Environmental Chemistry and Microbiology
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Module - 3
Lecture - 14
Chemical Kinetics - IV

Welcome everyone to our online NPTEL course of Environmental Chemistry and Microbiology. The course will be taught by Professor Sudha Goel and myself, Professor Anjali Pal. We are both from the Civil Engineering Department of IIT Kharagpur. We have divided this course into 2 parts, Environmental Chemistry and Environmental Microbiology. The first part, Environmental Chemistry will be covered by me and the second part, Environmental Microbiology will be taught by Professor Sudha Goel. I was explaining the chemical kinetics in my previous lectures.

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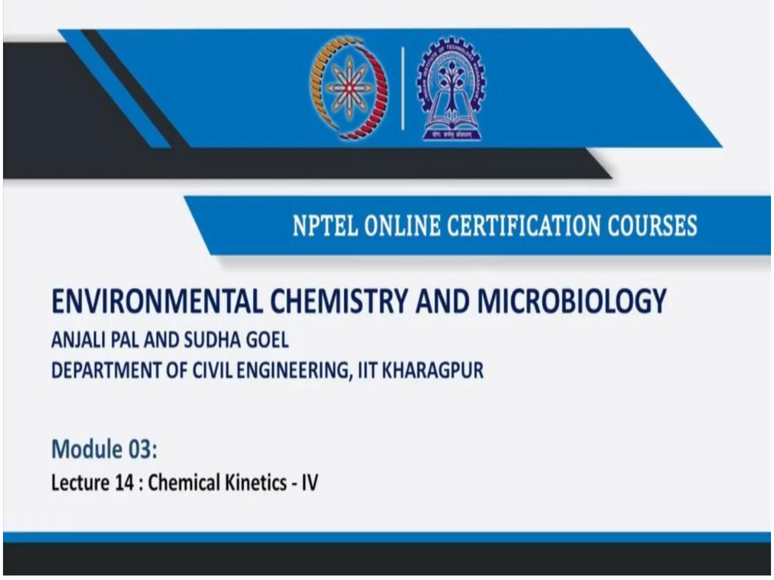

NPTEL ONLINE CERTIFICATION COURSES

ENVIRONMENTAL CHEMISTRY AND MICROBIOLOGY
ANJALI PAL AND SUDHA GOEL
DEPARTMENT OF CIVIL ENGINEERING, IIT KHARAGPUR

Module 03:
Lecture 14 : Chemical Kinetics - IV

This is the module 3. And in module 1, I have explained acids, bases and salts. In Module 2, I have explained the chemical equilibrium. And this is my fourteenth lecture in which we will discuss the chemical kinetics.

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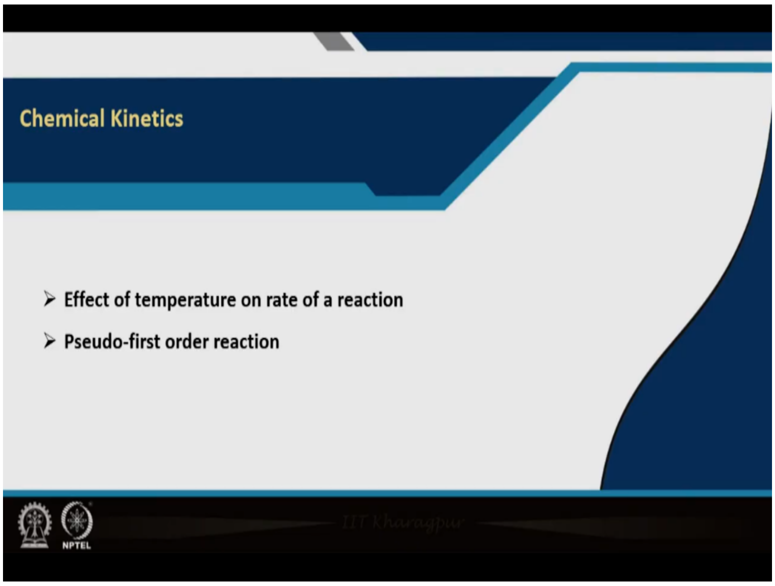

Chemical Kinetics

- ➢ Effect of temperature on rate of a reaction
- ➢ Pseudo-first order reaction

Now, in this lecture, I will tell about the effect of temperature on rate of a reaction and pseudo-first order reaction.

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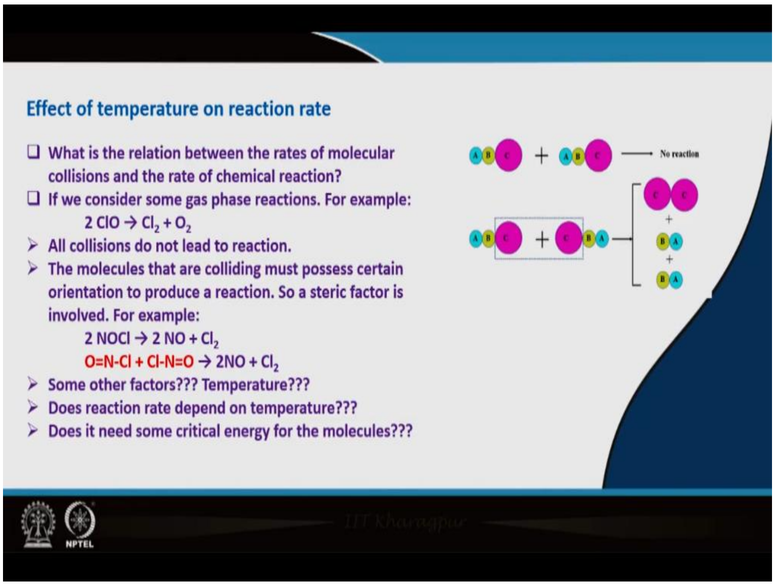

Effect of temperature on reaction rate

- ☐ What is the relation between the rates of molecular collisions and the rate of chemical reaction?
- ☐ If we consider some gas phase reactions. For example:

  $2\,ClO \rightarrow Cl_2 + O_2$
- ➢ All collisions do not lead to reaction.
- ➢ The molecules that are colliding must possess certain orientation to produce a reaction. So a steric factor is involved. For example:

  $2\,NOCl \rightarrow 2\,NO + Cl_2$

  $O{=}N{-}Cl + Cl{-}N{=}O \rightarrow 2NO + Cl_2$
- ➢ Some other factors??? Temperature???
- ➢ Does reaction rate depend on temperature???
- ➢ Does it need some critical energy for the molecules???

Hopefully you have noticed from my previous lectures that I used K for equilibrium constant and k for rate constant. In many books, I have observed that this is not maintained. But this is a good practice and it should be always maintained. I already told you that both equilibrium constant and the specific rate constant depend on temperature. So, how does it depend? It means, what is the effect of temperature on the rate of a reaction? It is known that when some reaction goes on, the molecules have to collide with each other. In case of small molecules, the collision frequency (number of collisions per unit time) is very large.

If we think then we can visualize that each collision will give rise to reaction. But it will not match. In many reactions, we see the rate is much lower compared to the number of collisions per unit time. So, the question is coming that all collisions give rise to reaction or not? The answer is no. All collisions do not give rise to reaction. Some specific orientation is needed for the molecules to react or to give some product. The collision should occur in some specific orientation. I am giving you a simple example here. Say, for example, NOCl is decomposed to NO and Cl_2.

$2NOCl \rightarrow 2NO + Cl_2$……………………………………..(1)

$O=N-Cl + Cl-N=O \rightarrow 2NO + Cl_2$…………………………(2)

So, here we can see that if we write in the above mentioned way (2), then we will see that there is the bond between nitrogen and chlorine. In the product, bond is formed between two chlorine atoms. So, bond between nitrogen and chlorine in the reactant needs to be broken and that between the chlorine atoms in the product needs to be created. If this has to happen, then how the collision should be? It means 3-dimensional. If we think that what is the orientation of collision? In the last slide you can see the atoms have been named as A, B, C. A stands for oxygen, B for nitrogen and C for chlorine. Two possible orientations of collisions have been shown and it is clear that in the first type where two chlorine atoms are not side by side placed no reaction occurs. But in the second case reaction occurs giving rise to chlorine chlorine bond. So, we have seen that there is another factor. It is called steric factor. Is there any other factor? We can think that if the molecules collide in proper orientation, then also all collisions should not give rise to, may not give rise to product. Then, what is the other factor? Is there any other factor? Is there temperature? Is there some some critical energy? That is our topic of discussion.

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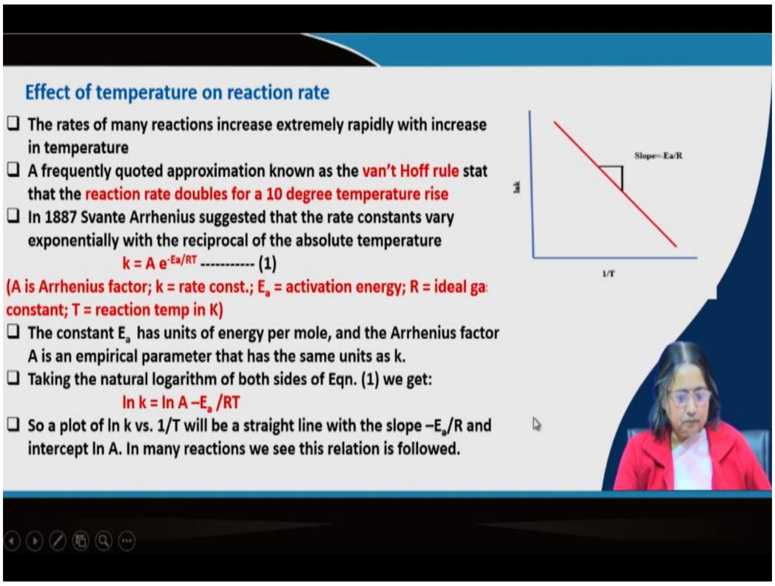

Effect of temperature on reaction rate

- ☐ The rates of many reactions increase extremely rapidly with increase in temperature
- ☐ A frequently quoted approximation known as the **van't Hoff rule** stat that the **reaction rate doubles for a 10 degree temperature rise**
- ☐ In 1887 Svante Arrhenius suggested that the rate constants vary exponentially with the reciprocal of the absolute temperature

$k = A\,e^{-Ea/RT}$ ----------- (1)

(A is Arrhenius factor; k = rate const.; E_a = activation energy; R = ideal ga constant; T = reaction temp in K)

- ☐ The constant E_a has units of energy per mole, and the Arrhenius factor A is an empirical parameter that has the same units as k.
- ☐ Taking the natural logarithm of both sides of Eqn. (1) we get:

$\ln k = \ln A - E_a/RT$

- ☐ So a plot of ln k vs. 1/T will be a straight line with the slope $-E_a/R$ and intercept ln A. In many reactions we see this relation is followed.

Now, it has been observed that the rate of reaction increases rapidly with increase in temperature. We can think easily that, when the temperature is increased, the molecules will run in a fast way. It means, they will run fast and they will collide more. That is okay. But is there any other effect?

It is the van 't Hoff rule where it is said that reaction rate doubles for a 10 degree rise in temperature. This is an observed thing and this is approximate. This is not quantitative but this is approximate thing.

Then, in 1887, Arrhenius suggested that the rate constants vary exponentially with the reciprocal of the absolute temperature. And he gave the following expression:

$$k = Ae^{-\frac{Ea}{RT}} \text{.................}(3)$$

k is the rate constant, A is known as Arrhenius factor, R is the universal gas constant and T is the temperature in absolute scale and E_a is some energy which is called activation energy.

. Now, if this is the expression, then it appears that what is the unit of Arrhenius factor? So, and what is the unit of E_a? E_a has the units of energy per mole. It is called activation energy and it has the unit of energy per mole. A is an empirical parameter that has the same unit as that of k. If we take the ln both sides, then we will get

$\ln k = \ln A - E_a/RT$………………(4)

So, from this expression, we can tell that if we plot lnk versus 1/T we will get a straight line with a negative slope. Slope is the $-E_a/R$ and you can get lnA from the intercept. So, what we will do? We will do the same reaction at 4 or 5 different temperatures and we will determine the k value. k is the rate constant. We, by now, we know how to determine the rate constant; what is the order of the reaction; how to determine the order. All those things we know. Then, after determining the k, we can plot lnk versus 1/T. So, we will get a straight line. From the straight line, we will get the activation energy, E_a and also, Arrhenius factor.

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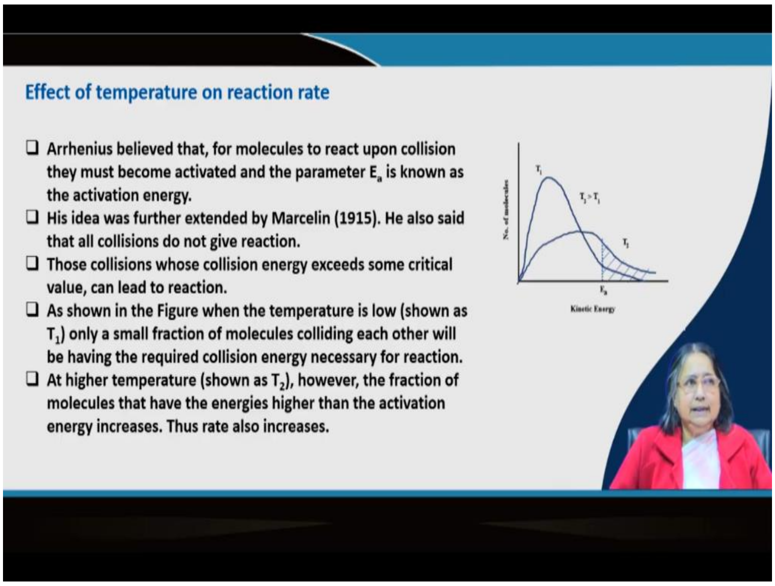

Effect of temperature on reaction rate

- ☐ Arrhenius believed that, for molecules to react upon collision they must become activated and the parameter E_a is known as the activation energy.
- ☐ His idea was further extended by Marcelin (1915). He also said that all collisions do not give reaction.
- ☐ Those collisions whose collision energy exceeds some critical value, can lead to reaction.
- ☐ As shown in the Figure when the temperature is low (shown as T_1) only a small fraction of molecules colliding each other will be having the required collision energy necessary for reaction.
- ☐ At higher temperature (shown as T_2), however, the fraction of molecules that have the energies higher than the activation energy increases. Thus rate also increases.

So, this is a very good experiment, to determine the activation energy. What is activation energy? Now, activation energy is some type of energy which the molecules must possess to do the reaction. To do the reaction means, not only the collision but also the number of collisions. It is important, but it is not the only one. So, number of collisions per unit time (frequency) is an important factor. And then, important is the steric factor. And then, some energy. This is the critical energy, to get the reaction. So, Arrhenius believed that for molecules to react upon collision, they must become activated. And the parameter E_a is known as the activation energy.

His idea also extended or refined by further by other scientists such as Marcelin, 1950. He also said, that all collisions do not give reaction. Those collisions whose collision energy exceed some critical value can lead to reaction. This is the main thing.

In the last slide the Boltzmann Maxwell distribution curve at temperature T_1 and T_2 has been shown ($T_2>T_1$). With the increase in temperature this curve is spreading. So, what you see that, in case of T_1, the number of molecules that is possessing the kinetic energy higher than E_a is much less compared to the number of molecules having the higher energy than the E_a at T_2. Here, number of molecules are higher. That is why, these molecules will give rise to the reaction. So, reaction rate increases.

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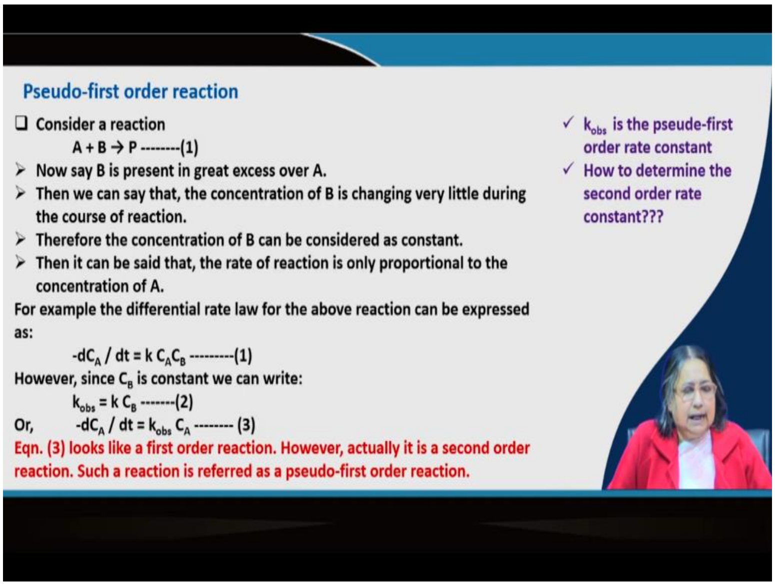

Pseudo-first order reaction

☐ Consider a reaction

$A + B \rightarrow P$ --------(1)

- Now say B is present in great excess over A.
- Then we can say that, the concentration of B is changing very little during the course of reaction.
- Therefore the concentration of B can be considered as constant.
- Then it can be said that, the rate of reaction is only proportional to the concentration of A.

For example the differential rate law for the above reaction can be expressed as:

$-dC_A / dt = k\,C_A C_B$ ---------(1)

However, since C_B is constant we can write:

$k_{obs} = k\,C_B$ -------(2)

Or, $-dC_A / dt = k_{obs}\,C_A$ -------- (3)

Eqn. (3) looks like a first order reaction. However, actually it is a second order reaction. Such a reaction is referred as a pseudo-first order reaction.

✓ k_{obs} is the pseude-first order rate constant

✓ How to determine the second order rate constant???

Now, what is the pseudo-first order reaction? You already know the first order reaction. But what is pseudo? Pseudo means false. We know Pseudopod. Now, pseudo-first order means, it is false first order. Consider an example, A + B giving P. Here, B is present in large excess over A. Then, we can say that there is almost no change for B in between the initial and final stages. Therefore, during the course of the reaction, the concentration of B can be considered as constant. B is not affecting or contributing. Actually, it is a second order reaction. If it is a first order with respect to A and first order with respect to B, then it is a second order reaction. But because B is in very large excess, so, we can consider that it is only proportional to the concentration of A. That means, it is first order with respect to A. But it is not actually first order. Overall reaction is not first order. That is why it is called pseudo-first order reaction. If we write the rate expression:

$-dC_A/dt=kC_AC_B$……………..(5)

As we are considering only A. But C_B is constant. So, $k \times C_B$ is also another constant and we denote it by k_{obs}. It is $k_{observed}$.

So, dC_A/dt, this is the rate. This is nothing but $k_{obs} \times C_A$. This is the first order. Now, you can ask that If I really want to know the second order rate constant then, what we will do? It means, we want to know the k value. Then, we will determine the k_{obs} at different concentrations of B. Then, we will draw a curve. And then, from the slope, we can determine the k. This is the second order rate constant. So, we understand that pseudo-first order reaction may be basically a second order reaction. It is because of the presence of excess of one component, we can consider that the concentration of that component is not changing. So, basically it is the first order reaction with respect to the other component. There are many examples of pseudo-first order reaction.

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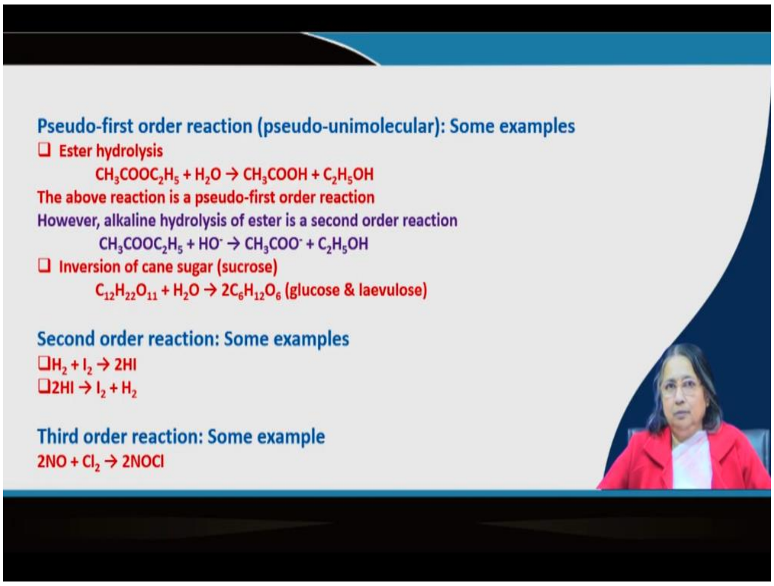

Pseudo-first order reaction (pseudo-unimolecular): Some examples

☐ Ester hydrolysis

$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$

The above reaction is a pseudo-first order reaction

However, alkaline hydrolysis of ester is a second order reaction

$CH_3COOC_2H_5 + HO^- \rightarrow CH_3COO^- + C_2H_5OH$

☐ Inversion of cane sugar (sucrose)

$C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6$ (glucose & laevulose)

Second order reaction: Some examples

☐ $H_2 + I_2 \rightarrow 2HI$

☐ $2HI \rightarrow I_2 + H_2$

Third order reaction: Some example

$2NO + Cl_2 \rightarrow 2NOCl$

Many of them are very important reactions. It is also called pseudo-unimoleculer. You have seen

$A+B \rightarrow P$…………………(6)

In equation (6), 1 mole is involved. That is why it is called unimolecular and by chance, it is also first order also. We have explained in terms of first order.

Now, let us see ester hydrolysis. Ester is a substance that is produced from a carboxylic acid and alcohol by elimination of water. It is a condensation reaction between a carboxylic acid and an alcohol, okay. So, ester, when it is hydrolysed in water (water is present in very large excess) and in that case, it is decomposed again to acid and alcohol. As water is present in a large excess, that is why, even if it is a bimolecular reaction or second order reaction, but still it is a pseudo-first order reaction and it is only dependent on the concentration of the ester. But this same reaction can be made a second order reaction. If some alkali is there it can be made alkaline hydrolysis. In that case, alkali is taking part. Alkali is not excess, water is excess. But alkali is present in low concentration. This is acting as catalyst (alkaline hydrolysis). Then, this reaction is no more pseudo-first order reaction. In this case, it is second order reaction.

There is another example. In another solvent if you want to do hydrolysis, some water is required. Lysis means, breaking. Like photolysis, using photon you are breaking something. In thermolysis, by using heat you are breaking something. In electrolysis, by passing electricity you are breaking something. So, lysis means breaking. Hydrolysis means, it is breaking up some molecules by using water. So, here you see, by using water, you are breaking this molecule. Now, if you want to break this molecule in another solvent, it is not water you use little amount of water. In that case, water is not in large excess. In that case, it will not be in pseudo-first order. In that case, you also have to consider water concentration. In that case, it will again be bimolecular or it may be second order reaction. So, depending on the condition it will vary.

Now, let us see another important reaction. It is the inversion of cane sugar. You know, cane sugar is sucrose.

$C_{12}H_{22}O_{11}+H_2O \rightarrow 2C_6H_{12}O_6$ (glucose and laevulose)…….(7)

By polarimeter, you can measure the optical rotation. You may not be very familiar. But people from chemistry background are very familiar with this reaction. By starting with dextrorotated molecule you can get back levorotated molecule. That is why it is called inversion of cane sugar. You are getting molecules which is glucose and laevulose. So, these 2 molecules, finally we will give the inversion (means optical rotation will be changing). Now, let us see second order reaction.

$H_2+I_2 \rightarrow 2HI$……………..(8)

$2HI \rightarrow I_2+H_2$……………..(9)

You see, I have given this example for chemical equilibrium. I have said that hydrogen and iodine, in gas phase reaction produces hydroiodic acid (444°C). Both are present in gas phase. So, you will get some percentage conversion if you allow the equilibrium. Now, if you start with HI also you will get H_2 and I_2. This is not in this chapter, but just I am telling. So, it is a bimolecular reaction. At the same time, it is a second order reaction. Here only 1 species but 2 molecules are involved. That is why it is also bimolecular reaction.

Third order reaction is there, but it is not very common.

$2NO+Cl_2 \rightarrow 2NOCl$…………….(10)

Reaction represented by (10) is an example of third order reaction. This is also termoleculer, because 3 molecules are involved; two NO molecules, one Cl_2 molecule. So, it is also third order reaction and termoleculer reaction. There are many examples. Only a few examples are shown.

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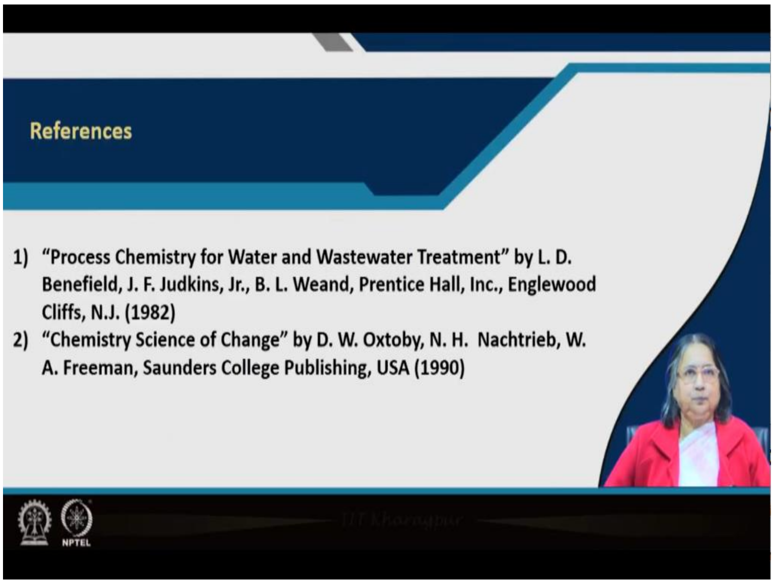

References

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)

Now, for this concept, you can get from same books that I mentioned in the earlier lectures,. You can read more. Thank you.