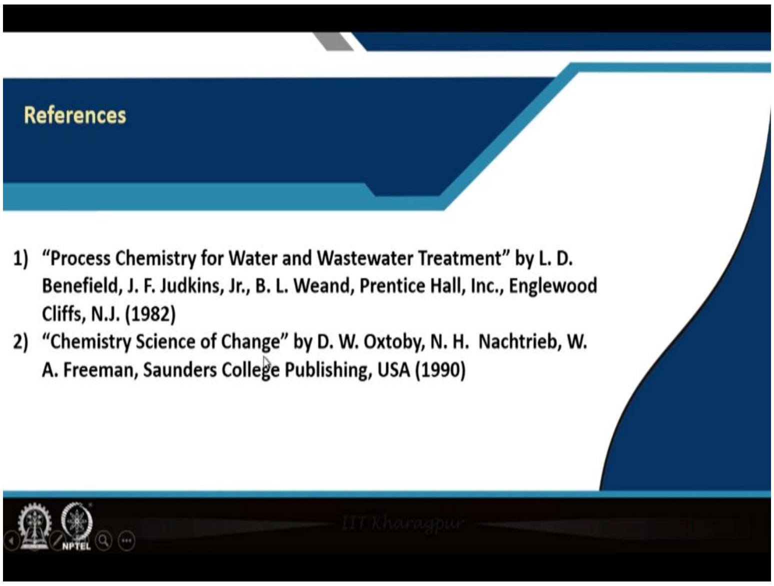

To have more idea or better idea you can read from these two books: i) Process Chemistry for Water and Wastewater Treatment by L. D. Benefield and Judkins and Weand (full reference is given in the slide), ii) Chemistry Science of Change, by D. W. Oxtoby.

So, what we have understood from the lecture 11 is that what is the chemical reaction? What is the average rate? What is the instantaneous rate of the chemical reaction? Thank you.