# Advanced Thermodynamics and Combustion
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## Module - VI
## Chemical Kinetics
## Lecture - 24
## Reaction Mechanisms (Part I)

Dear learners, greetings from IIT, Guwahati. We are in the MOOCs course Advanced Thermodynamics and Combustions, module - 6 that is Chemical Kinetics.

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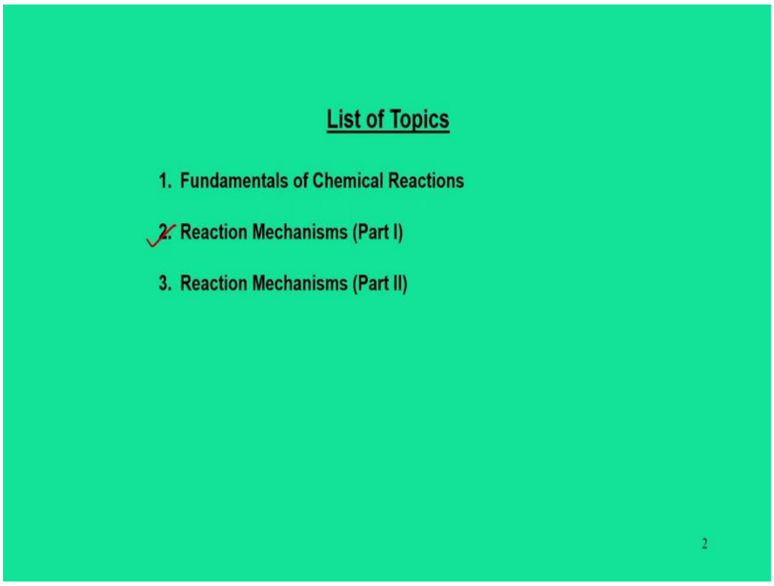

**List of Topics**

1. Fundamentals of Chemical Reactions
2. ✓ Reaction Mechanisms (Part I)
3. Reaction Mechanisms (Part II)

In the previous lecture we covered the fundamental chemical reactions and tried to find out what are the different reactions that are possible. Now, with our next view point, we are trying to study the reaction mechanisms and in some particular specific mechanisms hydrogen, oxygen systems then nitric oxide formations, carbon monoxide formation, all these things.

And in fact, typically these are the reactions that occur when the fuel reacts with the oxygen or air. But before you go to those aspects, let us understand some of the theoretical aspects of reaction mechanisms. And I call this theoretical reaction mechanisms is the part 1 and in the part 2 of this reaction mechanism we are going to cover some practical examples of certain reactions, how it occurs in reality. So, let us start the first one that is reaction mechanism part 1.

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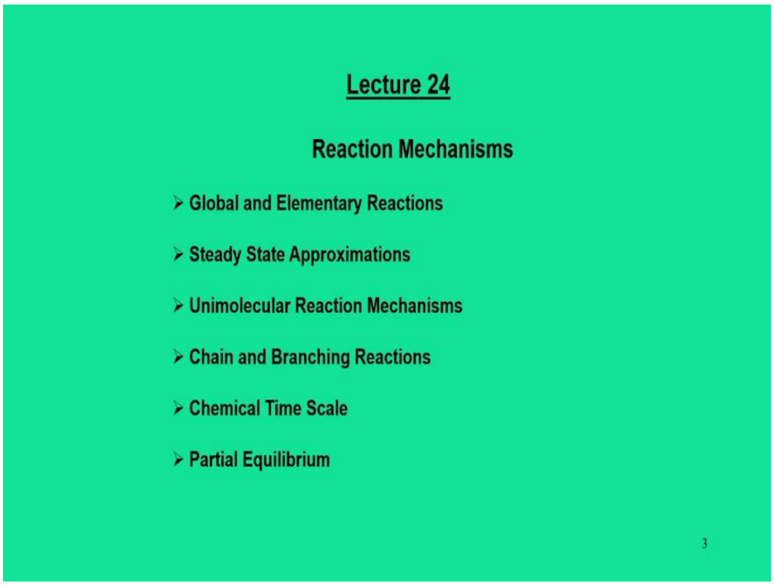

**Lecture 24**

**Reaction Mechanisms**

- Global and Elementary Reactions
- Steady State Approximations
- Unimolecular Reaction Mechanisms
- Chain and Branching Reactions
- Chemical Time Scale
- Partial Equilibrium

And in this lecture, we are going to brief out the global and elementary reactions which we covered in our previous lecture. Then here onwards we are going to do some approximations, first approximation is steady state approximations and this will tell you, I mean how you are going to proceed.

Normally, the reaction systems are very fast and it is in transient and for such transient situations if I want to do a realistic approximation, how I am going to do that. So, that is known as steady state approximations.

Now, with this view point if we want to apply that steady state approximations for uni-molecular system, then how it should look like and based on that we can formulate relations among the rate coefficients. Then moving further, we will be discussing something about chain and branching reactions, because normally when the reaction occurs, we see a global reaction. But there are many elementary reactions that occurs in the background and normally many species get formed and they get also destroyed during the reaction process.

But in a global form they do not really appear and such things they are termed by either chain reactions or chain branching reactions, all those concepts will be dealt with. And most important thing we will be talking about a chemical time scale, like when you talk about a time scale, some object is moving with certain velocity, we have some time scale either in the terms of hour, minutes or seconds.

But when you deal with the chemical reactions what are the time scale we are talking about? Normally those reactions are in the milliseconds or less duration so that means, that event takes place in very short duration time scale and we call this as a time scale. And how do you quantify this time scale?

So, this is this part we are going to define today. Then last part is that partial equilibrium: many a situation what happens some reactions are very fast and some reactions are also slow and some radicals are also form in between. Now, what happens is that in the study of partial equilibrium that means, the reaction has not reached the final chemical equilibrium state, but we can pair out some of the intermediate reactions in such a way that as if a complete equilibrium situation can be modelled.

So, this has also many benefits because it almost resembles the final form of equilibrium conditions. So, those concepts are termed as partial equilibrium. So, this is all about the overview of this lecture number 24 that is Reaction Mechanisms and here we will be dealing with the only theoretical aspects.

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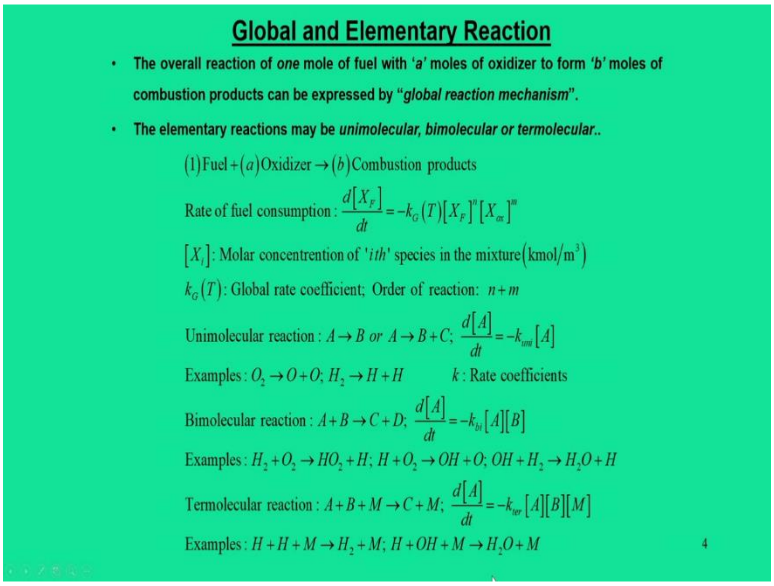

**Global and Elementary Reaction**

- **The overall reaction of *one* mole of fuel with '*a*' moles of oxidizer to form '*b*' moles of combustion products can be expressed by "*global reaction mechanism*".**
- **The elementary reactions may be *unimolecular, bimolecular or termolecular*..**

$(1)\text{Fuel} + (a)\text{Oxidizer} \rightarrow (b)\text{Combustion products}$

Rate of fuel consumption: $\frac{d[X_F]}{dt} = -k_G(T)[X_F]^n[X_{ox}]^m$

$[X_i]$: Molar concentrention of '$ith$' species in the mixture$(\text{kmol/m}^3)$

$k_G(T)$: Global rate coefficient; Order of reaction: $n+m$

Unimolecular reaction: $A \rightarrow B$ or $A \rightarrow B + C$; $\frac{d[A]}{dt} = -k_{uni}[A]$

Examples: $O_2 \rightarrow O + O$; $H_2 \rightarrow H + H$ $k$: Rate coefficients

Bimolecular reaction: $A + B \rightarrow C + D$; $\frac{d[A]}{dt} = -k_{bi}[A][B]$

Examples: $H_2 + O_2 \rightarrow HO_2 + H$; $H + O_2 \rightarrow OH + O$; $OH + H_2 \rightarrow H_2O + H$

Termolecular reaction: $A + B + M \rightarrow C + M$; $\frac{d[A]}{dt} = -k_{ter}[A][B][M]$

Examples: $H + H + M \rightarrow H_2 + M$; $H + OH + M \rightarrow H_2O + M$

So, if you understand reactions in our last class, we discussed about global and elementary reactions. What we have told is that 1 mole of fuel when it mixes with a mole of oxidizer; it gives b moles of combustion products. So, from which we can find out what is the rate of fuel consumptions, in the form of global rate coefficients and the concentration of fuels and oxidizers. So, this we see in a global form and we call this as a global reaction.

Besides this, there are possibilities that there may be some intermediate reactions that may take place and those reactions are called as elementary reactions and they can be unimolecular, bimolecular or termolecular. So, we have given the examples, one for each of the reactions we can define their rate coefficients in these expressions.

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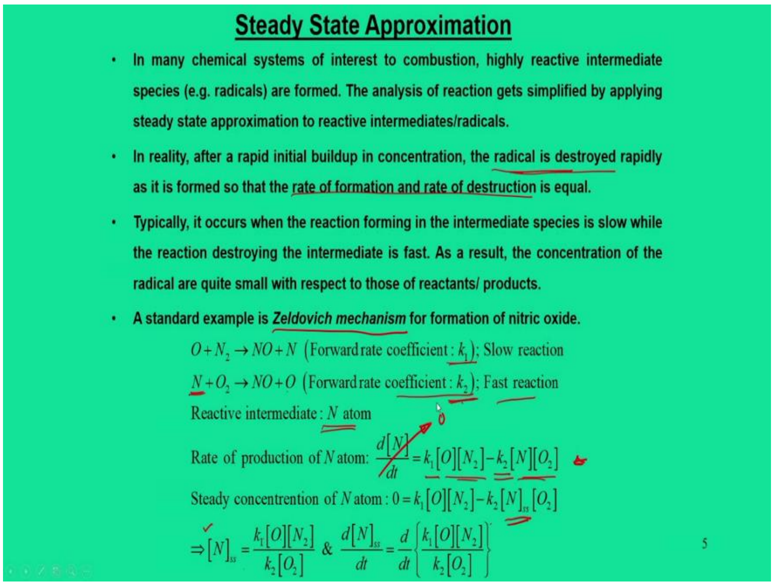

## Steady State Approximation

- In many chemical systems of interest to combustion, highly reactive intermediate species (e.g. radicals) are formed. The analysis of reaction gets simplified by applying steady state approximation to reactive intermediates/radicals.
- In reality, after a rapid initial buildup in concentration, the radical is destroyed rapidly as it is formed so that the rate of formation and rate of destruction is equal.
- Typically, it occurs when the reaction forming in the intermediate species is slow while the reaction destroying the intermediate is fast. As a result, the concentration of the radical are quite small with respect to those of reactants/ products.
- A standard example is *Zeldovich mechanism* for formation of nitric oxide.

$O + N_2 \rightarrow NO + N$ (Forward rate coefficient: $k_1$); Slow reaction

$N + O_2 \rightarrow NO + O$ (Forward rate coefficient: $k_2$); Fast reaction

Reactive intermediate: $N$ atom

Rate of production of $N$ atom: $\cancel{\frac{d[N]}{dt}} = k_1[O][N_2] - k_2[N][O_2]$

Steady concentrention of $N$ atom: $0 = k_1[O][N_2] - k_2[N]_{ss}[O_2]$

$\Rightarrow [N]_{ss} = \frac{k_1[O][N_2]}{k_2[O_2]}$ & $\frac{d[N]_{ss}}{dt} = \frac{d}{dt}\left\{\frac{k_1[O][N_2]}{k_2[O_2]}\right\}$

Now with this view point let us see that how you are going for a steady state approximation. So, normally if you have seen this either elementary or global reactions, they are unsteady in nature. So, under what circumstances we can assume a steady state conditions? So, what happens is that during a given or elementary reactions, some of the radicals they form, at the same time those radicals also get destroyed.

Although this rate of formation and rate of destruction is a tangent phenomenon, but how you are going to model is that, we need to find out that at what rate it forms and what rate it destroys and with respect to that we can make some balance so that we can say that what is the steady state concentration for that species.

So, how do you do that? So, to do that we need to analyze certain equations. So, one particular example in this process I can explain is that, a formation of nitric oxide and this is fundamentally known as Zeldovich reaction mechanism.

So, here what happens is that during the nitric oxide formations we can say oxygen atom can react with nitrogen atom to form NO plus N. So, this is typically a slow reaction and we can say its rate coefficient as $k_1$ and when this N forms it can again reacts with oxygen molecule to form NO plus O. So, this is another reaction for which the rate coefficient is $k_2$, but it is a fast reaction.

But in this process what happens? When the reaction gets initiated, the radical atom what we have mentioned here that the radical is formed and destroyed; so, there is a formation of radical destruction. So, basically in a rapid initial build up of concentration, radical is destroyed rapidly as it is formed so that rate of formation and rate of destruction are equal.

So, with this philosophy, let us see our radical is nitrogen atom and we want to find out what is the rate of production of nitrogen atoms. And this nitrogen atoms appears in the both the reactions and one for slow reaction, other for fast reactions. From this we can find out the concentration of nitrogen or rate of production of nitrogen atom with respect to time, we can find out based on the rate coefficients $k_1$, $k_2$ with their respective concentrations.

So, if you look at the 1st reactions, $k_1$ is the forward reaction and if you look at the 2nd reaction $k_2$ is the forward reactions. So, there is a negative sign here because nitrogen atoms appear here in the reactant side, in the 2nd equation. So, now from this equation when I say steady state concentrations, I can make this term $\frac{d[N]}{dt}$ 0; that means, steady state concentration of nitrogen atom, I can make it 0.

So, based on that we can replace this nitrogen atom as the steady state concentration of nitrogen, from this we can frame a equation what is the steady state concentration of nitrogen atom, which is a function of k1, k2 and nitrogen molecule concentration and oxygen molecule concentrations.

And we can differentiate this equation to find out what is the steady state, how the steady state concentration changes with time. Now, the beauty of this approximation is that instead of solving this particular equations, it is easy to solve this steady state concentration equations in this form so, this particular concept which we are going to use in the subsequent mechanisms.

$$[N]_{ss} = \frac{k_1[O][N_2]}{k_2[O_2]} \,\&\, \frac{d[N]_{ss}}{dt} = \frac{d}{dt}\left\{\frac{k_1[O][N_2]}{k_2[O_2]}\right\}$$

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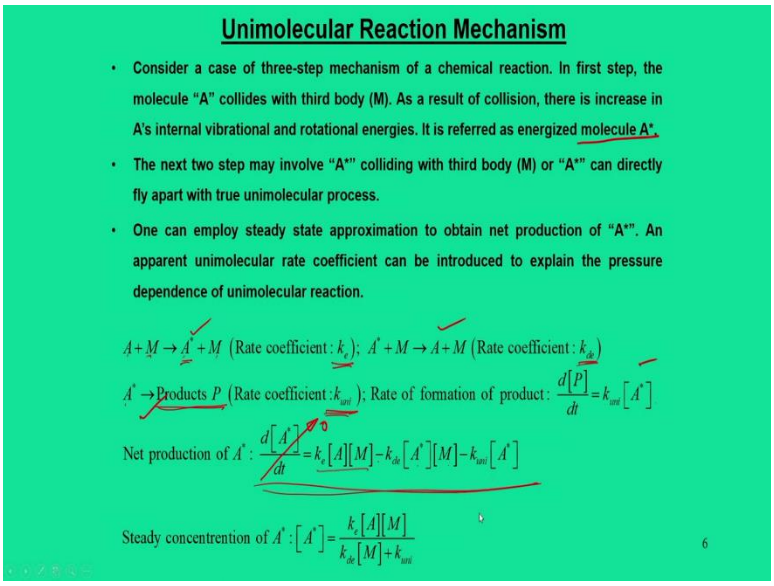

## Unimolecular Reaction Mechanism

- Consider a case of three-step mechanism of a chemical reaction. In first step, the molecule "A" collides with third body (M). As a result of collision, there is increase in A's internal vibrational and rotational energies. It is referred as energized molecule A*.
- The next two step may involve "A*" colliding with third body (M) or "A*" can directly fly apart with true unimolecular process.
- One can employ steady state approximation to obtain net production of "A*". An apparent unimolecular rate coefficient can be introduced to explain the pressure dependence of unimolecular reaction.

$A + M \rightarrow A^* + M$ (Rate coefficient : $k_e$); $A^* + M \rightarrow A + M$ (Rate coefficient : $k_{de}$)

$A^* \rightarrow$ Products $P$ (Rate coefficient : $k_{uni}$); Rate of formation of product : $\frac{d[P]}{dt} = k_{uni}[A^*]$

Net production of $A^*$ : $\frac{d[A^*]}{dt} = k_e[A][M] - k_{de}[A^*][M] - k_{uni}[A^*]$

Steady concentrention of $A^*$ : $[A^*] = \frac{k_e[A][M]}{k_{de}[M] + k_{uni}}$

Now, let us see how this concept we are going to apply for a unimolecular reaction system, when I say unimolecular reaction systems there are two possibilities. We can say that when $A + M \rightarrow A^* + M$.

What is this happening is that, so basically during the reaction process the molecule A collides with a third body, as a result of collision, there is an increase in vibrational or rotational kinetic energies of the molecules and this goes to a elevated state and we call this as a energized molecule $A^*$.

So, basically $A + M \rightarrow A^* + M$, M remains same for which the rate coefficient is $k_e$. Now, $A^* + M \rightarrow A + M$. So, it is a maybe same reaction which is getting reversed. So, you can say $k_{de}$ means it is a reverse of $k_e$, this is one part.

Other part is what we see globally is that we get the products P. So, $A^*$ gives the product with this unimolecular coefficient $k_{uni}$. So, from this equation we can frame the rate of formation of the product $\frac{d[P]}{dt} = k_{uni}[A^*]$.

Now, if you look at these three reactions 1, 2 and 3; this three reaction, we can find out what is the net production in this process. So, $\frac{d[A^*]}{dt} = k_e[A][M] - k_{de}[A^*][M] - k_{uni}[A^*]$. So, why this negative sign? Because $A^*$ appears in the reactant side. Whereas, the first equation $A^*$ appears in the product side.

So, when you have framed these particular equations, then we can find the steady state concentration of $A^*$. So, here we make the approximation of steady state approximation, making this $\frac{d[A^*]}{dt} = 0,$ and after that we can make steady state concentration $[A^*] = \frac{k_e[A][M]}{k_{de}[M]+k_{uni}}$. So basically, we have now used the steady state approximation to find the steady state concentration.

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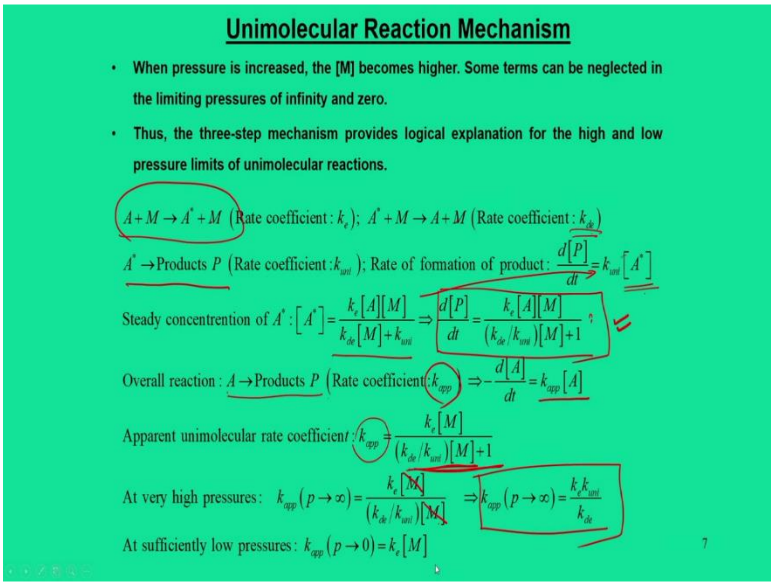

## Unimolecular Reaction Mechanism

- **When pressure is increased, the [M] becomes higher. Some terms can be neglected in the limiting pressures of infinity and zero.**
- **Thus, the three-step mechanism provides logical explanation for the high and low pressure limits of unimolecular reactions.**

$A + M \rightarrow A^* + M$ (Rate coefficient : $k_e$); $A^* + M \rightarrow A + M$ (Rate coefficient : $k_{de}$)

$A^* \rightarrow$ Products $P$ (Rate coefficient : $k_{uni}$); Rate of formation of product : $\frac{d[P]}{dt} = k_{uni}[A^*]$

Steady concentrention of $A^*$ : $[A^*] = \frac{k_e[A][M]}{k_{de}[M]+k_{uni}} \Rightarrow \boxed{\frac{d[P]}{dt} = \frac{k_e[A][M]}{(k_{de}/k_{uni})[M]+1}}$

Overall reaction : $A \rightarrow$ Products $P$ (Rate coefficient : $k_{app}$) $\Rightarrow -\frac{d[A]}{dt} = k_{app}[A]$

Apparent unimolecular rate coefficient : $k_{app} = \frac{k_e[M]}{(k_{de}/k_{uni})[M]+1}$

At very high pressures : $k_{app}(p \rightarrow \infty) = \frac{k_e\cancel{[M]}}{(k_{de}/k_{uni})\cancel{[M]}} \Rightarrow \boxed{k_{app}(p \rightarrow \infty) = \frac{k_e k_{uni}}{k_{de}}}$

At sufficiently low pressures : $k_{app}(p \rightarrow 0) = k_e[M]$

Then we have to move further in a different perspective, like if you look this particular equation again 3rd reaction which is a global and you try to find out what is the rate of product formation $\frac{d[P]}{dt}$, then we can write from this equation as $\frac{d[P]}{dt} = k_{uni}[A^*]$. Already we find the steady state concentration of $A^*$.

So, by putting this equation in this equation here, we get the expression of formation of products concept is $\frac{d[P]}{dt} = \frac{k_e[A][M]}{\left(\frac{k_{de}}{k_{uni}}\right)[M]+1}$. So, this is what we get and our main philosophy is that when you look at the reaction point of view, reaction occurs at certain pressure and temperatures and we will see that how these equations gets affected at different regimes of pressure and temperatures.

So, one case is that, if the pressure is increased concentration of M becomes higher. So, many terms of these equations can be neglected and through this process we can find out the validity of these equations with certain regimes of pressure.

So, what we look at is that we have already arrived at these particular expressions and this particular expression has rate coefficient of these elementary reactions, but when you take the overall reactions what you see are in a global reaction, a gives the products and for this the rate coefficient is defined as k apparent.

So, basically the we call this is a global rate coefficient and we can write this as $-\frac{d[A]}{dt} = k_{app}[A]$. By comparing these two equations and we can find out what is the expression of apparent molecular rate coefficient or uni molecular rate coefficient in terms of the concentration of M and the rate coefficient of that the elementary reactions.

So, this concentration of M we want to get eliminated, because normally there is no role of M in the global reactions. So, this needs to be eliminated. Now, when this needs to be eliminated? For example, when the reaction appears at very high pressure, then the denominator part, this particular term gets dominated.

So, we can write this denominator as $\left(\frac{k_{de}}{k_{uni}}\right)[M]$ so that this concentration of M gets cancelled from the numerator and denominator side we can find the expression apparent rate coefficients as a function of the rate coefficients in their elementary systems. $k_{app}(p \to \infty) = \frac{k_e k_{uni}}{k_{de}}$

Now, when the reactions are occurring at very low pressure, mean pressure close to 0. So, only the fast reactions are dominated. So, means at low pressure you need not worry about the rate coefficient k de and k unimolecular rate coefficient. And this approximation tells that what is the link between the global rate coefficient that is in this case is k apparent and the rate coefficients in their individual unimolecular steps or reactions.

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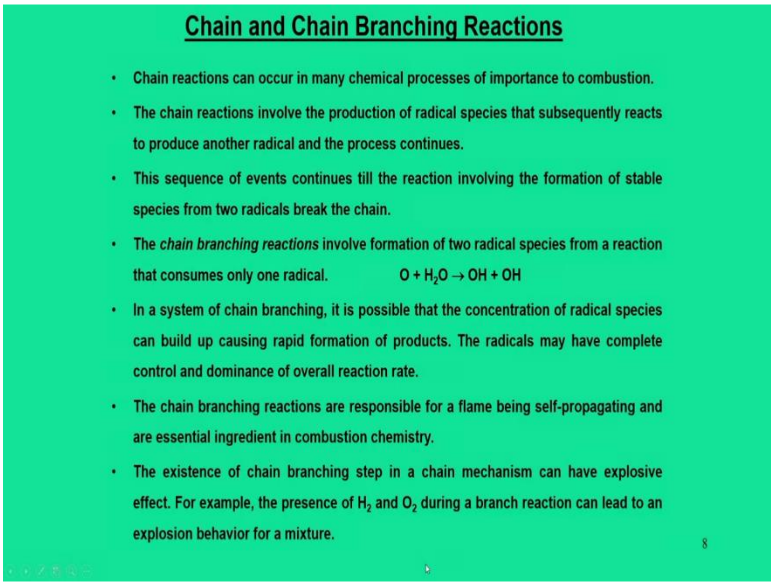

## Chain and Chain Branching Reactions

- Chain reactions can occur in many chemical processes of importance to combustion.
- The chain reactions involve the production of radical species that subsequently reacts to produce another radical and the process continues.
- This sequence of events continues till the reaction involving the formation of stable species from two radicals break the chain.
- The *chain branching reactions* involve formation of two radical species from a reaction that consumes only one radical. $O + H_2O \rightarrow OH + OH$
- In a system of chain branching, it is possible that the concentration of radical species can build up causing rapid formation of products. The radicals may have complete control and dominance of overall reaction rate.
- The chain branching reactions are responsible for a flame being self-propagating and are essential ingredient in combustion chemistry.
- The existence of chain branching step in a chain mechanism can have explosive effect. For example, the presence of $H_2$ and $O_2$ during a branch reaction can lead to an explosion behavior for a mixture.

So, this philosophy also can be extended for bimolecular and termolecular reactions, but we are not going into details of those aspects. But what we have seen is that how steady state approximation helps us in finding out the unimolecular reaction mechanism steps.

Then we will move to the new concept that is chain and chain branching reactions. So in fact, about this chain reactions I have already explained in the previous lecture and in fact, the chain reaction is very vital because for many chemical processes and it has lot of importance to the combustions.

Normally, the reaction proceeds with the formation of certain radicals, although those radicals or those molecules have no role, but they are called as chain initiation systems that will accelerate further sequence of events of the reactions. So, the chain reactions involve the production of radical species, that subsequently react to produce another radical and this process goes on.

This sequence of event continues till the reaction involving the formation of stable species of two radicals break down the chain. Then we come across the chain branching reactions and it involves the formation of two radical spaces from the reaction that consume only one radical. So, in the chain reaction radical species are formed, in the chain branching reactions it also gives multiple number of radical species.

So, that means, one forms and it subsequently accelerates the next chain and this keeps on branching. For example, when oxygen atom is formed in some form and if it sees $H_2O$, it can form this branch OH and OH.

So, everywhere we have O and $H_2O$, it will have OH radicals formation. So, these are called chain branching systems and this OH will again react with some O atom or some other atom to form another component. So, this branching process keeps on happening. And in the system of chain branching, it is possible that concentration of radical species can build up causing rapid formation of products.

Although it starts with a chain initiation and after this branching when subsequent number of radicals are formed, it accelerates the chemical processes. And some point of time they take the complete hold of the entire reaction mechanism systems or they have a dominance of overall reaction steps. So, in fact, this is the concept that the chain branching reactions are responsible for a flame being self-propagating and are essentially ingredient for the combustion chemistry.

So, in the combustion view point, if you want to retain a sustained flame then we must keep on generating this chain branching systems and the flame can propagate on its own. Many a times what happens? This chain branching systems have serious consequence, may be they are basically create an explosive species.

For example, when we have hydrogen and oxygen, when they exist in molecule form and they do not oxidize, then there is no question, they are safe. But as long as they start reacting through this branching systems, they can lead to explosive behaviour of the mixture. We will explain this fact when you discuss in our next lecture regarding the application of the reaction mechanisms.

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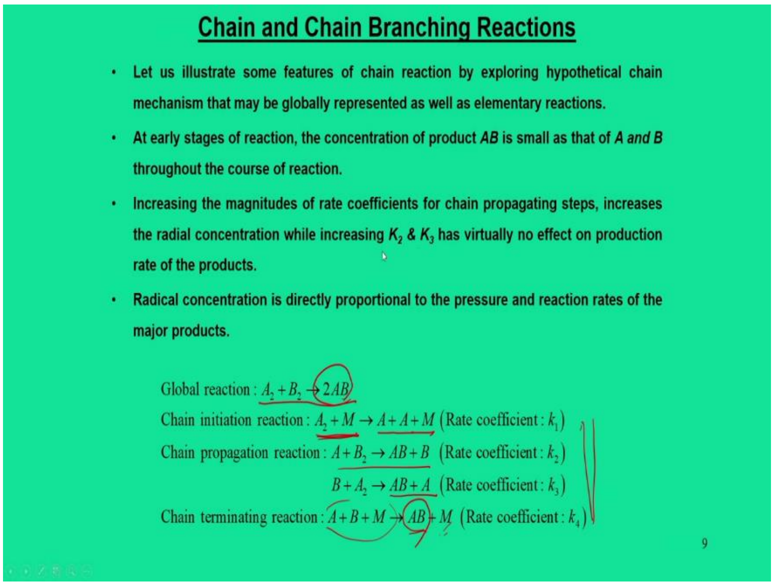

## Chain and Chain Branching Reactions

- Let us illustrate some features of chain reaction by exploring hypothetical chain mechanism that may be globally represented as well as elementary reactions.
- At early stages of reaction, the concentration of product *AB* is small as that of *A and B* throughout the course of reaction.
- Increasing the magnitudes of rate coefficients for chain propagating steps, increases the radial concentration while increasing $K_2$ & $K_3$ has virtually no effect on production rate of the products.
- Radical concentration is directly proportional to the pressure and reaction rates of the major products.

Global reaction : $A_2 + B_2 \rightarrow 2AB$

Chain initiation reaction : $A_2 + M \rightarrow A + A + M$ (Rate coefficient : $k_1$)

Chain propagation reaction : $A + B_2 \rightarrow AB + B$ (Rate coefficient : $k_2$)

$B + A_2 \rightarrow AB + A$ (Rate coefficient : $k_3$)

Chain terminating reaction : $A + B + M \rightarrow AB + M$ (Rate coefficient : $k_4$)

Then moving further, let us understand how you want to view this chain initiation or chain propagation mechanisms. So, if you look at global reactions, which you normally see $A_2 + B_2 \rightarrow 2AB$, it is a hypothetical reaction and for this 2AB formations there may be series of a sequence of events. So, first we may have $A_2 + M \rightarrow A + A + M$.

And this $A + B_2 \rightarrow AB + B$ when $B + A_2 \rightarrow AB + A$. So, through this process AB concentration gets built up, and when the chain terminates finally, what remains is AB. So, all $A + B + M \rightarrow AB + M$ and this M vanishes. And through this process we get different rate coefficients and we need to find out what are the relation among them and those relations can be built up with the knowledge of the equilibrium products.

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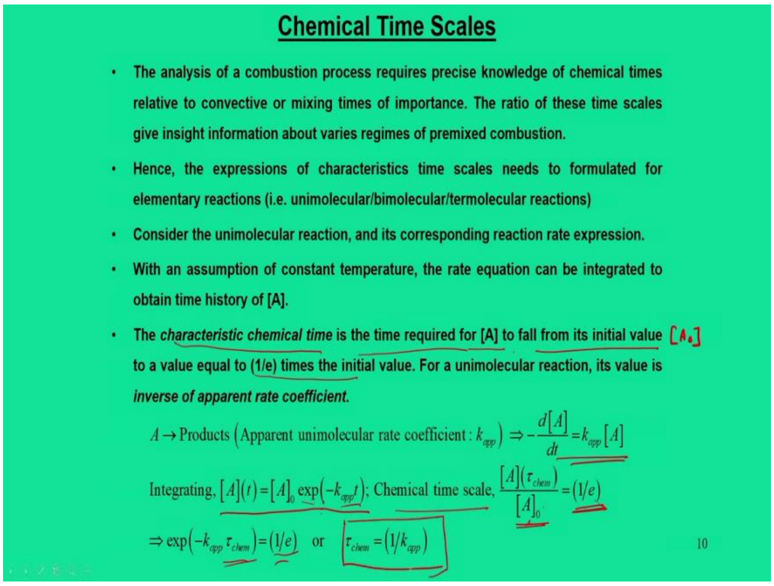

## Chemical Time Scales

- The analysis of a combustion process requires precise knowledge of chemical times relative to convective or mixing times of importance. The ratio of these time scales give insight information about varies regimes of premixed combustion.
- Hence, the expressions of characteristics time scales needs to formulated for elementary reactions (i.e. unimolecular/bimolecular/termolecular reactions)
- Consider the unimolecular reaction, and its corresponding reaction rate expression.
- With an assumption of constant temperature, the rate equation can be integrated to obtain time history of [A].
- The *characteristic chemical time* is the time required for [A] to fall from its initial value $[A_0]$ to a value equal to (1/e) times the initial value. For a unimolecular reaction, its value is ***inverse of apparent rate coefficient.***

$$A \rightarrow \text{Products}\left(\text{Apparent unimolecular rate coefficient}: k_{app}\right) \Rightarrow -\frac{d[A]}{dt} = k_{app}[A]$$

$$\text{Integrating, } [A](t) = [A]_0 \exp\left(-k_{app} t\right); \text{ Chemical time scale, } \frac{[A](\tau_{chem})}{[A]_0} = (1/e)$$

$$\Rightarrow \exp\left(-k_{app}\tau_{chem}\right) = (1/e) \quad \text{or} \quad \boxed{\tau_{chem} = \left(1/k_{app}\right)}$$

Then another important aspect that we are going to discuss is the chemical time scale. So, we all aware of the timescales, timescales is normally represented either in hour, meter, second, year, depending on the nature of the event, but in the chemistry we see the time scales in a very short duration phenomena or it is a very small event.

So, how do you view this? Now, we have unimolecular, bimolecular, termolecular reactions and all of them will have a different time scale. And if at all you need to define a time scale, how do you quantify this? So, this is the basic philosophy for determining the chemical time scales in a combustion process.

The analysis of combustion process requires precise knowledge of chemical times relative to convecting mixing time of importance. So, what it means is that so when the combustion phenomena normally takes place, either it is has to be done through a pre-mixed mode or diffusion mode and the flame gets established and it keeps on propagating.

And to keep it in a sustained mode, we need to find out that fuel and air mixes properly and this mixing process has some finite time. At the same time, during the mixing process it may so happen that, but your chemical time scale during the mixing process and chemical time scales they should be at par. That means, if your chemical time scale is in milliseconds your mixing time should be in the similar durations, so that we can ensure that maximum fuel is burnt.

So, the precise knowledge of chemical time scale is very vital. So, for that purpose we need to find the expression for characteristics time scale to be formulated for the elementary reaction that is unimolecular, bimolecular, termolecular reactions. So, let us start with an assumption that we are looking at a unimolecular reaction.

So, when I say unimolecular reactions element A gives the products with its apparent molecular rate coefficient k apparent. So, we can find an expression that how the rate of the concentration of A changes, because its negative sign says that concentration drops with time and that is $-\frac{d[A]}{dt} = k_{app}[A]$.

Now, this particular equation can be integrated to find out $[A](t) = [A]_0 \exp(-k_{app}t)$. Now, here we introduce the term what is called as chemical time scale or many a times you call as characteristics chemical time and it is the time required for concentration of A to fall from its initial value and this initial value means $A_0$ to have a value equal to 1.8 times of its initial value.

So, concentration of A, when you multiply by this, so we will have $\frac{[A](\tau_{chem})}{[A]_0} = \left(\frac{1}{e}\right)$. So, why it is called 1 by e? Because with this number this logarithmic expression gets simplified. Then by putting this expression here we can write $\exp(-k_{app}\tau_{chem}) = \left(\frac{1}{e}\right)$ or $\tau_{chem} = \left(\frac{1}{k_{app}}\right)$. So, from this we can find for a unimolecular system, chemical time scale is equal to $\frac{1}{k_{app}}$.

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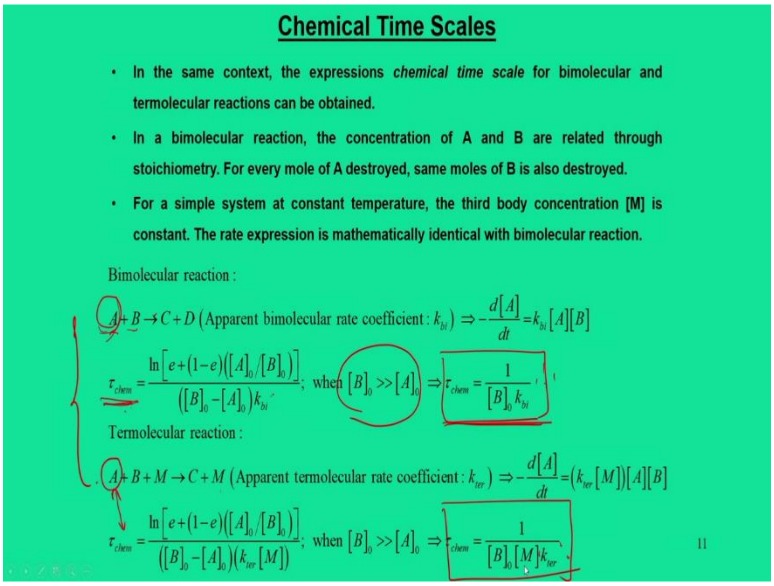

## Chemical Time Scales

- In the same context, the expressions *chemical time scale* for bimolecular and termolecular reactions can be obtained.
- In a bimolecular reaction, the concentration of A and B are related through stoichiometry. For every mole of A destroyed, same moles of B is also destroyed.
- For a simple system at constant temperature, the third body concentration [M] is constant. The rate expression is mathematically identical with bimolecular reaction.

Bimolecular reaction :

$$A+B\rightarrow C+D \text{ (Apparent bimolecular rate coefficient} : k_{bi}) \Rightarrow -\frac{d[A]}{dt}=k_{bi}[A][B]$$

$$\tau_{chem}=\frac{\ln\left[e+(1-e)\left([A]_0/[B]_0\right)\right]}{\left([B]_0-[A]_0\right)k_{bi}};\ \text{when } [B]_0>>[A]_0 \Rightarrow \boxed{\tau_{chem}=\frac{1}{[B]_0 k_{bi}}}$$

Termolecular reaction :

$$A+B+M\rightarrow C+M \text{ (Apparent termolecular rate coefficient} : k_{ter}) \Rightarrow -\frac{d[A]}{dt}=(k_{ter}[M])[A][B]$$

$$\tau_{chem}=\frac{\ln\left[e+(1-e)\left([A]_0/[B]_0\right)\right]}{\left([B]_0-[A]_0\right)\left(k_{ter}[M]\right)};\ \text{when } [B]_0>>[A]_0 \Rightarrow \boxed{\tau_{chem}=\frac{1}{[B]_0[M]k_{ter}}}$$

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This is what we called as a characteristics time scale. Now, in the same context the expressions for chemical time scales for bimolecular and termolecular reactions can be obtained. So, in a bimolecular reaction with the same philosophy we can have expressions tau chemical, because in a bimolecular reaction we require two species, concentration of A, concentration of B. It gives C and D and we need to find out the chemical time scale for A.

So, first term should be A. Now, when I write this chemical time scale, this expression refers to for the characteristic time scale for species A, for this species A we need to find what is the initial concentration $A_0$. And similarly, if the reaction is termolecular, then we also need to find out the 1st term that is species A and this refers to this this characteristic time scale for the species A.

So, for simple system at constant temperature, the third body concentration A is constant. So, the rate expression is mathematically identical for bimolecular systems.

So, basically bimolecular and tri molecular they remain same, what remains the final expressions is that when $[B]_0 >> [A]_0 \Rightarrow \tau_{chem} = \frac{1}{[B]_0 k_{bi}}$, this chemical time scale refers to a very simple expressions for unimolecular reaction and for termolecular reactions.

Now, if you look at these two particular reactions and if you compare the original reaction $A + B \rightarrow C + D$and $A + B + M \rightarrow C + M$, then both chemical characteristic time scale for bimolecular and termolecular reactions appears to be same, only just a difference in the concentration.

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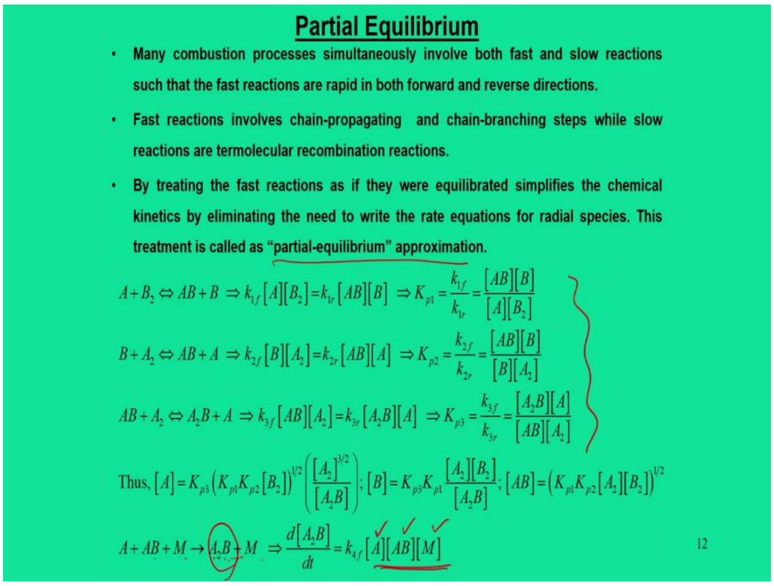

## Partial Equilibrium

- Many combustion processes simultaneously involve both fast and slow reactions such that the fast reactions are rapid in both forward and reverse directions.
- Fast reactions involves chain-propagating and chain-branching steps while slow reactions are termolecular recombination reactions.
- By treating the fast reactions as if they were equilibrated simplifies the chemical kinetics by eliminating the need to write the rate equations for radial species. This treatment is called as "partial-equilibrium" approximation.

$$\left.\begin{aligned}
&A+B_2 \Leftrightarrow AB+B \Rightarrow k_{1f}[A][B_2]=k_{1r}[AB][B] \Rightarrow K_{p1}=\frac{k_{1f}}{k_{1r}}=\frac{[AB][B]}{[A][B_2]}\\
&B+A_2 \Leftrightarrow AB+A \Rightarrow k_{2f}[B][A_2]=k_{2r}[AB][A] \Rightarrow K_{p2}=\frac{k_{2f}}{k_{2r}}=\frac{[AB][B]}{[B][A_2]}\\
&AB+A_2 \Leftrightarrow A_2B+A \Rightarrow k_{3f}[AB][A_2]=k_{3r}[A_2B][A] \Rightarrow K_{p3}=\frac{k_{3f}}{k_{3r}}=\frac{[A_2B][A]}{[AB][A_2]}
\end{aligned}\right\}$$

$$\text{Thus, } [A]=K_{p3}\left(K_{p1}K_{p2}[B_2]\right)^{1/2}\left(\frac{[A_2]^{3/2}}{[A_2B]}\right);\ [B]=K_{p3}K_{p1}\frac{[A_2][B_2]}{[A_2B]};\ [AB]=\left(K_{p1}K_{p2}[A_2][B_2]\right)^{1/2}$$

$$A+AB+M \rightarrow A_2B+M \Rightarrow \frac{d[A_2B]}{dt}=k_{4f}\underline{[\overset{\checkmark}{A}][\overset{\checkmark}{AB}][\overset{\checkmark}{M}]}$$

Now, next topic of discussion that we are going to explain is about partial equilibrium. Many a times what happens, complete equilibrium analysis may not be feasible in certain situations, so why? Because some reactions are very fast and some reactions are slow, many times forward reactions are fast reverse reactions are slow. That is because for example, when you say termolecular reactions, they are basically chain terminating mechanisms. So, that is the stopping time.

So, whatever species are formed, they try to recombine and settle down. So, when this happens, the analysis may be difficult if you wait till the complete equilibrium situations; what has been a probable or feasible approach is to consider partial equilibrium. So, for this consideration, we say the fast and slow reactions has to happen such a way that and they can happen in forward and reverse fashion. Now, out of all the reactions in a given system, one can pair out some particular reactions that a gives similar products or same products.

For example, in this situation $A + B_2 \Leftrightarrow AB + B, B + A_2 \Leftrightarrow AB + A$ and both the reactions can form the species AB and in the both the cases, we can pair them out. So, they can be considered as a one single pair. By while doing so, it is logical to assume that rate of forward reaction and rate of reverse reactions are known and you can express them in terms of their equilibrium constants.

And from this, it is possible to evaluate the concentration of the actual reaction which is occurring. So, actual reaction which is this is $A + AB + M \rightarrow A_2B + M$. So, $A_2B$ is the real need of our requirement for which we need to find out. So, we need information about the concentration of A, concentration of AB, concentration of M. So, these individual concentrations can be formulated by assuming through what we call as a pair mechanism and they fall under the criteria of partial equilibrium approximations.

So, by treating fast reactions as if they were equilibrated, this simplifies the chemical kinetics by eliminating the need to write the rate reactions for radical species. What it means is that when the elementary reactions get started or chain gets built up, chain initiation has been done, branching has been done and through this that radical has been formed. So, we need to make a partial equilibrium assumption to find out the equilibrium concentration for the final species and this process avoids the need to write the rate equations for individual radical species.

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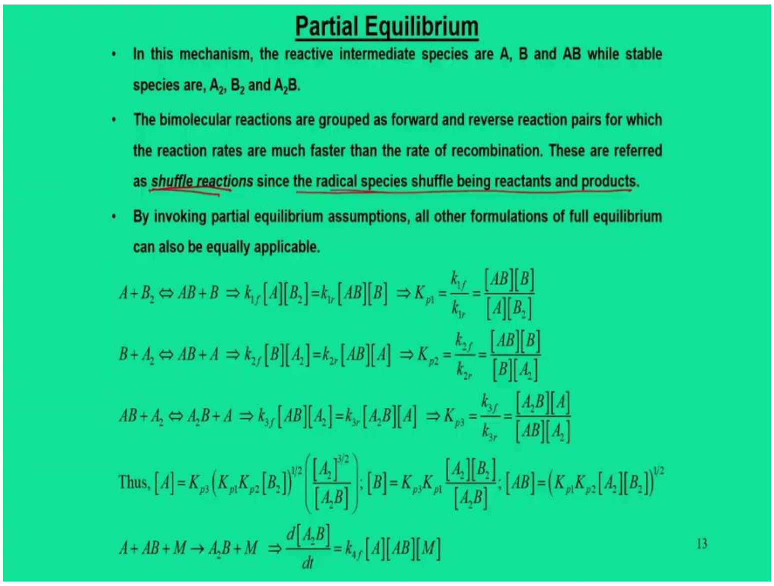

## Partial Equilibrium

- In this mechanism, the reactive intermediate species are A, B and AB while stable species are, $A_2$, $B_2$ and $A_2B$.
- The bimolecular reactions are grouped as forward and reverse reaction pairs for which the reaction rates are much faster than the rate of recombination. These are referred as *shuffle reactions* since the radical species shuffle being reactants and products.
- By invoking partial equilibrium assumptions, all other formulations of full equilibrium can also be equally applicable.

$$A + B_2 \Leftrightarrow AB + B \Rightarrow k_{1f}[A][B_2] = k_{1r}[AB][B] \Rightarrow K_{p1} = \frac{k_{1f}}{k_{1r}} = \frac{[AB][B]}{[A][B_2]}$$

$$B + A_2 \Leftrightarrow AB + A \Rightarrow k_{2f}[B][A_2] = k_{2r}[AB][A] \Rightarrow K_{p2} = \frac{k_{2f}}{k_{2r}} = \frac{[AB][B]}{[B][A_2]}$$

$$AB + A_2 \Leftrightarrow A_2B + A \Rightarrow k_{3f}[AB][A_2] = k_{3r}[A_2B][A] \Rightarrow K_{p3} = \frac{k_{3f}}{k_{3r}} = \frac{[A_2B][A]}{[AB][A_2]}$$

$$\text{Thus, } [A] = K_{p3}\left(K_{p1}K_{p2}[B_2]\right)^{1/2}\left(\frac{[A_2]^{3/2}}{[A_2B]}\right); [B] = K_{p3}K_{p1}\frac{[A_2][B_2]}{[A_2B]}; [AB] = \left(K_{p1}K_{p2}[A_2][B_2]\right)^{1/2}$$

$$A + AB + M \rightarrow A_2B + M \Rightarrow \frac{d[A_2B]}{dt} = k_{4f}[A][AB][M]$$

And here I need to try to emphasize there are some reactions, which are paired and they are called as shuffle reactions and because these species are shuffled, among those reactions between the reactants and products. And this helps us to find out which is a faster reaction.

Faster reactions are normally bimolecular reactions in the forward or reverse fashion and slow reactions may be termolecular reactions, because they are in the phase of recombination or rearrangement or those reactions settle down soon, they are very slow. With this we come to the end of this lecture and based on our understanding we will try to solve a numerical problem.

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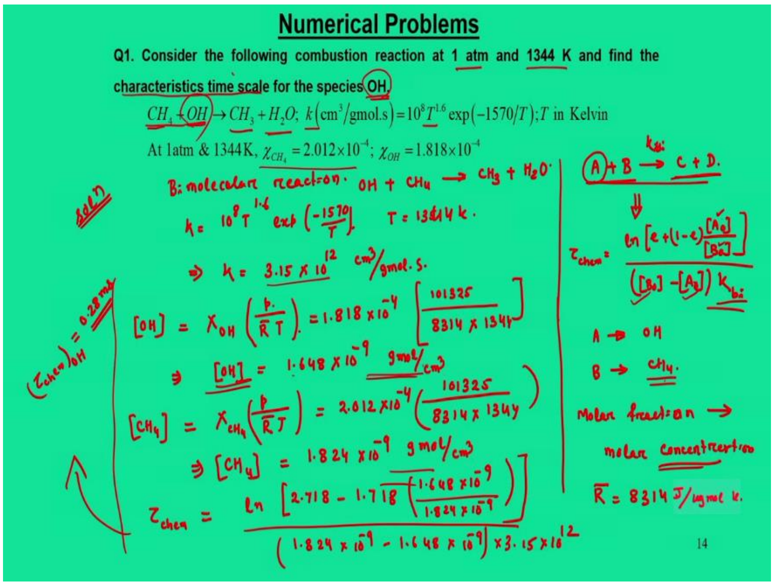

## Numerical Problems

Q1. Consider the following combustion reaction at 1 atm and 1344 K and find the characteristics time scale for the species OH.

$CH_4 + OH \rightarrow CH_3 + H_2O$; $k(\text{cm}^3/\text{gmol.s}) = 10^8 T^{1.6} \exp(-1570/T)$; $T$ in Kelvin

At 1atm & 1344K, $\chi_{CH_4} = 2.012\times10^{-4}$; $\chi_{OH} = 1.818\times10^{-4}$

Soln

Bimolecular reaction. $OH + CH_4 \rightarrow CH_3 + H_2O$.

$k = 10^8 T^{1.6} \exp\left(-\frac{1570}{T}\right)$ $T = 1344$ K.

$\Rightarrow k = 3.15\times10^{12}$ cm³/gmol. s.

$[OH] = X_{OH}\left(\frac{p}{\bar{R}T}\right) = 1.818\times10^{-4}\left[\frac{101325}{8314\times1344}\right]$

$\Rightarrow [OH] = 1.648\times10^{-9}$ gmol/cm³

$[CH_4] = X_{CH_4}\left(\frac{p}{\bar{R}T}\right) = 2.012\times10^{-4}\left(\frac{101325}{8314\times1344}\right)$

$\Rightarrow [CH_4] = 1.824\times10^{-9}$ gmol/cm³

$$\tau_{chem} = \frac{\ln\left[2.718 - 1.718\left(\frac{1.648\times10^{-9}}{1.824\times10^{-9}}\right)\right]}{(1.824\times10^{-9} - 1.648\times10^{-9})\times3.15\times10^{12}}$$

$(\tau_{chem})_{OH} = 0.28$ ms

$A + B \xrightarrow{k_{bi}} C + D.$

$\Downarrow$

$$\tau_{chem} = \frac{\ln\left[e + (1-e)\frac{[A_0]}{[B_0]}\right]}{([B_0] - [A_0])\,k_{bi}}$$

A → OH

B → $CH_4$.

Molar fraction → molar concentration

$\bar{R} = 8314$ J/kgmol K.

So, this numerical problem is all about finding out the characteristic time scale for a certain reaction. So, we have already defined the nature of time scales for unimolecular, bimolecular and termolecular reactions. What has been given is that one particular reaction that is $CH_4 + OH \rightarrow CH_3 + H_2O$.

So, this is one particular elementary or I mean you can say chain initiation or chain branching reaction and for which the rate coefficients are defined in terms of centimeter cube per gram mole seconds and it is a function of temperature as $k = 10^8 T^{1.6} \exp(-1570/T)$.

And the reaction is happening at one atmosphere, but 1344 kelvin and this reaction is a bimolecular reaction, because we have two species $CH_4$ and OH. And what has been asked for? Characteristics time scale for OH. So, basically we are finding out characteristic time scale for OH, then you have to rewrite the equation keeping OH first. So, we will write this expression $OH + CH_4 \rightarrow CH_3 + H_2O$.

So, this refers to the fact A plus B, gives rise to C plus D and for this in a generic term we are looking at the characteristics time scale for A. And when you do that the basic definition says

$$\tau_{chem} = \frac{\ln\left[e + (1-e)\frac{[A_0]}{[B_0]}\right]}{([B_0] - [A_0])k}$$

And in our case this k is giving as this expression, $= 10^8 T^{1.6} \exp{(-1570/T)}$. Now, putting T is equal to 1344 kelvin and all the parameters are known, then we can find out $k = 3.15 \times 10^{12} cm^3/gmol - s$. But what other thing you require? We require initial concentration $A_0$ and $B_0$.

Now, let us see in our case what is A. So, our case A stands for OH, B stands for $CH_4$ and we need to find out their concentrations. So, OH concentration we can find out and this concentration we have to find out because we have given with the molar fractions. So, molar fraction needs to be converted to molar concentration and for this we require the expression or information about the pressure and temperatures. So, I if I can write that conversion, then I can write

$$[OH] = X_{OH}\left(\frac{p}{\bar{R}T}\right) = 1.818 \times 10^{-4}\left[\frac{101325}{8314 \times 1344}\right] = 1.648 \times 10^{-9} gmol/cm^3$$

$$[CH_4] = X_{CH_4}\left(\frac{p}{\bar{R}T}\right) = 2.012 \times 10^{-4}\left[\frac{101325}{8314 \times 1344}\right] = 1.824 \times 10^{-9} gmol/cm^3$$

So, we can find out chemical time scale as

$$\tau_{chem} = \frac{\ln\left[2.718 - 1.718\frac{1.648 \times 10^{-9}}{1.824 \times 10^{-9}}\right]}{(1.824 \times 10^{-9} - 1.648 \times 10^{-9})3.15 \times 10^{12}} = 0.28\, millisecond$$

So, this gives the information that in a bimolecular chemical reactions, the order of characteristics time scale is about milliseconds and in this case, the time scale for OH species is 0.28 millisecond. With this I conclude.

Thank you for your attention.