Environmental Chemistry and Microbiology
Prof. Dr. Anjali Pal
Department of Civil Engineering
Indian Institute of Technology – Kharagpur

Lecture –17
Chemical Kinetics Reaction Mechanism (Part B)

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 both are from Civil Engineering Department, IIT Kharagpur. We have divided this course into two parts. The first part environmental chemistry will be covered by me and the second part i.e., environmental microbiology will be taught by Professor Sudha Goel.

I discussed in my module 1 the acids, bases and salts. In the second module I discussed about the chemical equilibrium. In the third module I discussed about the chemical kinetics. I elaborated the reaction rate, reaction order, how to determine the order and how to use the differential rate law and integrated rate law to find out the order. This is my 17th lecture and this is chemical kinetics reaction mechanism (Part B).

You know that in chemical kinetics, the reaction mechanism is very important to know not only the order and rate, but we have to know how the reaction is going on and what are the steps it is following. It has some relation with the rate expression and that we have to determine. This need some knowledge and speculation. I will tell you that.

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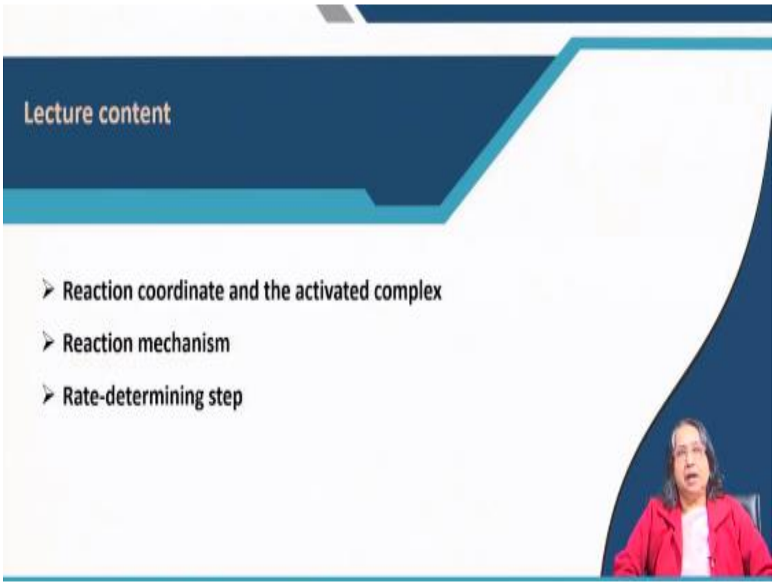

Lecture content

- Reaction coordinate and the activated complex
- Reaction mechanism
- Rate-determining step

In this lecture the content is the reaction coordinate and activated complex, reaction mechanism and rate determining step.

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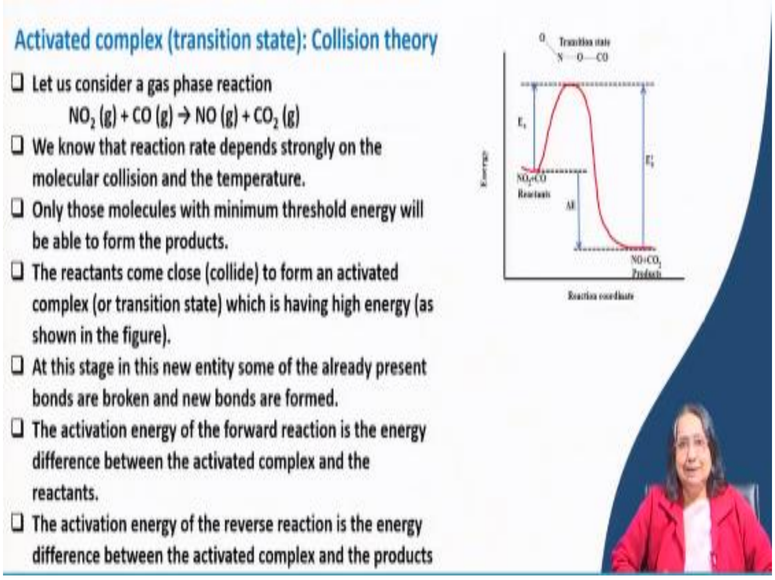

Activated complex (transition state): Collision theory

- ☐ Let us consider a gas phase reaction
  $NO_2 (g) + CO (g) \rightarrow NO (g) + CO_2 (g)$
- ☐ We know that reaction rate depends strongly on the molecular collision and the temperature.
- ☐ Only those molecules with minimum threshold energy will be able to form the products.
- ☐ The reactants come close (collide) to form an activated complex (or transition state) which is having high energy (as shown in the figure).
- ☐ At this stage in this new entity some of the already present bonds are broken and new bonds are formed.
- ☐ The activation energy of the forward reaction is the energy difference between the activated complex and the reactants.
- ☐ The activation energy of the reverse reaction is the energy difference between the activated complex and the products

You know that we played one game in our childhood days. What is the game? We had some marbles and then we wanted to push the marbles. We wanted the marbles to cross a small hill and how we will do it? We will push the marble with sufficient energy. Then the marbles will go up the hills and then it will cross the hill and it will fall on the other side. So, what we have seen that when we push the marbles then some of the marbles came back because the pushing was not done with sufficiency energy. So, some of the marbles will come back and some of the marbles will manage to cross the hill and go to the other side. So, when one marble is going up then the kinetic energy is decreasing, potential energy is increasing. When it is at the top of the hill then potential energy is maximum and kinetic energy zero. And then, when it crosses the hill then again potential energy is decreasing and kinetic energy is increasing. So, this model actually can be applied here to understand the activated complex and how the mechanism is going on. Here, you can see that there is one reaction (gas phase):

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

Now in the last slide you can see that the potential energy is plotted against the reaction coordinate. You can see the reactant molecules on the left and the product molecules on the right. Now the reactant molecules will react when they come close with sufficient speed, sufficient energy and they have to collide. We know that reaction rate depends strongly on the molecular collision and the temperature. I have explained that in my third module when I talked about the dependence of reaction rate on temperature. So whenever two molecules will react, they have to collide. But all collisions will not produce the reaction. Some of the collisions may not produce the reaction. Only those collisions with sufficient energy, will cause the reaction. Only those molecules with minimum threshold energy will be able to form the products. The reactants come close (collide) to form an activated complex (transition state). So, they are colliding and they are crossing uphill that means they are crossing energy state. Now at this stage here when the activated complex is formed some of the already present bonds are broken and new bonds are formed. In reaction (1) you can see that NO_2 and CO react to form CO_2 and NO. So here one NO bond has to be broken and one bond has to be formed between carbon and oxygen so here it is being formed. Now let us come to the activation energy of the forward reaction. So, when you consider the reactant is going to product, then it is a forward reaction. The activation energy of the forward reaction is the energy difference between the activated complex and the reactants. So reverse reaction is also possible if you think about this NO and CO_2 is going back to form CO and NO_2. So, activation energy of the reverse reaction is the energy difference between the activated complex and the products.

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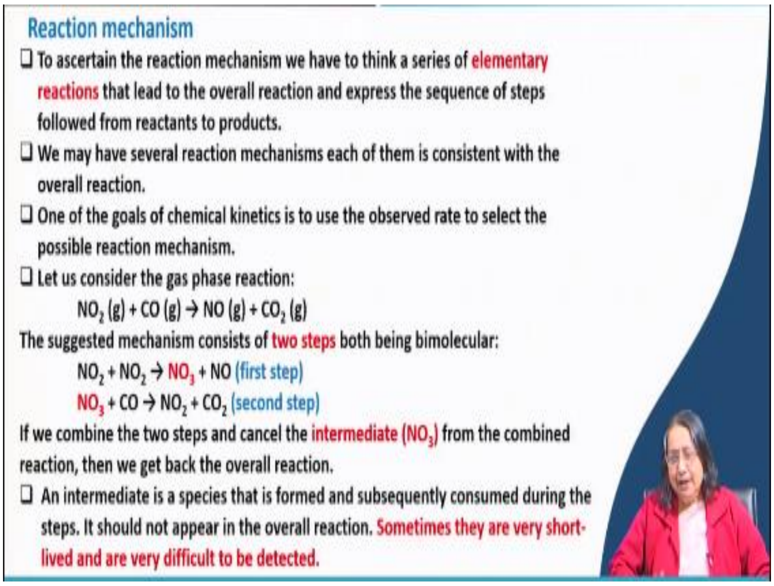

Reaction mechanism

☐ To ascertain the reaction mechanism we have to think a series of elementary reactions that lead to the overall reaction and express the sequence of steps followed from reactants to products.

☐ We may have several reaction mechanisms each of them is consistent with the overall reaction.

☐ One of the goals of chemical kinetics is to use the observed rate to select the possible reaction mechanism.

☐ Let us consider the gas phase reaction:

$$NO_2\,(g) + CO\,(g) \rightarrow NO\,(g) + CO_2\,(g)$$

The suggested mechanism consists of two steps both being bimolecular:

$$NO_2 + NO_2 \rightarrow NO_3 + NO \text{ (first step)}$$

$$NO_3 + CO \rightarrow NO_2 + CO_2 \text{ (second step)}$$

If we combine the two steps and cancel the intermediate (NO_3) from the combined reaction, then we get back the overall reaction.

☐ An intermediate is a species that is formed and subsequently consumed during the steps. It should not appear in the overall reaction. Sometimes they are very short-lived and are very difficult to be detected.

Now let us come to the reaction mechanism. I told you that reaction mechanism is very important to know. It comes under the scope of chemical kinetics. To ascertain the reaction mechanism, we have to think of elementary reactions (already discussed in the previous lecture). Most of the reactions are not occurring in a single step. And when you consider the elementary reaction, you cannot think anything. You have to think the elementary reaction such a way that after combining all the elementary reactions you should get the overall reaction and then you should get what is the reactant and what is the product.

The reactant and product should match with this proposition. Now we may have several mechanism reactions and each of them is consistent with the overall reaction. Suppose you have written several possible mechanisms then which one will be the correct one? One of the goals of chemical kinetics is to use the observed rate. So, when you have several possible mechanisms, then you have to think about the rate. Say, let us again consider the reaction represented in (1). This is gas phase reaction. Now the suggested mechanism consists of two steps as follows:

$NO_2+NO \rightarrow NO_3+NO$ (first step)…………….(2)

$NO_3+CO \rightarrow NO_2+CO_2$ (second step)………..(3)

From steps represented by (2) and (3) you can see that NO_3 is the intermediate. NO_3 is not there in the actual reaction. So, if NO_3 is produced it has to be consumed. Now adding the intermediate steps, you should get the overall reaction (actual reactant and product). If we combine the two steps and cancel the intermediate (NO_3) from the combined reaction then we get back the overall. So, when you a combination of elementary reactions for actual reaction then you have to keep this thing in mind that you may produce some intermediates. But intermediate should not be there anymore in the balanced equation. It should be consumed. I told already that proposition of mechanism is difficult. You need to perform a lot of experiments also to do. Now if you want to see the intermediate formed as a proof then you must have some instrument. But sometimes the intermediates are so short-lived (transient existence) that it is very difficult to absorb them. There are very sophisticated instruments also which can detect those short-lived intermediates, but here I am not discussing that.

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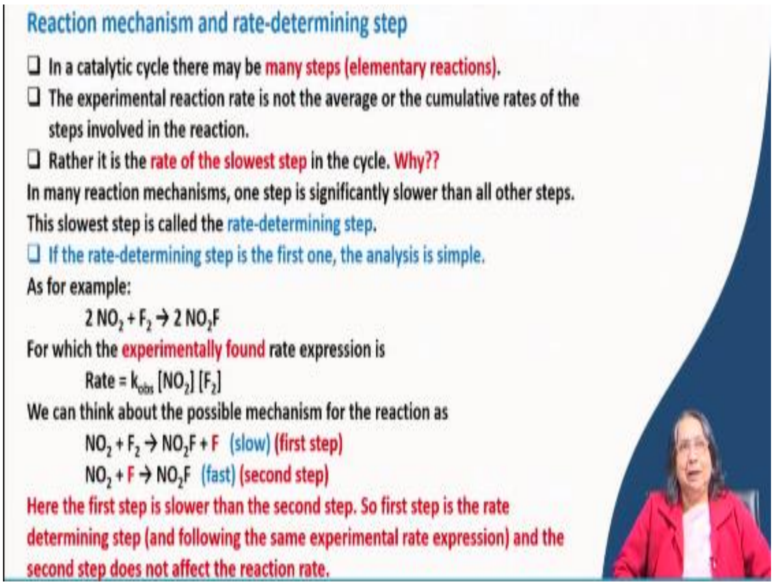

Reaction mechanism and rate-determining step

☐ In a catalytic cycle there may be many steps (elementary reactions).

☐ The experimental reaction rate is not the average or the cumulative rates of the steps involved in the reaction.

☐ Rather it is the rate of the slowest step in the cycle. Why??

In many reaction mechanisms, one step is significantly slower than all other steps.
This slowest step is called the rate-determining step.

☐ If the rate-determining step is the first one, the analysis is simple.

As for example:

$$2\,NO_2 + F_2 \rightarrow 2\,NO_2F$$

For which the experimentally found rate expression is

$$\text{Rate} = k_{obs}\,[NO_2]\,[F_2]$$

We can think about the possible mechanism for the reaction as

$NO_2 + F_2 \rightarrow NO_2F + F$ (slow) (first step)

$NO_2 + F \rightarrow NO_2F$ (fast) (second step)

Here the first step is slower than the second step. So first step is the rate determining step (and following the same experimental rate expression) and the second step does not affect the reaction rate.

Now let us come to the rate determining step. This is a very important thing for proposing reaction mechanism. In catalytic cycle there may be many steps. I already told you that in any reaction there may be many steps and those are called elementary reactions. Now the experimental reaction rate is not the average of the or the cumulative of the rates of the steps involved in the reaction. So, rate of the overall reaction is the rate of the slowest step. I told you just now in the previous lecture that slowest step is very important in the cycle. I am giving another example to make you understand in a better way. Say for example, I want to send one file with particular documents to a person of high authority. Say for example, I want to send my file from table number 1 to table number 10. Now in between there are many tables. So, it will go from 1 to 2, then 2 to 3, then 3 to 4 and so on. Ultimately it will go to table number 10. Now say, for example, the persons who are sitting in all tables except one are very fast and efficient. They do it very fast, the person at the remaining table is slow. Let the slow person is sitting at table 5. So, to go to table number 5 via table number 2, 3, 4 it takes 2 hours time and then from table number 5 to table number 6 it takes 10 days. Again, after table number 6 to go to table number 10 it takes only 2, 3 hours. Then ultimately it is taking 11 days. But main time is taken by that table number 5 to reach table number 6. So, it is the slowest step that is taking maximum time. The slowest step is nothing, but the rate determining step. If you really want to make transfer of file faster then you have to speed up the transfer from table 5 to 6. It is the rate determining step and actual rate is governed by that one. In many reaction mechanisms one step is significantly slower than all other steps. This slowest step is called the rate determining step. Unlike the case of file, in case of reactions it is very important. If the rate determining step is first one then analysis is very simple. Let us consider an example:

$2NO_2+F_2\rightarrow 2NO_2F$……………(4)

Experimentally rate expression has been found as:

$\text{Rate}=k_{obs}[NO_2][F_2]$……………(5)

So, we can think about the possible mechanism for the reaction as

$NO_2+F_2\rightarrow NO_2F+F$ (slow)……………..(6)

$NO_2+F\rightarrow NO_2F$ (fast)…………………..(7)

In this reaction the step represented by (6) is the slow step. It is therefore rate determining step. The second step (7) does not affect the rate of the reaction. F is the intermediate and it is consumed. Hence, the rate expression is given by (5). So here you see it is a simple case as first step is rate determining step (told earlier in the lecture). But when there are series of step then it is not so easy to tell about the mechanism.

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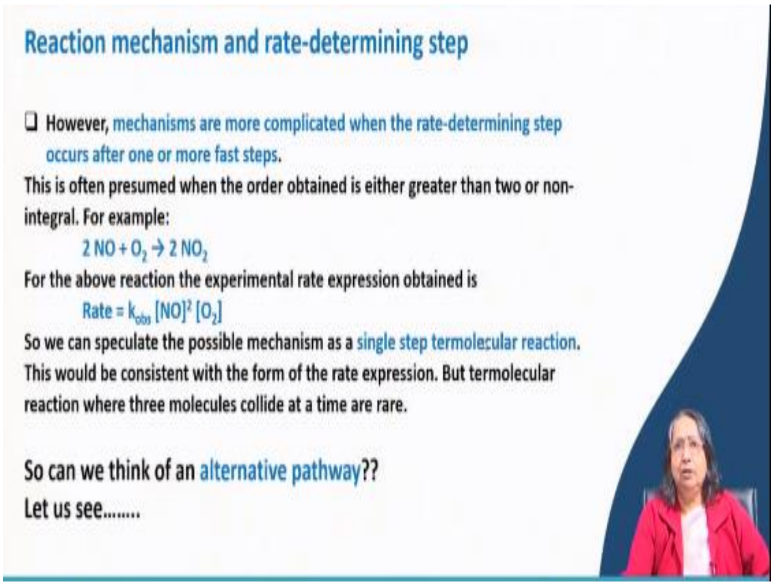

Reaction mechanism and rate-determining step

- ❑ However, mechanisms are more complicated when the rate-determining step occurs after one or more fast steps.

This is often presumed when the order obtained is either greater than two or non-integral. For example:

$$2\,NO + O_2 \rightarrow 2\,NO_2$$

For the above reaction the experimental rate expression obtained is

$$Rate = k_{obs}\,[NO]^2\,[O_2]$$

So we can speculate the possible mechanism as a single step termolecular reaction. This would be consistent with the form of the rate expression. But termolecular reaction where three molecules collide at a time are rare.

So can we think of an alternative pathway??

Let us see........

Mechanisms are more complicated when the rate determining step occurs after one or more fast steps. In the previous one first step was the slowest, but always it is not like that. It is more complicated when rate determining step occurs after one or more fast steps. Say, for example:

$2NO+O_2 \rightarrow 2NO_2$…………..(8)

In case of (8) rate expression is given as:

$Rate=k_{obs}[NO]^2[O_2]$……..(9)

So, you can say that this is one step mechanism, but we have already discussed that single step termolecular reaction is not common. If we have other possible mechanism, we have to consider that. It should be consistent with the form of the rate expression. So, can we think an alternative pathway? Let us see, whether we can do it.

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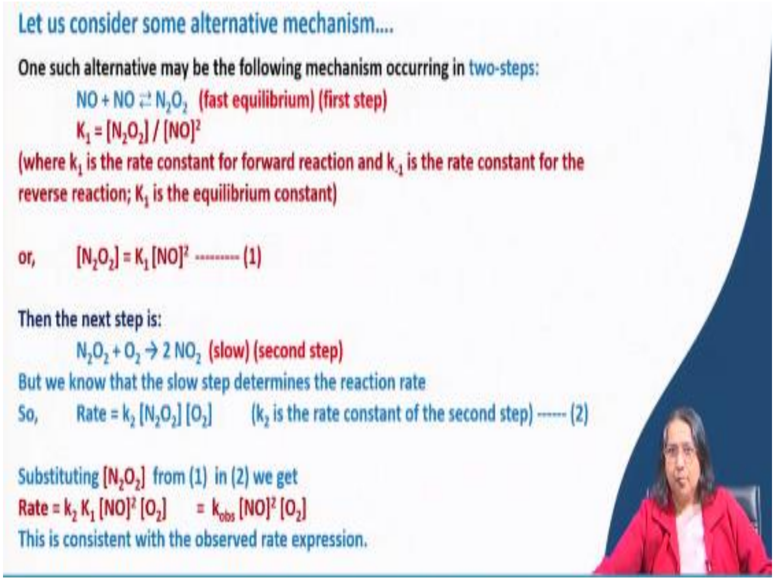

Let us consider some alternative mechanism....

One such alternative may be the following mechanism occurring in two-steps:

$NO + NO \rightleftarrows N_2O_2$ (fast equilibrium) (first step)

$K_1 = [N_2O_2] / [NO]^2$

(where k_1 is the rate constant for forward reaction and k_{-1} is the rate constant for the reverse reaction; K_1 is the equilibrium constant)

or, $[N_2O_2] = K_1 [NO]^2$ --------- (1)

Then the next step is:

$N_2O_2 + O_2 \rightarrow 2\ NO_2$ (slow) (second step)

But we know that the slow step determines the reaction rate

So, Rate $= k_2 [N_2O_2] [O_2]$ (k_2 is the rate constant of the second step) ------ (2)

Substituting $[N_2O_2]$ from (1) in (2) we get

Rate $= k_2 K_1 [NO]^2 [O_2] \quad = k_{obs} [NO]^2 [O_2]$

This is consistent with the observed rate expression.

It can be thought as it is composed of two following steps:

$NO+NO \leftrightharpoons N_2O_2$ (fast equilibrium) (first step)…………………..(10)

$N_2O_2+O_2 \rightarrow 2NO_2$ (slow) (second step)…………………………(11)

The first step (10) represents fast equilibrium reaction and equilibrium equation can be expressed as:

$k_1=[N_2O_2]/[NO]^2$

or, $[N_2O_2]=k_1[NO]^2$………………………………………………(12)

Reaction represented by (11) denotes the slow step and therefore it is the rate determining step. Its rate expression can be written as follows:

$Rate=k_2[N_2O_2][O_2]$……………………………………………….(13)

Substituting (12) in (13):

$Rate=k_1k_2[NO]^2[O_2]$

$=k_{obs}[NO]^2[O_2]$…………………………………………………(14)

(14) is consistent with the expression (9).

So, this alternative mechanism is not considering a termolecular reaction, but it is considering the first step (fast equilibrium) and then second step (slow one). So maybe this mechanism is correct. So just I have shown that how we can think. What are the different things we have to keep in mind when we develop the elementary reactions?

Now, these are the general concepts. I have shown you with very simple reactions, but actually the reactions are not so simple. They are complicated. They may not involve two steps. They may involve more than two steps. So, some knowledge is required to think about the elementary steps. But at least we can think what is the elementary step. We know what is the balanced equation. Experimentally we can find out the rate expression, order of the reaction. Then our thinking should comply with all those things and it should match. Then only we can tell that it is okay.

Sometimes we can determine the intermediates to proof that our speculative mechanism is right.

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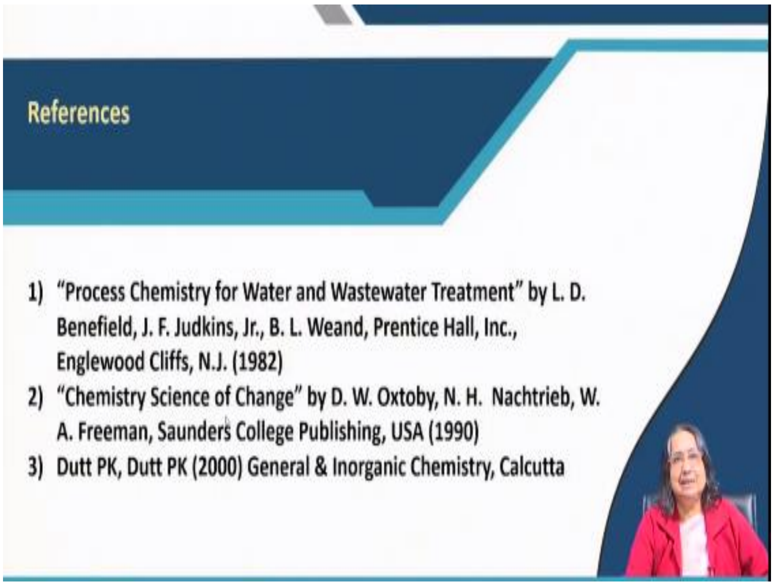

References

1) "Process Chemistry for Water and Wastewater Treatment" by L. D. Benefield, J. F. Judkins, Jr., B. L. Weand, Prentice Hall, Inc., Englewood Cliffs, N.J. (1982)
2) "Chemistry Science of Change" by D. W. Oxtoby, N. H. Nachtrieb, W. A. Freeman, Saunders College Publishing, USA (1990)
3) Dutt PK, Dutt PK (2000) General & Inorganic Chemistry, Calcutta

You can follow the references given in the last slide for studying this portion.

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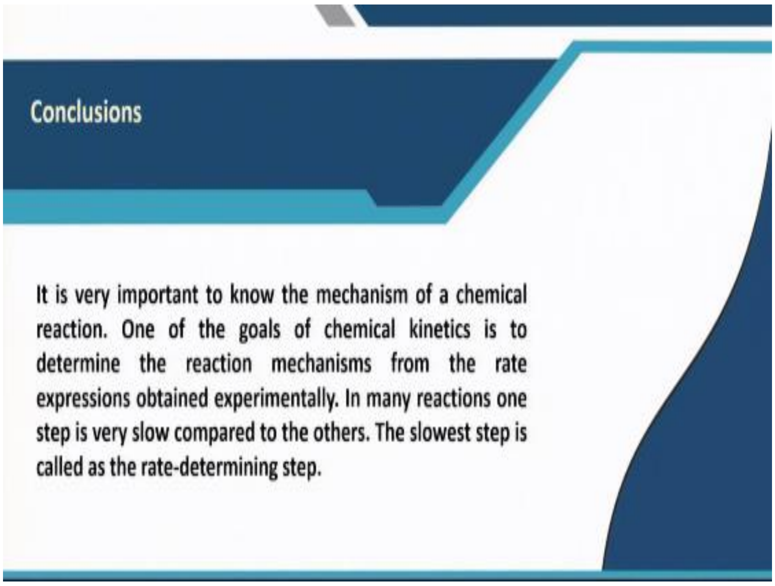

Conclusions

It is very important to know the mechanism of a chemical reaction. One of the goals of chemical kinetics is to determine the reaction mechanisms from the rate expressions obtained experimentally. In many reactions one step is very slow compared to the others. The slowest step is called as the rate-determining step.

Now as a conclusion I can tell that it is very important to know the mechanism of a chemical reaction. One of the goals of chemical kinetics is to determine the reaction mechanism from the rate expression obtained experimentally. In many reactions one step is very slow compared to the others. The slowest step is called the rate determining steps. So, these are the main things that I have covered in this lecture. Thank you.