Environmental Chemistry and Microbiology
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Module - 4
Lecture - 16
Chemical Kinetics - Reaction Mechanism (Part-A)

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 Civil Engineering Department of IIT Kharagpur. We have divided this course into 2 parts. The first part is Environmental Chemistry. It will be covered by me and the second part is environmental microbiology. It will be taught by Professor Sudha Goel.

Now, in our module 1, we have discussed about the acids, bases and salts. In Module 2, I have discussed about chemical equilibrium; and in the module 3, I discussed about chemical kinetics. I have told about the reaction rate; reaction order; how to determine the reaction order; and also I discussed about the differential rate law and integrated rate law. In this lecture, I will cover the environmental chemical kinetics under environmental chemistry and the mechanism of reactions. This is the part A and it is the lecture 16.

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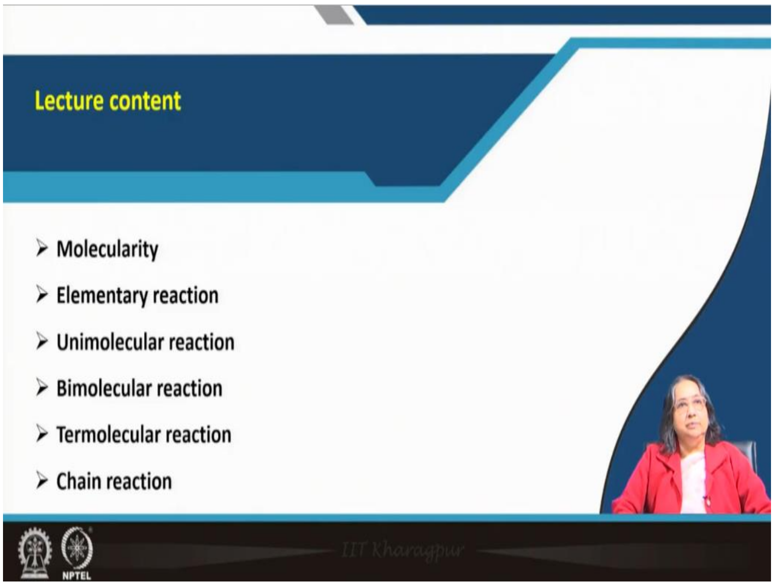

Now, the current lecture content is molecularity, elementary reaction, unimolecular reaction, bimolecular reaction, termolecular reaction and chain reaction. You all know that in the general way, we show a reaction by balanced equation, but it is very important to know the detailed mechanism of the reaction. To know the detailed mechanism, we need to have the idea on these topics that I just mentioned.

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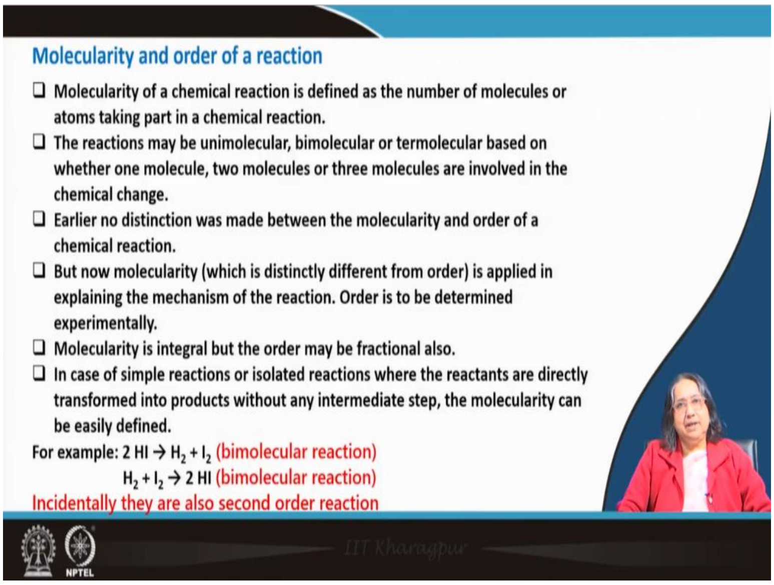

Now, what is the molecularity and order? What is the difference between the molecularity and order of a reaction? By molecularity of a chemical reaction; usually we mean the number of molecules that is reacting in a balanced equation. In that sense, the reaction may be unimolecular, where only 1 molecule is reacting. Then it can be bimolecular, where 2 molecules are reacting. It may be termolecular, where 3 molecules are reacting. Earlier, we did not distinguish between the molecularity and order of a chemical reaction. But now, after the discussion of chemical kinetics in the module 3, you all know that molecularity and order are not the same. We apply the term molecularity to explain the mechanism of a chemical reaction. But on order, we have no control; it is the experimentally determined parameter and it can be a fraction also, it can be an integer also. But molecularity is always an integer. Now, in case of simple reaction or isolated reaction or elementary reaction where the reactants are directly transformed into products without any intermediate step, molecularity can be easily defined. Say for example, consider the simple reaction of decomposition of hydroiodic acid (1).

$2HI \rightarrow H_2 + I_2$……….(1)

This is hydroiodic acid decomposition, where 2 molecules of hydroiodic acid are producing 1 molecule of hydrogen and 1 molecule of iodine. It is very simple here to tell because 2 molecules are involved, so you can easily tell that this is a bimolecular reaction. But if you see the opposite reaction (2) where 1 molecule of hydrogen is combining with 1 molecule of iodine and produces 2 molecules of HI.

$H_2+I_2 \rightarrow 2HI$…………………(2)

If you see this reaction (2), then also you can tell that opposite reaction is also a bimolecular reaction. But incidentally, it is also second order reaction. But it is not necessary that molecularity and the order will be same. It may be different also. That, we will discuss in this lecture.

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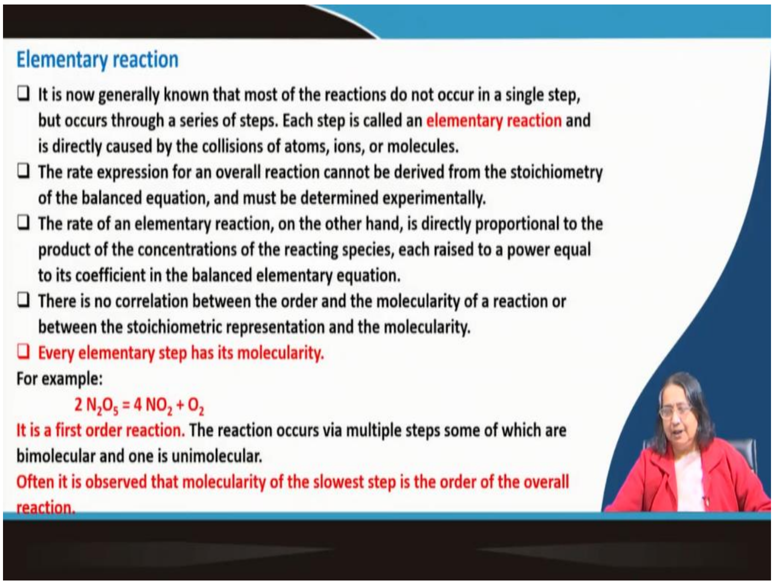

What is elementary reaction? It is generally known that most of the reactions do not occur in a single step. In our school days we never bothered about the mechanism of a reaction. We only have shown the balanced equation. But now, while talking about the mechanism, we must consider the different steps. Most of the reactions do not occur in a single step, but occurs through a series of steps. Each step is called an elementary reaction and is directly caused by the collisions of atoms, ions or molecules.

We all know that a reaction cannot occur unless there is the collision and during the collision it must have a particular threshold energy i.e., activation energy. So, when any elementary step occurs, it has to fulfil that condition. Now, the rate expression of an overall reaction cannot be derived from the stoichiometry of the balanced equation. Unless we know the order, we cannot write the rate expression. That is why, order is important and to know the order, we have to do the experiment.

Each step is called the elementary reaction and the rate of elementary reaction on the other hand is directly proportional to the product of the concentrations of the reacting species. That means, in elementary steps, it is very easy to find out the molecularity of that particular elementary step. So, if we see the balanced elementary equation, then we can easily find out the rate expression for that particular elementary equation (each term raised to a power equal to its coefficient in the balanced elementary equation). However, there is no correlation between the order and the molecularity of a reaction or between the stoichiometric representation and the molecularity.

Now, let us see another example (decomposition of nitrogen pentoxide into NO_2 and oxygen).

$2N_2O_5=4NO_2+5O_2$…………………(3)

You can see that it is a balanced equation (3). You can also see here that the stoichiometry is 2. You can easily tell that it is a bimolecular reaction. But if you tell that this is a second order reaction, then you are not correct. Experimentally, when we find out the order, we see it is a first order reaction. Why it is so? Why it is not matching? It is so because the reaction occurs by multiple steps, some of which are bimolecular and one is unimolecular. So, all steps are not occurring at equal speed. That is another thing. Some steps are slow and some steps are fast. So, how will you determine the molecularity and the order? Order experimentally determined. But how will you tell the molecularity? Often it is observed that molecularity of the slowest step is the order of the overall reaction. So, slowest step is a very important term to tell about the mechanism of a particular reaction. I will tell you later, what does it mean?

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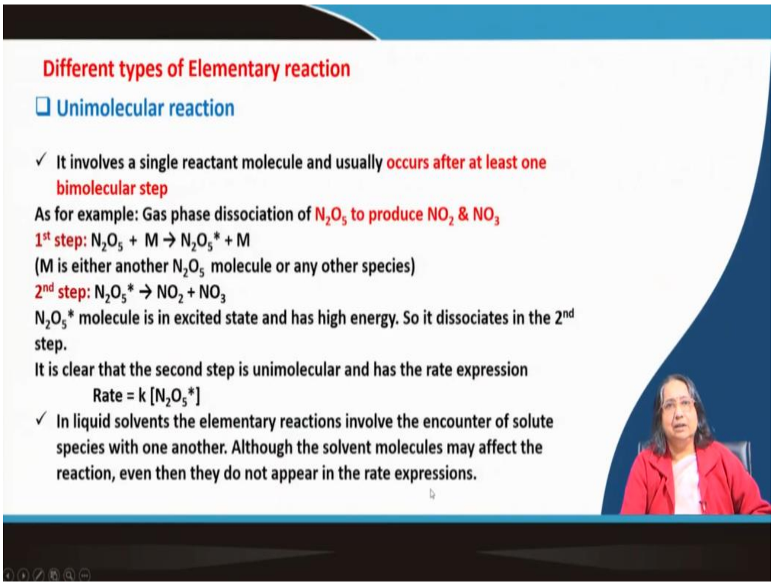

What is the elementary reaction? It is the slowest step. What does it mean? I will give you some idea. Say for example I am going from Kharagpur to Delhi. But to go from Kharagpur to Delhi, I cannot go directly there like same as the reaction, What I have to do? First, I have to go to Kharagpur station by taxi or something. Then, from Kharagpur station, I have to catch a train to go to Kolkata. Then, from Kolkata airport, I will catch a flight to go to Delhi. Now, say for example, in this journey, one step is very slow. Say for example, it is a very slow-moving train going from Kharagpur to Kolkata. It takes maybe 10 hours to go. When you catch the flight to go to Delhi, it takes one and a half hours. So, the slow step is nothing but the slow-moving train going from Kharagpur to Kolkata. Now, altogether it is taking too much time. Now, if you want to go fast, then which step you have to consider mostly? You have to consider the slow step. If you want to go fast, you have to make slow step fast. So, you have to either go by a car or you have to go by a fast-moving train, so that it takes only 1 hour time. And then, you can say I can reach Delhi in a very small time period. So, it means, the slowest step is the governing factor to tell you whether the overall process is fast or slow. Same thing is also followed in case of chemical reactions.

Now, I will tell first what are the different molecularity. You have heard of unimolecular reaction. So, what is uni? Uni means 1. So, unimolecular reaction involves a single reactant molecule and usually occurs after at least one bimolecular step. Why it is written "usually occurs after at least one bimolecular step"? Say for example, there is 1 molecule. So, to go for some reaction, if it is just 1 molecule, it will not be involved not in reaction. So, to take part in the reaction, it must collide with some other molecule, maybe with similar molecule or with a different molecule. Otherwise, it will not go for reaction.

Let us consider the gas phase decomposition of N_2O_5 into NO_2 and NO_3.

$N_2O_5+M \rightarrow N_2O_5^*+M$………………….(4)

$N_2O_5^* \rightarrow NO_2+NO_3$…………………….(5)

To do this decomposition, N_2O_5 must collide with some other species (it maybe the same molecule or something else). So, when it collides with sufficient energy, then what will happen to the original molecule? It will go to some excited state. And when it will go to excited state it will decompose into NO_2 and NO_3. We know that excited molecules cannot stay for long time. To show the excited molecule, we use the star sign. So, what we have seen that unimolecular reaction is following a bimolecular reaction. In the first step 2 things are there, N_2O_5 and M. So, it is a bimolecular reaction. In the second step, it is a unimolecular reaction because it involves a single reactant and usually occurs after at least one bimolecular step. The second step is unimolecular and has the rate expression like this:

Rate=k[N_2O_5*]…………..(6)

Now, here it is a gas phase reaction. So, it is colliding with another molecule or it may be colliding with something else. But in liquid solvents, the elementary reactions involve the encounter of solute species with one another. So, in solvent system, it is possible that 2 ions or 2 molecules or whatever, they can encounter. Sometimes, solvent molecule can affect the reaction, but we already we have learnt that when it is solvent molecule, then it will not come in the rate expression. So, accordingly you have to write the rate expression.

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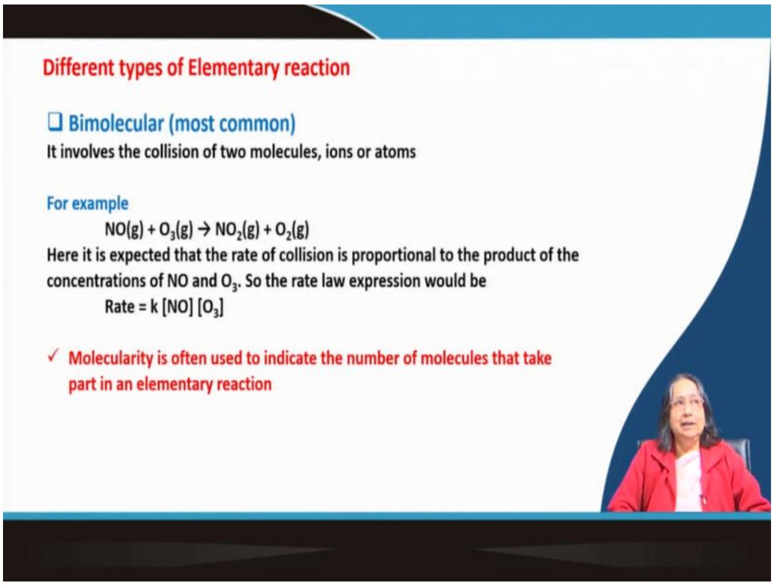

Now, let us see bimolecular reaction. Bimolecular reaction is most common. We have already seen that the decomposition of HI to hydrogen and iodine; or the reaction of hydrogen and iodine to form the hydroiodic acid are both bimolecular reactions. Apart from this many other reactions are also bimolecular reactions. Say for example reaction of NO with ozone to form NO_2 and oxygen. Here it is expected that the rate of collision is proportional to the product of the concentration of NO and O_3. As there are 2 species here, so, it is very simple to write the rate expression:

Rate=k[NO][O_3]…….(7)

Molecularity is often used to indicate the number of molecules that take part in the elementary reaction. For elementary reaction, to tell the molecularity is very easy.

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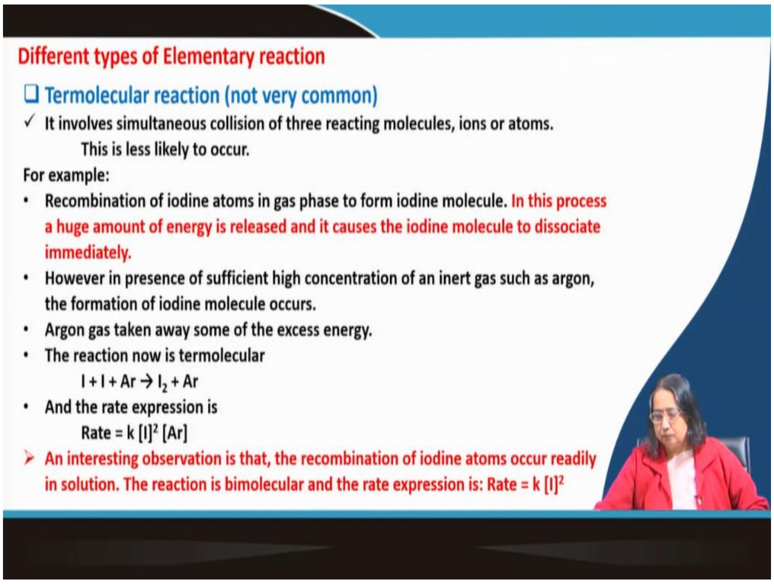

Now, let us consider the termolecular reaction. Ter means 3. It is also not very common. I visualise in this way. Say for example, two people are running in a particular corridor. So, when two people are running, there is enough chance that they will collide with each other. But if there are three people running, it is not very easy to think that, at a particular time, three of them will come at a particular spot to collide. That is nothing but the termolecular reaction. Let us see the example of recombination of iodine atoms in gas phase to form iodine molecules. In this process, a huge amount of energy is released and it causes the iodine molecule to dissociate immediately. That means, this reaction theoretically is possible, but it will not occur because, once it is formed, then it releases a huge amount of energy and that energy will cause them to fly apart. However, in presence of sufficient high concentration of inert gas like argon this reaction can occur because then, the argon will take out some of the energy.

$I+I+Ar \rightarrow I_2+Ar$…………(8)

The reaction now can occur and it is nothing but a termolecular reaction.

The rate expression will be :

$Rate=k[I]^2[Ar]$…………..(9)

It is shown here that argon is necessary or any inert gas is necessary, so that excess energy will be taken away. But if the reaction is done in some solution, then what will happen? Then, solvent can take out excess energy and then, the reaction will occur. The reaction is bimolecular and the rate expression is:

$Rate=k[I]^2$……………(10)

So, termolecular reaction is possible. But it is not very common like the bimolecular reaction.

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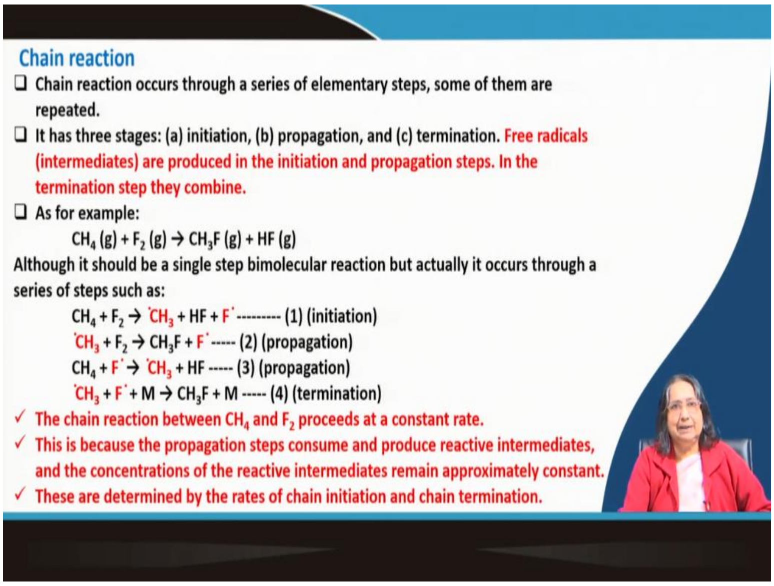

Now, let us see the chain reaction. In many environmental segments, we see that chain reaction is going on. The specialty of chain reaction is that it occurs through various steps. First step is initiation, then propagation and then termination. During these steps of initiation and propagation, free radicals and which are nothing but intermediates are produced. Finally, in the termination step, they will combine and they will terminate the reaction. Let us see an example. For example, in gas phase methane reacts with fluorine and produces CH_3F and HF.

$CH_4(g)+F_2(g) \rightarrow CH_3F(g)+HF(g)$…….(11)

But is it occurring in a single step or it is occurring through multiple steps? Now, if it is a single step reaction, then we can tell easily that it is a bimolecular reaction. But actually, it occurs through a series of steps such as:

$CH_4+F_2 \rightarrow {}^{\cdot}CH_3+HF+F^{\cdot}$…………..(12) (Initiation)

${}^{\cdot}CH_3+F_2 \rightarrow CH_3F+ F^{\cdot}$ …………..(13) (Propagation)

$CH_4+ F^{\cdot} \rightarrow {}^{\cdot}CH_3+HF$…………….(14) (Propagation)

${}^{\cdot}CH_3+F^{\cdot}+M \rightarrow CH_3F+M$………..(15) (Termination)

In the initiation step (12), you can see that methyl radical and another radical ($F^{\cdot}$) is generated. The dot (.) means free radical. That means it has unpaired electron. Now, these free radicals are very reactive and they can react with something else again to form another free radical. The next step is propagation. Propagation means, there are many steps where other free radicals are being generated ((13) and (14)). Now, you see that in the step (15), the free radicals are recombined and then it is producing some compound. So, there is no more free radical left. This way, it will go on continuously producing more and more free radicals and it takes place in various steps. So, the important thing about it is that, the chain reaction between methane and fluorine, proceeds at a constant rate. Why? It is so because the propagation steps consume and produce the intermediates. These free radicals are called intermediates and the concentrations of the reactive intermediates remain approximately constant. That is why the rate is also constant. These are determined by the rates of chain initiation and chain termination. You will see this when I will discuss about the radioactivity. There, free radical is not generated, but there, some daughter elements are generated and you will see that radioactive equilibrium.

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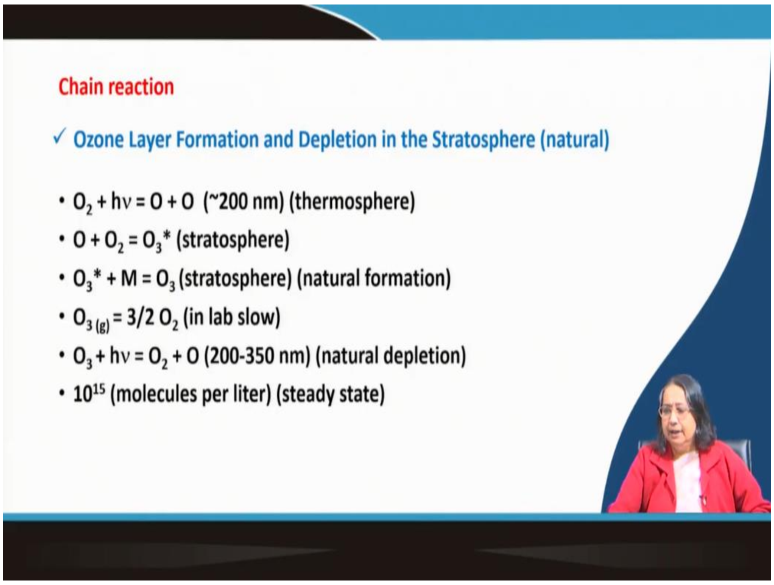

I told you that in nature also chain reaction is happening. You know ozone layer is present in the stratosphere. Naturally it is produced in the stratosphere. How naturally it is produced? It is produced by a series of reactions:

O_2+hν=O+O (~200nm) (thermosphere)………………..(16)

O+O_2=O_3* (stratosphere)……………………………….(17)

O_3*+M=O_3 (stratosphere) (natural formation)…………(18)

O_3(g)=3/2O_2 (in lab slow)……………………………….(19)

O_3+ hν=O_2+O (200-350nm) (natural depletion)…………(20)

In the stratosphere there is oxygen and then, high energy photon is coming and it is breaking it into O and O (16). It is 200 nanometre from the thermosphere. So, in the thermosphere, it is happening. Now, this O is combining with oxygen to form the ozone and it is happening in stratosphere (17). Now, in case of ozone, you see it is excited molecule (*). It is coming down to the ground state by colliding with something M (M is anything). So, it is coming to the ground state. This is a natural formation. So, I have shown 3 steps to explain the natural formation. Now, you forget (19). This is a reaction that happens in a lab. Ozone can form the oxygen, but it is a slow reaction. Now, ozone can react with photon (20). But you can see here, this is the light of 200 nanometre. This light wavelength (200 to 350 nm) means higher wavelength. So, energy is less. So, what is happening? Ozone forms oxygen and O. So, natural depletion. So, formation and depletion are going on naturally to maintain this concentration of ozone in the atmosphere. At a steady state 10^{15} molecules of ozone per litre is maintained. So, this is maintained and it is protecting us from the UV light. We all know that the ozone layer is a protective layer. It is protecting us from the UV light. Now, what is happening?

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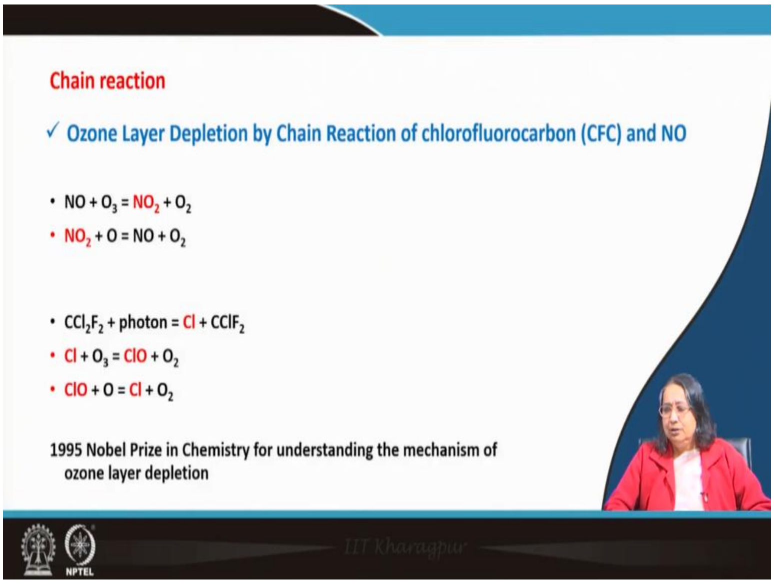

Due to some manmade activities, this ozone layer is getting depleted. How it is going on?

$NO+O_3=NO_2+O_2$……………..(21)

$NO_2+O=NO+O_2$……………….(22)

CCl_2F_2+photon=$Cl+CClF_2$…….(23)

$Cl+O_3=ClO+O_2$…………………(24)

$ClO+O=Cl+O_2$…………………..(25)

There are nitrogen oxides (NO, nitric oxide). It is reacting with ozone to form some intermediates. That intermediate again is combining with oxygen to form the NO and O_2. It can go on as a chain reaction.

Finally, you see, ozone is decomposed to oxygen (22). So, this is the manmade activity that is going on. Another manmade activity is that chlorofluorocarbon ((23)-(25)). From the refrigerators and many sprays, chlorofluorocarbon is coming. It reacts with photon and produces the free radical (chlorine free radical). This free radical can destroy the ozone through a series of chain reactions. So, this is the reason that ozone layer is depleted and it is making ozone holes in many places. Then the UV light is coming to the earth and it is creating lot of hazards for our health. The mechanism of ozone layer depletion was first described by 3 scientists and Nobel Prize in 1995 was given for this (for the understanding of the mechanism of ozone layer depletion). Similarly, we know about photochemical smog formation. We know that in the industrial areas, a brown haze is formed, which irritates our eyes and creates breathing problem. That is also like a cyclic chain type of chain reaction and it is producing NO_2, several types of nitrogen oxides (NO_x). It is a very dangerous thing. So, there also, if you go through that photochemical smog formation, then you will see that these types of reactions (chain reaction) are going on.

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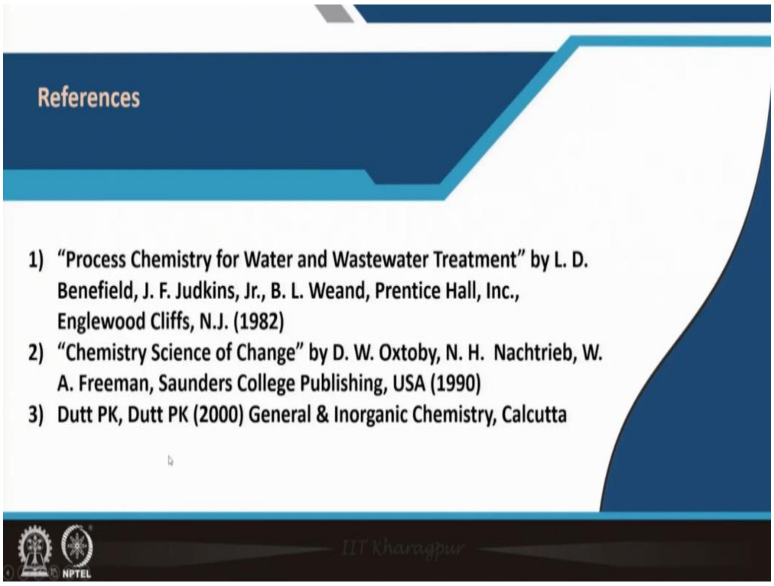

You can have all the things that I discussed in the references written in the last slide in a more elaborative way. So, you can read these 3 books.

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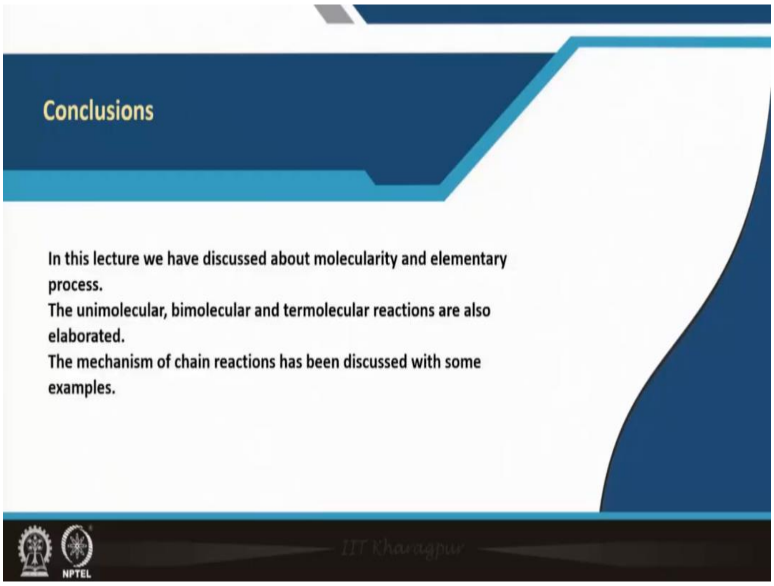

So, in this lecture, what we have covered? We have discussed about the molecularity and elementary process. We have also explained that what is unimolecular reaction, bimolecular reaction, termolecular reaction and also chain reaction. Thank you.