Fundamentals of Combustion

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Lecture - 20
Fundamental of Combustion Kinetics – Part 1
Global and Elementary Reactions

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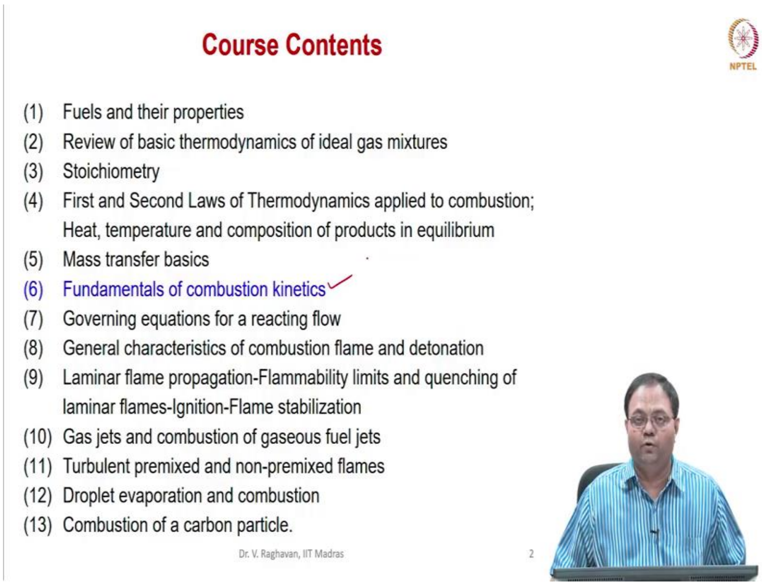

Next topic is Fundamentals of Combustion Kinetics, chemical kinetics. So, this is very important to understand how fast the reaction is going to be completed.

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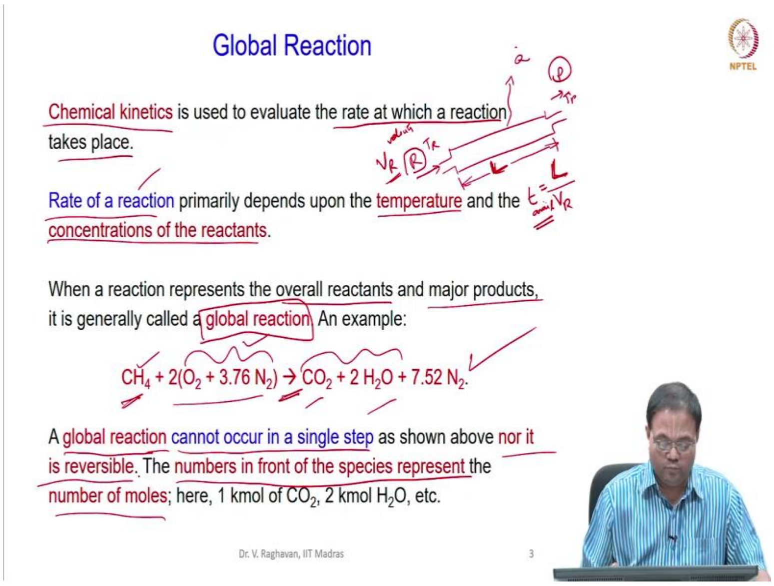

So, chemical kinetics or combustion kinetics is used to evaluate the rate at which a reaction takes place. It is very important for us.

For example, if there is a combustion chamber, so, this inlet and there is an outlet. So, the products leave here, and reactants enter. So, some dimension we will keep for this, say L.

So, reactant let us pre-mix the fuel and oxidizer, that reactants enter at some temperature say T and the product leave at T product. So, some heat transfer is allowed to take place from this control volume.

Now, if L is the length of the combustion chamber, these reactants are entering at some velocity, say, V_R is the velocity of the reactants. So, I want to burn more amount of reactants, more amount of fuel, so, for that we need to supply enough amount of oxidizer. So, the reactant is supplied at a particular flow rate or a velocity say V_R and reaction is expected to be completed within this length.

So, if you do not have an idea of whether the reaction will be completed within this length; that means, the time available for the reaction to complete is this length divided by V_R so, that is the velocity.

So, this is length in m and this is the time scale time for time available I would say. So, time available for the reaction to complete is the length divided by V_R velocity at which the reactants are passed.

So, this is the time available, the reaction will be completed within this time, if not, I have to either increase the length or reduce the velocity. If I do not do this, the time available will not be sufficient for the reaction to complete, so, the product will not be formed completely and the reactant may come out.

So, the rate at which the reaction takes place is very important. At least we should have some idea or else know we cannot construct the combustion chamber; proper dimensioning cannot be done.

So, this study of chemical kinetics is very important in determining the rate at which a chemical reaction will be complete and we have to understand several things here. How a particular fuel is going to react and what are the factors influencing the chemical kinetics and so on.

So, the rate of reaction basically depends on two things, temperature and the concentration of the reactants. If you have good volume of reactants and a good temperature, so, if the both are available, then the rate of reaction will be sufficiently fast. So, we will see one by one.

First of all, let us take some reactants like say methane and air combustion. So, when a reaction represents the overall reactants like methane is the fuel, air is the oxidizer and products are the major products, If I write a reaction like this it is called global reaction.

In the sense I know what are the reactants and I write this is in the mole base like 1 kmol of methane reacts with so much kmol of air forming 1 kmol of carbon dioxide, 2 kmol of water vapor and so on.

So, this global reaction will give you an idea of the overall mechanism representing the reactants and the major products. However, this global reaction cannot occur in a single step. I have written in a single step like this. So, reactants forming products in a single step I am writing this.

But it is impossible for the reaction to occur like this. One more thing is you can see this arrow, this is one directional arrow, that means the reactants can form products but products cannot form (we have already discussed this the product cannot form reactants) reactants like this, CO_2 and H_2O if you put in a combustion chamber it will not produce the required reactants. So, that mean that is impossible.

See, you can even think about this, it is not possible because this has several steps into account. It is not going to complete in only 1 second, that is it has some definite time for completion and it has several steps. So, methane CH_4 is not going to directly convert into CO_2 and H_2O.

So, the number in front of the species represent the number of moles. So, here 1 kmol of CO_2, 2 kmol of H_2O etcetera, so, that means we are not talking about a molecular level.

See, what is 1 mole? Several number of molecules contribute a mole. So, we are talking about several molecules present in this particular scheme, reaction scheme.

But if you can write the reaction in molecular level then only we can say that can happen in one step or not. So, global reaction cannot happen in one step, single step that is for sure and we have to understand and it is not reversible.

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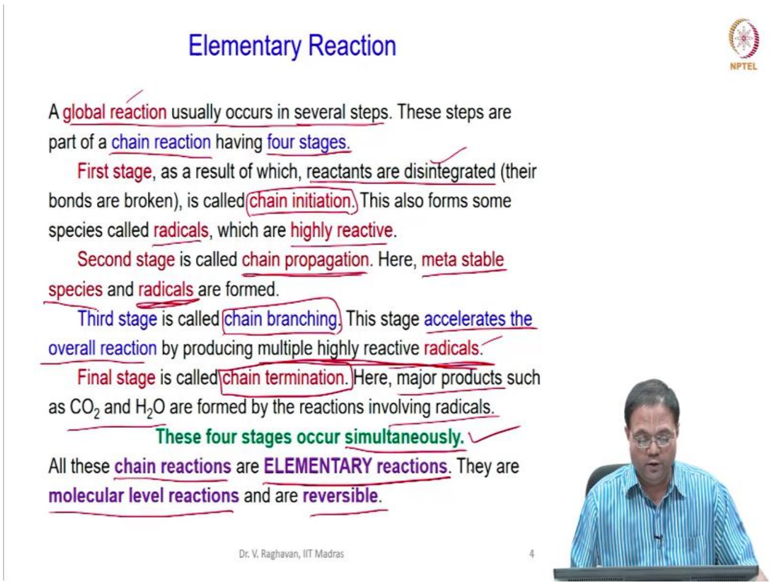

So, how it occurs? It occurs in several steps like global reaction usually occurs in several steps. These steps are part of a chain reaction which can be divided into four stages. So, what happens is first the reactants should break for example, O_2 should break to O atoms, CH_4 should break into say CH_3, H and so on CH_2, H_2O.

So, several ways the reactants are going to be disintegrated because the bond should be broken. So, in one step, only one bond can be broken and one bond can be formed and so on. So, in that case, if the reactants collide with each other, they can lose one of the bonds and form one of the bonds and so on.

So, this initiation step is the first step during which the reactants are disintegrated and what is formed are called radicals or other some species which are formed due to that first step, initiation step which is much reactive, highly reactive than the reactants themselves.

Now, the second stage is called chain propagation. The chain has been initiated first and this chain reaction is now propagating to the next step producing two types of species one is called meta stable species name itself suggests meta stable is not completely stable.

Stable species say CO_2, H_2O they are stable species much stable, but meta stable species are not so weak, but they are not strong also, they are meta stable. So, they can under certain conditions, react with some other species to form products or some other species.

Then again, the highly reactive species called radicals are also formed in the chain propagation reaction. So, chain propagation keeps the reaction mechanism live. Next, the third stage is called chain branching. Actually, this is a very important stage where multiple radicals are formed.

For example, in chain propagation, only one radical may be formed. Let us define radical later, see that in detail but in the chain branching step multiple radicals are formed. More than one radical can be formed.

Once the radical concentration increases, the reaction rate is accelerated the overall reaction rate is accelerated. So, it may also end up in explosive nature. That means much faster reaction can happen. This is called chain branching step or stage.

The final stage is called chain termination step where the major products stable products like CO_2 and H_2O are formed due to the reaction between radicals. So, actually even though we can categorize this in four stages all occur simultaneously.

The reactions which are contributing to the chain reactions mentioned above, the four steps or stages of chain reactions they are called elementary reaction as opposed to the global reaction, they are called elementary reactions. They are molecular level reactions, they can occur in one step plus they are reversible also.

So, the global reactions cannot occur in one step, they are not reversible. Elementary reactions are molecular level reactions, global reactions are molar level reactions and elementary reactions are reversible and they can occur in single step.

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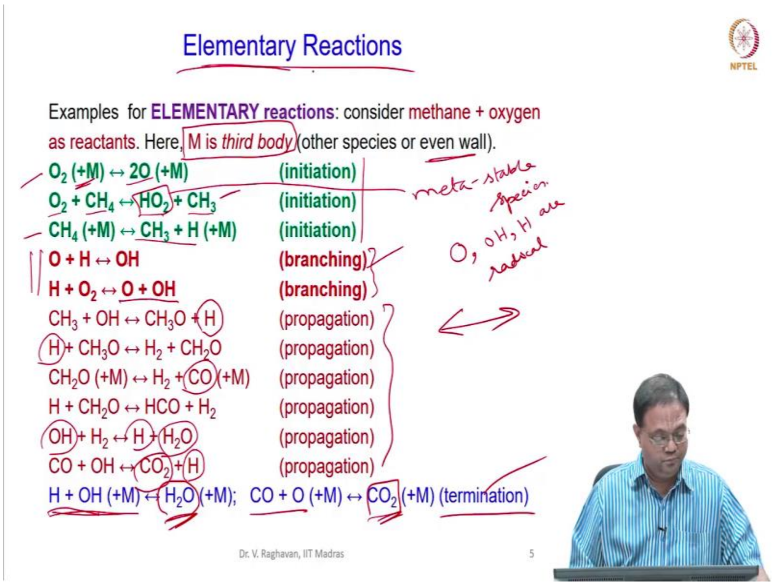

Now, I have given some elementary reactions here and also indicated the chain reaction stages. See for example, as I told you oxygen breaks. Now, hopefully understand that here there is a contribution from a third body called M, normally M represents third body, it may be other species or a group of other species.

See the oxygen can collide with any other species like C_1 or even some partially formed products, so, CO, CO_2 anything can be used to collide with oxygen.

So, this M can be anything but that particular species is heavier and they may be the walls also, even the wall of the reactor. So, that will contribute to just breakage of the bonds. For example, O_2 breaks to 2O.

Now, we can see that O_2 with CH_4 they are reactants basically can form HO_2 and CH_3 so, one of the methane H is now disintegrated and CH_3 is formed and that H reacts with the O_2 to form HO_2. This HO_2 is the meta stable species I am talking about, this is a meta stable species. This O is a radical.

So, actually O, OH, H are radicals they are very reactive species. This HO_2 is a meta stable species which is formed here. Again, CH_3 should undergo some more disintegration so, CH_3 one more H will break to form CH_2 and CH will form and so on.

So, this is one step where the methane is broken into CH_3 plus that H is contributed to formation of HO_2. Similarly, CH_3 now breaks and so on. So, several reaction steps are there in this I have just listed this few. Similarly, this also can happen.

So, CH_4 with the third body can produce CH_3 plus H and so on. So, when the reactants are disintegrated, initiation steps are got. Now, chain branching as I told multiple radicals are formed. So, $H + O_2 \leftrightarrow O + OH$, both are very reactive.

So, similarly OH splitting into O and H. So, we can see multiple radicals are formed or this radical is very fast, very fast chain branching reactions, this will lead to acceleration of the overall reaction rate.

Then I have several propagation steps. Propagation step you can see that one radical is surely formed here. Similarly, in this reverse reaction here I can see this. You can see O_2 CO is also a very highly reactive and we can see H etcetera. It is in the reverse reaction OH is formed.

So, when the radicals are involved, and these reactions will maintain the chain for the reaction to propagate. It may not accelerate the chain reaction as the branching reactions do but they will maintain the chain reaction and till the completion total overall mechanism is complete.

But termination reaction if you see that the radicals recombine, it is called recombination. $H + OH \leftrightarrow H_2O$, $CO + O \leftrightarrow CO_2$, they recombine to form the final products here. So, here you can see that $CO + OH \leftrightarrow CO_2 + H$, here also a final product is formed. Similarly, $OH + H_2 \leftrightarrow H + H_2O$, a final product can be formed.

When the final product is formed along with the radical that is called propagation reaction, but only if the final product is formed like this then that is a termination reaction.

So, these are the steps in the chain reaction: initiation, branching, propagation and the termination reactions and you can see that for methane, we can define say about 400-500 reactions like this and everything should be properly understood.

So, these all are reversible reactions; see the arrow here, these are reversible reactions and the molecular level reactions. So, when I say $O_2 \leftrightarrow 2O$, I indicate that one molecule of O_2 reacts to form 2 atoms of O and so on. So, everything is molecular level reaction.

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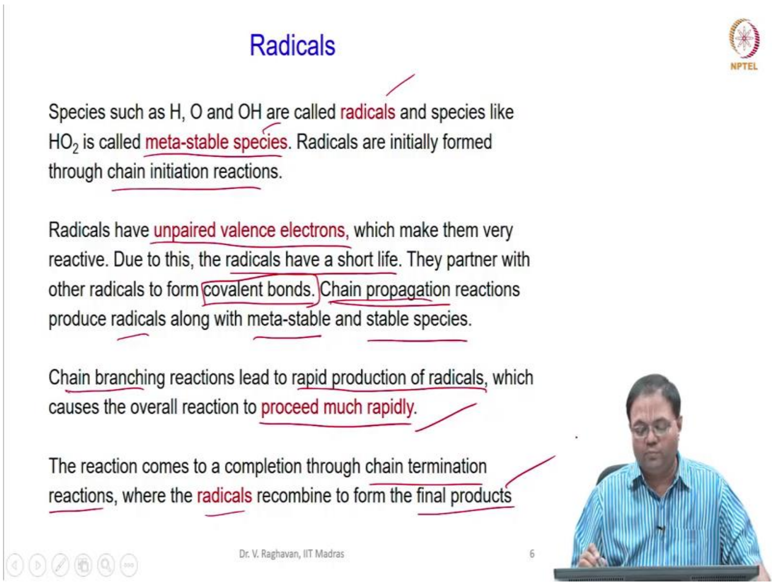

Species such as H, O and OH are called radicals and species like HO_2 are called meta-species. Radicals are initially formed through chain initiation reactions. Radicals have unpaired valence electrons which make them very reactive. These electrons are fond of reacting with the other radicals or other species. So, basically, they have very short life. They partner with other radicals and other species to form covalent bond. That is molecular level bond are formed when they react with the other species.

So, chain propagation reactions produce radicals along with meta stable species or stable species or final products also, that is very important. So, these keep the reactions running, till it completes totally.

Chain branching reaction due to rapid production of radicals produce more than one radical at a time, so that the reaction may become explosively fast or very much rapid. The reaction comes to completion through chain termination reactions, where the radicals recombined. So, two radicals when are they formed as separate radicals, they can recombine to form the final products which we have discussed.

So, the global reaction which is given here will not occur in one step. You can also see several molecules are there here and only two molecules if they want to hit each other and form products disintegrate themselves and form products that is possible, but so many molecules it is not possible to really sense.

So, this is the only mechanism, overall mechanism represented by a global reaction which gives what are all the reactants present and what are all the final product which are formed. That is the important thing here.

So, these reactions, elementary reactions are molecular level reactions and are reversible reactions several of these steps will contribute to a global reaction. So, several of these steps written in a particular order is called mechanism, reaction mechanism and that reaction mechanism will contribute to say methane-air reaction or a hydrogen-air reaction and so on. Even a simple hydrogen, oxygen reaction has about say 15-20 steps reaction steps like this.

Now, in the four chain reaction steps, initiation, propagation, branching and termination reaction, if radicals and meta stable species are formed then you can see that the chain branching reactions will be very fast and chain propagation reactions maintain the reaction by producing a particular radical or meta stable species along with the stable species. Then, the termination reactions consume these radicals to form the final products.

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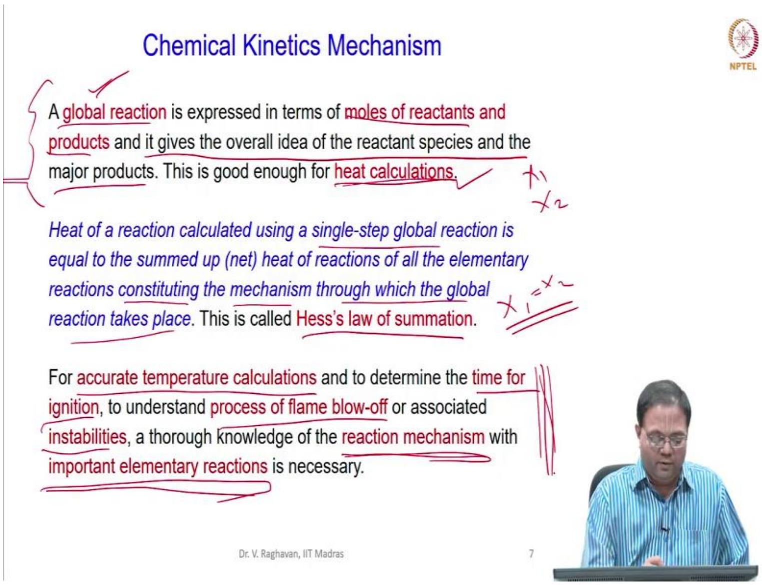

Now, chemical kinetic mechanism as I told you a global reaction which is expressed in terms of moles of reactants and moles of products. It is not going to occur in one step, and it needs several elementary reactions to define its pathway.

For example, if I say methane's oxidation, the methane oxidation has a definite pathway and several types of pathways and for that, we need to know the entire mechanism by a set of elementary reactions which will define the pathway.

Then why is global reaction is useful? because it gives the overall idea of the reactant species and the product major products which are formed. So, that is what is very important for heat calculations. When you want to calculate the heat release rate etcetera, that is what is going to be useful.

So, when you want to know what is heat release rate a single step global reaction is enough for us. Similarly, when you want to calculate the amount of air required for an amount of fuel fed into the reactor, single step reaction is enough. Now, how can you say that for heat calculation only one step is enough.

When say 400-500 steps are going to be involved in giving the mechanism of the entire reaction. This is because of this. Heat of a reaction calculated using a single step global reaction is equal to the summed up or the net heat of reactions of all the elementary reactions constituting the mechanism through which the global reaction takes place. So, you calculate the heat of reaction using a single step global reaction you will get a value say that is X1

You have a mechanism now, so, 300 steps elementary reactions, 300 elementary reactions contributing the entire mechanism and calculate the heat release from this, add and subtract them and evaluate the net heat release etcetera, so that may be X2.

Hess's law of summation says that X1 = X2. You calculate the heat based upon a single global step reaction or several elementary reactions, the result is same. So, when heat calculation is concerned you can just complete it by using a global single step reaction itself.

So, for a practical reactor design, when you want to know how much air should be supplied, what should be the product coming out so, what should be the amount of a diluent like nitrogen, how much should be supplied, what is the heat which is released during this process etcetera the global single step mechanism is enough for us. We do not need to go for the detailed mechanism with elementary reactions.

However, for accurate temperature calculation we need detailed mechanism. Even this global single step reaction can give some idea, some order of temperature, see if the actual temperature is say, 2200 K it may give a slightly higher temperature say, 2300 K or 2400 K something like that. But if you want accurate temperature calculations or to find the time for ignition, then you should go for detailed mechanisms. These are very important things.

So, time delay for example, how fast the ignition will occur or what is the time delay between the ignition source provided and the actual ignition to occur or under what conditions the flame will blow off, so, these types of instabilities are transient time dependent processes. When you want to take into account a thorough knowledge of the reaction mechanism with important elementary reactions is necessary.

Reaction mechanism can be as complicated as possible but at least we should know the sensitivity of these elementary reactions and choose important elementary reactions to constitute a reaction mechanism that will give you an idea of these factors. So, that is what is important. So, we need to know about this.

We know that when you handle several elementary reactions, your analysis is going to be complicated. Because you are going to solve several reactions together instead of just taking one reaction at a time and solving it. It is easier to do this. But if you want in several cases like this here, you need to go for some elementary reactions which will give you accurate calculations.

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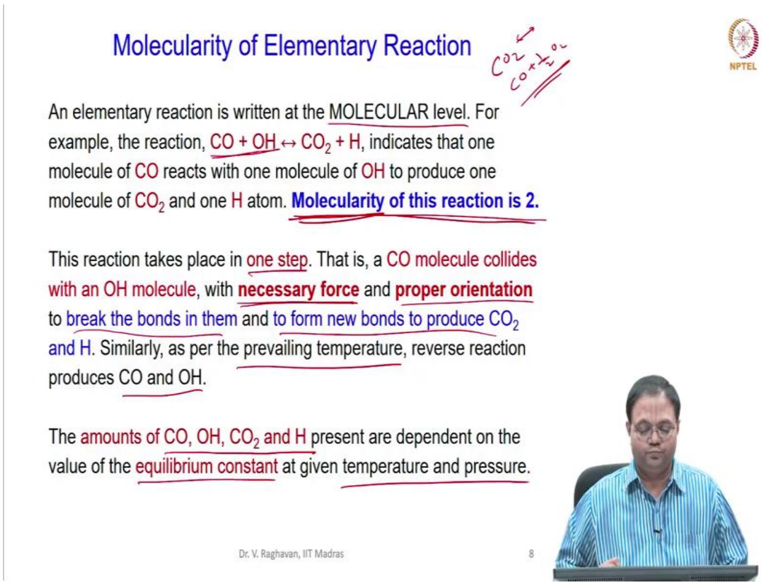

Now, molecularity of an elementary reaction. An elementary reaction is written at the molecular level as we have told that already. So, let us consider an important reaction called $CO + OH \leftrightarrow CO_2 + H$. So, this actually can be read as one molecule of CO reacts with one molecule of OH to produce one molecule of CO_2 and one H atom.

So, now if you take the forward reaction 2 molecules are involved. So, the molecularity of this reaction is 2. So, number of molecules participating in a reaction that is the molecularity. Obviously, a global reaction does not have a definition of molecularity because that is written in terms of moles.

So, I cannot say one mole of CH_4 + 2×4.76 moles of air, so, they cannot translate into molecules, that is not possible. Global reaction is not a molecular level reaction but elementary reactions are molecular level reactions. Molecularity is the number of molecules which is participating in a particular reaction.

For example, if you take this reaction $CO_2 \leftarrow\rightarrow CO + ½ O_2$, the forward reaction the molecularity is one because one molecule of CO_2 is involved and so on.

So, here also we can see that in the reverse reaction, you can say the molecularity is 2. So, this is ½ O_2, $CO + O \leftarrow\rightarrow CO_2$ and so on. So, this reaction, the elementary reaction takes place in one step.

So, when it reacts, one bond is broken and one bond is formed. That is what can happen in one collision. So, the collision should be proper, that is what I have written here.

CO molecules collide with an OH molecule with necessary force, it cannot just collide without any energy, with necessary energy and force and proper orientation to break the bonds in them and form new bonds. So, at a time one bond can be broken and one bond can be formed. So, that is possible in an elementary reaction and that is molecular level reaction what we are talking here.

So, again you can see that the similarly at the prevailing temperature, based upon the temperature, reverse reaction can also happen and CO and OH can be formed. So, this is also very important. So, under some conditions, the forward reaction will be favorable, under some other conditions, reverse will be favorable, which we have already seen in the chemical equilibrium.

So, the amounts of CO, OH, CO_2 and H present are dependent on the equilibrium constant which we have calculated. That is again a function of temperature and pressure. So, this elementary reaction can occur in a single step. It is a reversible reaction and based upon the number of molecules participating in the reaction, its molecularity is defined.

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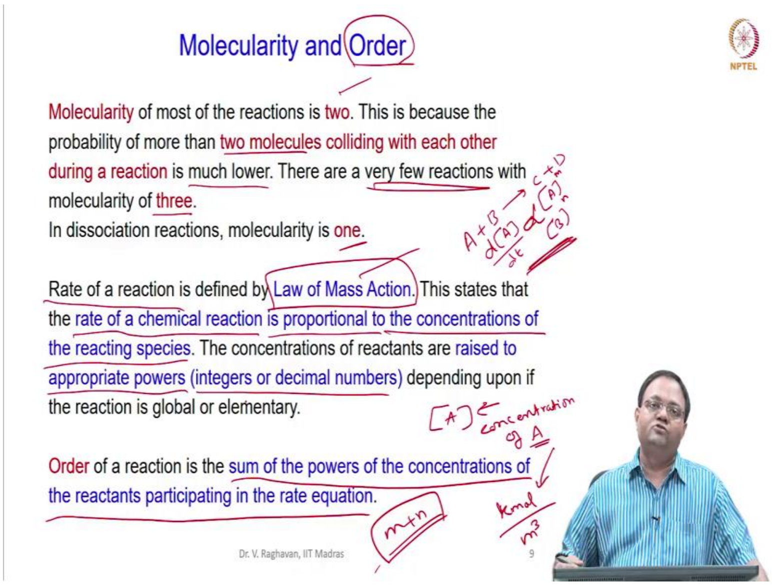

Then, what is the order? Order of a reaction, so, that is what we are going to see this order of a reaction. Molecularity of most of the reactions is two because two molecules can collide, and reaction can be favorable. Probability of more than two molecules colliding with each other during a reaction is much lower.

So, only a very few reactions of molecularity three, three molecules colliding at a time and forming species, only very few reactions are there and we can just number them. But more than 90-95 percent of the reactions are two molecules colliding with each other, that is the molecularity of those elementary reactions are two.

Now, dissociation reactions, I told you the molecularity is one. $CO_2 \leftarrow\rightarrow CO + O$, so that is molecularity is one there. Now, for defining the order of the reaction we need to know how the rate of a reaction is defined. So, how the rate of the reaction is defined?

It is defined using what is called law of mass action. What is law of mass action? The rate of a chemical reaction is proportional to the concentrations of the reacting species raised to some powers, appropriate powers. So, that is the law of mass action.

For example, if $A + B \rightarrow C + D$, I am considering the forward reaction in this elementary reaction. Then the rate of the reaction is nothing but the rate at which the concentration of a reactant reduces with time. Reactant concentration reduce and the product concentration should increase.

So, the concentration of product increases. This is proportional to the concentration of the reactants raised to some power. So, m and n are some appropriate powers. This is called law of mass action. The rate of a reaction, so, when I put say like this [A], it means concentration of A. Concentration is nothing but $kmol/m^3$.

So, concentration of A, how it varies with time? The rate of change of concentration of A with time is proportional to the concentration of the reactant species. A and B are the reactant species so, A^m, B^n. Now, these powers can be integers or decimal numbers, we have to see what are they based upon what type of reaction it is.

So, now what is order? Once you know the law of mass action, I know the reaction rate depends upon the concentration raised to appropriate powers of the reactants. So, order of the reaction is the sum of powers of the concentration of the reacting species in the rate equation. This is called rate equation.

The rate at which A reduces with time is proportional to the concentration of reactants, $d[A]/dt = [A]^m[B]^n$. We can also write the rate at which concentration of B reduces with time that is also proportional to A^m and B^n.

So, here, the order is nothing but m + n. The power of concentration of A is m, the power of concentration of B is n, the order of this reaction is m + n. So, this is what the definition of order.

So, law of mass action defines the rate of reaction as that is proportional to the concentrations of the reactant species raised to appropriate powers and the order is defined as the sum of the powers to which the concentrations are raised to.

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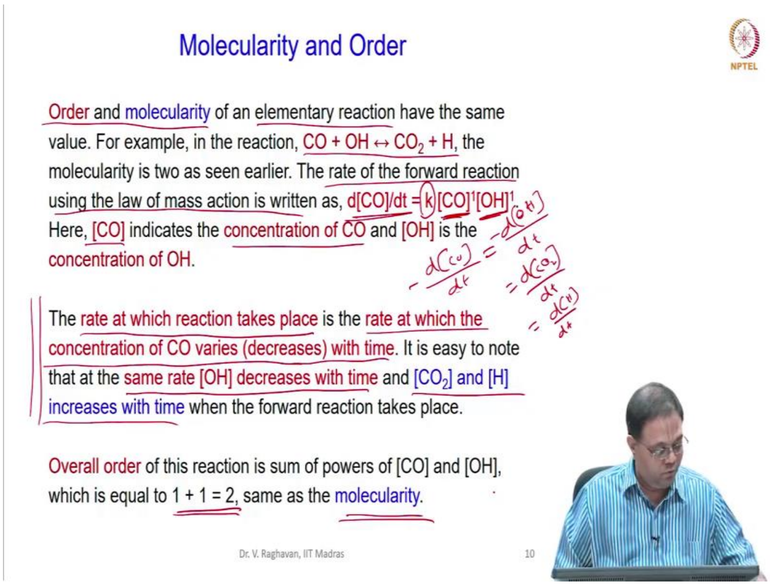

Now, order and molecularity of an elementary reaction is same. For example, CO + OH ←→ CO_2 + H, the molecularity is two, we can see that CO, OH two molecules are positive this.

When you write the rate of this reaction, let us say forward reaction, here the rate at which the concentration of CO changes with time d[CO]/dt, square bracket when I put that is the concentration of CO, so, this is the concentration of CO.

The rate at which the concentration of CO varies with time is proportional to concentration of CO raised to power 1 and concentration of OH raised to power 1, $d[CO]/dt = [CO]^1[OH]^1$. Now, this is the law of mass action. The proportionality constant is not a constant, but it is defined as rate coefficient which is k. So, k is the rate coefficient.

Now, we can see that the order of this reaction is 1 + 1 = 2, molecularity is also 2, order is also 2. So, elementary reactions, the stoichiometric coefficient here for CO is 1 stoichiometric coefficient for OH is 1 that is 1 molecule of CO, 1 molecule of OH, so, that is only used as the power to raise the concentration.

So, CO power its number of molecules and OH power number of its molecules, when you add them that will be the molecularity. So, order of the reaction and molecularity will be the same for an elementary reaction. Order of a reaction is defined from elementary reaction. It is defined for global reaction also, but molecularity is defined only for the elementary reaction.

Now, the rate at which reaction takes place is the rate at which the concentration of CO varies. Now, in this case it is a reactant, so, it should decrease with time. So, that is what we are representing like this, the rate of reaction is we can write -d[CO]/dt = -d[OH]/dt.

Both are correct because the rate at which this is decreasing, CO is decreasing, one molecule of CO if it partially consumed, then the same amount of OH should be consumed to form the products. So, we can write like this. So, it is easy to note that the OH will decrease with time and at the same rate, the concentrations of CO_2 and concentration of H will increase with time.

So, these are actually negative and this should be equal to d[CO_2]/dt which is equal to d[H]/dt, the rate at which the reactants are consumed that will be the rate at which the products are formed. So, this is the important thing we should remember.

The order of the reaction is the powers at which these concentrations are raised to in a rate equation given by the law of mass action. So, for this reaction it will be 1 + 1 = 2, same as the molecularity. Molecularity of an elementary reaction and order of an element reaction is the same.