Fundamentals of Combustion

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Lecture - 22

Fundamentals of Combustion Kinetics – Part 3

Steady State and Partial Equilibrium Approximation

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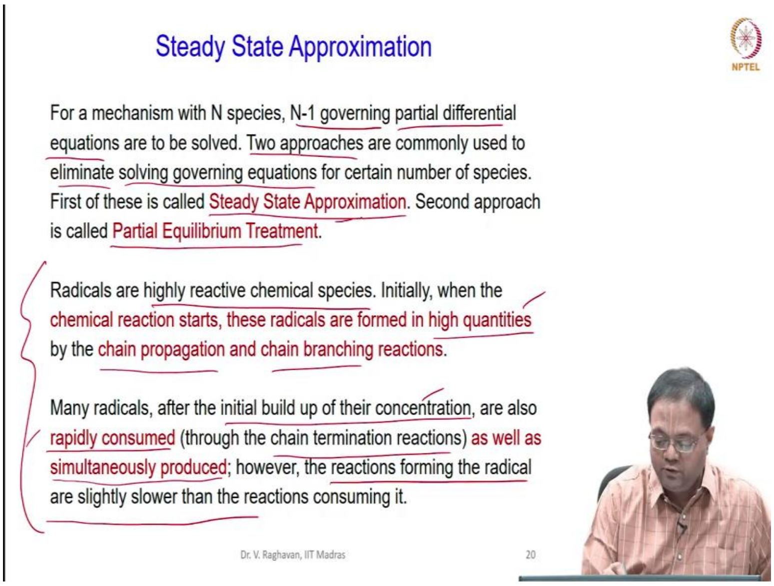

Steady State Approximation

For a mechanism with N species, N-1 governing partial differential equations are to be solved. Two approaches are commonly used to eliminate solving governing equations for certain number of species. First of these is called Steady State Approximation. Second approach is called Partial Equilibrium Treatment.

Radicals are highly reactive chemical species. Initially, when the chemical reaction starts, these radicals are formed in high quantities by the chain propagation and chain branching reactions.

Many radicals, after the initial build up of their concentration, are also rapidly consumed (through the chain termination reactions) as well as simultaneously produced; however, the reactions forming the radical are slightly slower than the reactions consuming it.

So, let us see this approximations which are made to reduce the number of species. So, if you have a multi component mixture, N species constituting that mixture then we need to solve N-1 governing equations. So, these governing equations are partial differential equations which involve non-linear source term.

So, the rate of production or consumption of each species kg/m^{3}s. We have seen already that the exponential dependence of the rate coefficient. So, for each species you have to calculate.

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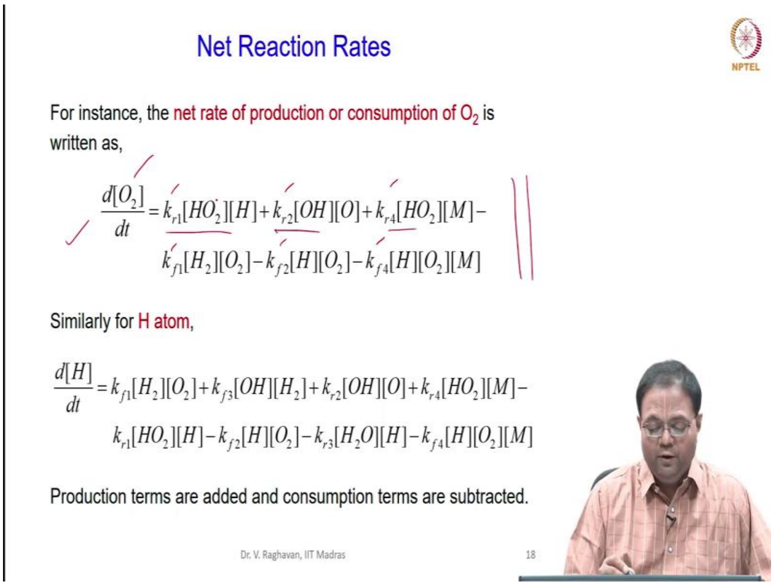

Net Reaction Rates

For instance, the net rate of production or consumption of O_2 is written as,

$$\frac{d[O_2]}{dt} = k_{r1}[HO_2][H] + k_{r2}[OH][O] + k_{r4}[HO_2][M] - k_{f1}[H_2][O_2] - k_{f2}[H][O_2] - k_{f4}[H][O_2][M]$$

Similarly for H atom,

$$\frac{d[H]}{dt} = k_{f1}[H_2][O_2] + k_{f3}[OH][H_2] + k_{r2}[OH][O] + k_{r4}[HO_2][M] - k_{r1}[HO_2][H] - k_{f2}[H][O_2] - k_{r3}[H_2O][H] - k_{f4}[H][O_2][M]$$

Production terms are added and consumption terms are subtracted.

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So, for example, you can see this. This is the way you calculate the net rate of production or consumption of particular species involving several reactions. This is a non-linear term because of all these rate coefficients are non-linear function of temperature.

So, involving this equation you get a non-linear source term. So, solving this N-1 governing equations are very tedious and more computational efforts are required.

So, it is better to always reduce the number of species especially when the problem which you are trying to solve is a bigger in scale. So, two approaches are used to eliminate the number of species. When we say eliminate, we do not eliminate the species itself we eliminate solving the governing equations. So, how to do that?

There are two approaches. The first one is called steady state approximation. Second one is called partial equilibrium treatment. So, these are the two approaches which are commonly used to eliminate the solution of governing equations.

So, these species are calculated as function of other species and say reaction rate coefficients and when you implement this partial equilibrium you involve the k_p value and so on. So, the first one, steady state approximation involves with the elimination of radicals which are highly reactive chemical species. What happens is when the chemical reaction starts radicals are formed in high quantities because of the chain propagation and chain branching reaction. So, chain propagation reaction produces at least one radical and chain branching reactions produces produce multiple radicals.

So, high quantities of radicals are produced because initially the concentration of reactants are very high. So, based upon the initial concentration of the reactants high quantities of radicals are produced.

Radicals are highly reactive. So, what happens is initially the concentration build up will occur. Due to the massive production the buildup of concentration will occur. Once the concentration reaches the higher value the reactions involving its consumption will have a higher rate. Obviously, because the rate of reaction is dependent on the concentration of the reactants also.

So, initial buildup of the concentration of the radicals will lead to higher reaction rates for the reactions involving these radicals. So, the radicals are also rapidly consumed now because of the higher rate of the reactions involving these radicals which consume them.

Now, basically this can be chain termination reactions also which can produce the major products. Now, once this is consumed, it is also simultaneously produced because of the other reactants being there and they are also producing radicals through propagation and branching reactions and they are consumed through termination reactions and so on.

So, they simultaneously occur, production and consumption. However, the reactions forming the radicals are at a lower phase are slightly slower than the reactions consuming this. So, now, the production of the radical become slower and the consumption becomes higher.

So, this happens to several radicals. So, that is the main thing you have to physically understand and I select these radicals and put them in what is called steady state approximation.

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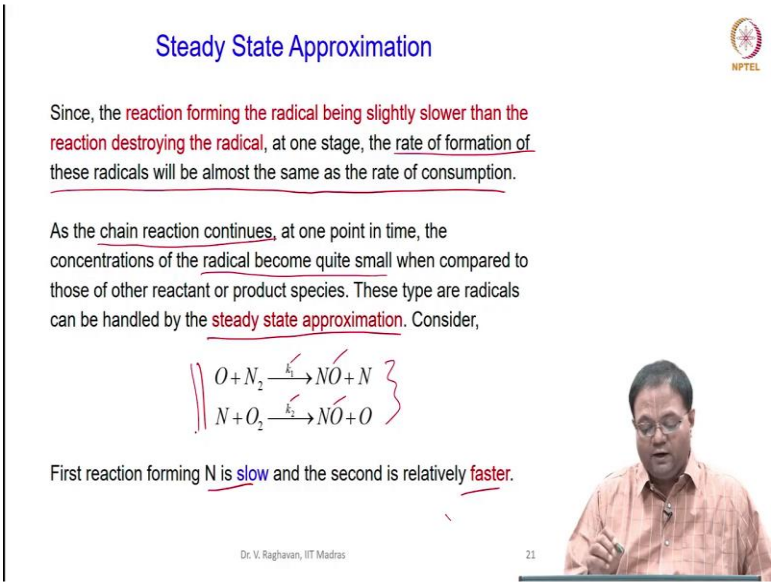

Steady State Approximation

Since, the reaction forming the radical being slightly slower than the reaction destroying the radical, at one stage, the rate of formation of these radicals will be almost the same as the rate of consumption.

As the chain reaction continues, at one point in time, the concentrations of the radical become quite small when compared to those of other reactant or product species. These type are radicals can be handled by the steady state approximation. Consider,

$$O + N_2 \xrightarrow{k_1} NO + N$$
$$N + O_2 \xrightarrow{k_2} NO + O$$

First reaction forming N is slow and the second is relatively faster.

Now, since the reaction forming the radical being slightly slower than the reaction destroying the radical at one stage, rate of formation of these radicals will be almost the same as the rate of its consumption. So, they form and they just destroyed all that is all.

So, that means that they do not have any time dependency at any time they will produce and they will be destroyed that is all.

What happens is then the chain reaction continues, at one point you will see that the concentration of radical becomes very small because they are produced at a slow rate and are consumed at a very faster rate.

So, the concentrations are there because the radicals become very small when compared to the major species, other reactant and the product species. So, under such condition these radicals are handled with steady state approximation.

So, we will consider example to illustrate how it is. So, let us consider here a set of reaction like this.

$$O + N_2 \xrightarrow{k} NO + N$$
$$N + O_2 \xrightarrow{k} NO + O$$

So, here you can see that it is a nitric oxide formation reaction. It is called Zeldovich mechanism, two important reactions producing nitric oxide. O + N_2 at a rate of the rate coefficient for that reaction is k_1 producing NO. N + O_2 forming NO, the rate coefficient is k_2 here.

The first reaction forming N is slow than the second reaction which is forming the N. So, the N is consumed at a slightly faster rate than it is produced in the first reaction that is what the important note you have to make. So, the first reaction forming N is slower than the second reaction consuming N.

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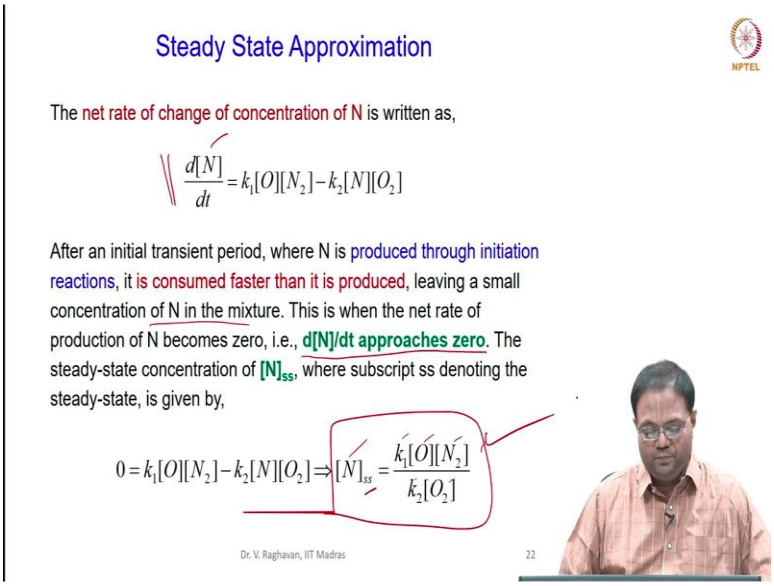

Steady State Approximation

The net rate of change of concentration of N is written as,

$$\frac{d[N]}{dt} = k_1[O][N_2] - k_2[N][O_2]$$

After an initial transient period, where N is produced through initiation reactions, it is consumed faster than it is produced, leaving a small concentration of N in the mixture. This is when the net rate of production of N becomes zero, i.e., **d[N]/dt approaches zero**. The steady-state concentration of **$[N]_{ss}$**, where subscript ss denoting the steady-state, is given by,

$$0 = k_1[O][N_2] - k_2[N][O_2] \Rightarrow \boxed{[N]_{ss} = \frac{k_1[O][N_2]}{k_2[O_2]}}$$

So, what happens is at the particular time the concentration of N decreases to a low value. So, the concentration of N with time is nothing but the first reaction where it is formed. So, d[N]/dt = $k_1[O][N_2]$ - $k_2[N][O_2]$ (in the second reaction it is produced).

So, after the initial transient period, initially this will not be zero during the transient period. So, there will be some buildup and consumption etcetera now after that transient period is over, then it is produced and it is consumed faster. Now, what happens is the value of N will be low and also the rate of change of concentration of N with time approaches a value of zero. So, it tends to zero.

$$0 = k_1[O][N_2] - k_2[N][O_2] \Rightarrow [N]_{ss} = \frac{k_1[O][N_2]}{k_2[O_2]}$$

So, we can say you can put left hand side zero here. So, 0 equal to the forward reaction rate of the first reaction minus the reaction of which is forming NO.

Now, from this we can write the concentration of N in terms of other species like this. So, here N I put a subscript steady state. So, SS is calculated as $k_1 \times [O][N_2]/k_2[O_2]$.

So, now the concentration of N is calculated and it is used in the calculation of properties and other diffusion coefficients etcetera. However, yet species concentration equation need not be solved for N because the concentration of N is calculated using concentration of other species like O, N_2 and O_2 and the k_1 and k_2 which are the rate coefficients of the first and second reactions what we saw.

So, in this way this species is right now eliminated from solving. But this species is still in the mechanism, we need not solve a separate governing equation for this. So, we can just calculate, once O, N_2 and O_2 are calculated, I can calculate the concentration of N and use it for other purposes.

For example, calculation of c_p of the mixture, diffusion coefficient of the particular species into mixture etcetera, for all other activities you will see that the concentration of N will be used, but a separate equation for N is not needed.

So, that is the advantage of doing this. So, in a steady state approximation which can be applied to radicals and fast reaction species which are produced initially at a higher rate, but also consumed much at a much higher rate in the subsequent procedure of the reaction can be calculated using a steady state approximation. So, that is what is illustrated here.

So, this is one of the approximation or methods which will be used to eliminate the species.

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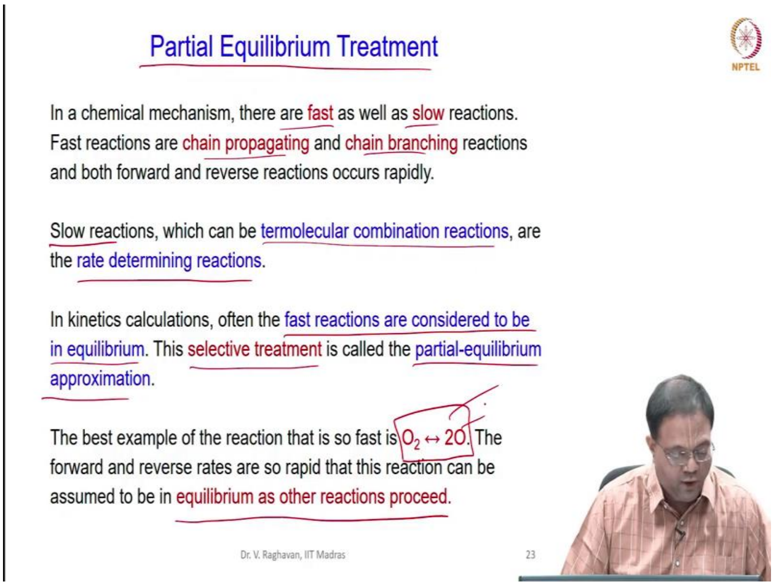

Partial Equilibrium Treatment

In a chemical mechanism, there are fast as well as slow reactions. Fast reactions are chain propagating and chain branching reactions and both forward and reverse reactions occurs rapidly.

Slow reactions, which can be termolecular combination reactions, are the rate determining reactions.

In kinetics calculations, often the fast reactions are considered to be in equilibrium. This selective treatment is called the partial-equilibrium approximation.

The best example of the reaction that is so fast is $O_2 \leftrightarrow 2O$. The forward and reverse rates are so rapid that this reaction can be assumed to be in equilibrium as other reactions proceed.

The second treatment, second way to eliminate the species like solving the conservation equation of species is partial equilibrium treatment. Now, the chemical mechanism has several reactions, out of them some are very fast, some are very slow and so on. Very extremely fast reactions are chain propagating reactions, chain branching reactions etcetera.

Slow reaction etcetera is termolecular, three molecules combination reactions etcetera or slow reactions. Normally, these slow reactions only will control the overall rate of the mechanism.

See for example, in a road if there is a slow moving vehicle that will actually decide the speed of the other vehicles following it and so on, so, similar to that the slow reactions are the rate determining reactions.

So, by the time the slow reactions are going to be completed the fast reaction would have been completed much faster and they would have reach reached the equilibrium condition. So, at a given temperature and pressure they would have complete and they would have reached the equilibrium, the slow reactions are still going on.

So, fast reactions can be considered to be in equilibrium. So, this selective I am not considering everything in equilibrium. I am not giving so much time to all the reaction to complete and all the products to come to equilibrium, we are not doing that. What we are trying to do is only the selective treatment of assuming equilibrium for certain reactions.

So, this approach is called partial-equilibrium treatment or a partial-equilibrium approximation. We will give an example again to say what we are trying to demonstrate here. So, consider the fastest reaction $O_2 \leftrightarrow 2O$. It is a very fast reaction.

Here, in the forward rate, O_2 is producing 2O atoms or the at the reverse rate 2O atoms combining to form O_2 are very fast. So, that this completes within a very quick time and after completion this becomes an equilibrium.

So, based upon the temperature and pressure certain amount of O_2 and certain amount of O will be there in the particular mixture. So, the equilibrium can be assumed for this reaction and other reactions are still going on. So, when you do this equilibrium for this I can eliminate O for example.

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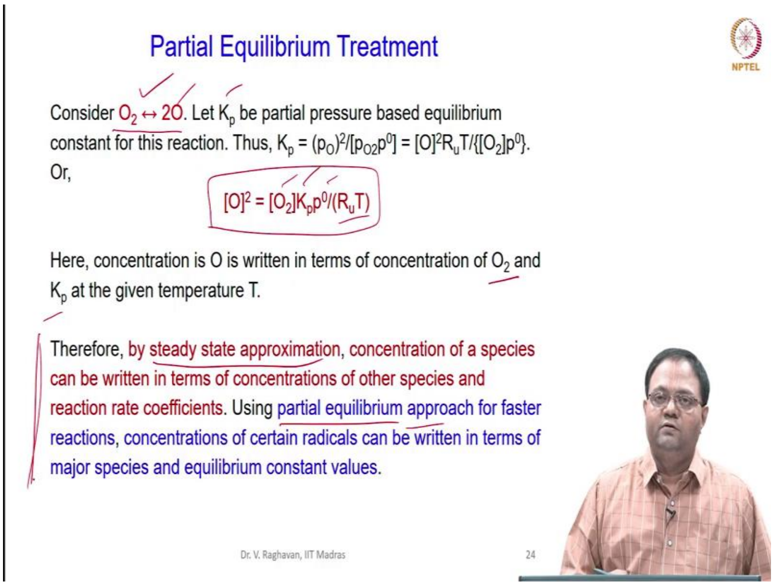

Partial Equilibrium Treatment

Consider $O_2 \leftrightarrow 2O$. Let K_p be partial pressure based equilibrium constant for this reaction. Thus, $K_p = (p_O)^2/[p_{O2}p^0] = [O]^2R_uT/\{[O_2]p^0\}$. Or,

$$\boxed{[O]^2 = [O_2]K_pp^0/(R_uT)}$$

Here, concentration is O is written in terms of concentration of O_2 and K_p at the given temperature T.

Therefore, by steady state approximation, concentration of a species can be written in terms of concentrations of other species and reaction rate coefficients. Using partial equilibrium approach for faster reactions, concentrations of certain radicals can be written in terms of major species and equilibrium constant values.

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So, what I would do here is I will consider the reaction $O_2 \leftrightarrow 2O$ that is the fastest reaction that should be in equilibrium and I calculate the equilibrium constant based upon partial pressure.

So, what is that? $K_p = (p_O)^2/[p_{O2}p^0] = [O]^2R_uT/\{[O_2]p^0\}$.. So, when you write that you will get partial pressure of O square divided by partial pressure of O_2 into p^o that is atmospheric pressure, the standard pressure.

Now, in terms of concentration you can write it as

$$[O]^2 = [O_2]K_pp^0/(R_uT)$$

So, now, I can calculate the concentration of O in terms of concentration of O_2 partial pressure-based equilibrium constant and the atmospheric pressure, R_u and T etcetera at a particular temperature.

I can calculate the concentration of O with this; that means, I need not solve a partial differential equation to calculate transportation of the O. So, O can be calculated by this equation. So, O is now eliminated for from the partial differential equations. So, concentration of O is written in terms of concentration of O_2 and K_p at a given temperature.

So, this way these two approaches we have seen that in the first approach steady state approximation can be used to write the concentration of radical, some radicals you know as a function of other species rate coefficients etcetera, so that a partial differential equation need not be solved for that radical. We can assume several radicals like that.

Similarly, this is one of the reactions which we consider to be in partial equilibrium. We can also consider other reactions which are much faster and those reactions can be assumed to be in partial equilibrium, so that the species radicals, again some radicals like that can be assumed to be in partial equilibrium. So that they can be calculated. The concentration of them can be calculated using the concentration of other species temperature and so on and K_p basically.

So, these two approaches like steady state approximation or the partial equilibrium approach are used to eliminate solving the partial differential equation or the concentration equation for several species. So that even though these species are going to be used for calculating the c_p values other properties such as diffusion coefficients, mixture enthalpy, mixture properties etcetera.

So, there is no need to solve a separate conservation equation for that because the concentration of these species can be solved using the concentration of other species and the reaction rate coefficients, partial pressure based equilibrium constants and so on. So, these two approaches help us in eliminating solution of partial differential equation.

So, if there are N equations, if you do not apply any of these rules or approximations, we will end solving N-1 partial differential equations. So, if N becomes very high then we will be solving too much of equations.

So, when you try to put some conditions for this and eliminate say 10 equations so, we need to only solve N-11 equations in that way. So, that is the advantage of this.

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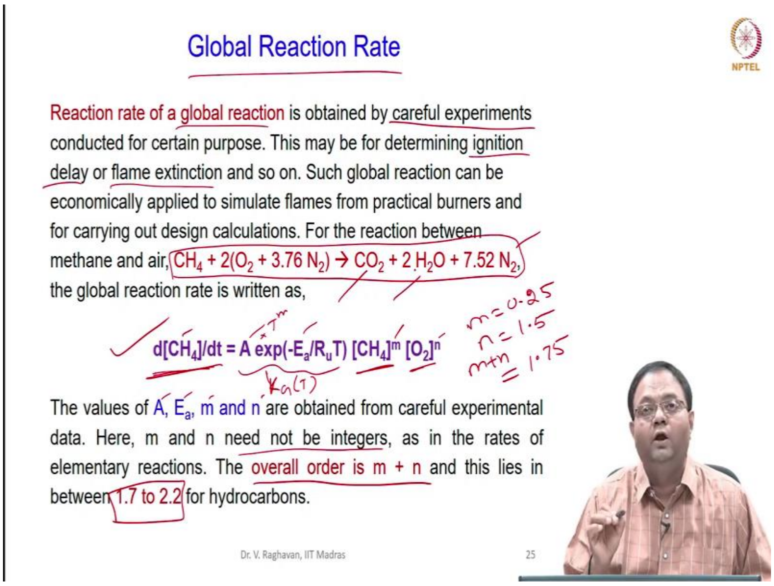

Global Reaction Rate

Reaction rate of a global reaction is obtained by careful experiments conducted for certain purpose. This may be for determining ignition delay or flame extinction and so on. Such global reaction can be economically applied to simulate flames from practical burners and for carrying out design calculations. For the reaction between methane and air, $\boxed{CH_4 + 2(O_2 + 3.76\ N_2) \rightarrow CO_2 + 2\ H_2O + 7.52\ N_2}$, the global reaction rate is written as,

$$d[CH_4]/dt = \underbrace{A \overset{\times T^m}{\exp}(-E_a/R_uT)}_{k_a(T)} [CH_4]^m [O_2]^n$$

$m = 0.25$
$n = 1.5$
$m+n = 1.75$

The values of A, E_a, m and n are obtained from careful experimental data. Here, m and n need not be integers, as in the rates of elementary reactions. The overall order is m + n and this lies in between $\boxed{1.7 \text{ to } 2.2}$ for hydrocarbons.

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Now, so far we have seen the rate coefficient for elementary reactions and the way for example, here we have seen in a mechanism several reactions are there from that a particular net rate of consumption or production of a particular reaction of species like O_2 how we have to write we have seen and all these equations r1, r2, r4 etcetera are elementary reactions.

So, elementary reaction rates involve the concentration of the reactants raised to the stoichiometric coefficients. Here, for example, HO_2 and H react to form O_2 and H_2. So, here this HO_2 the power of this HO_2 concentration is 1. That is stoichiometric coefficient of this particular reaction itself. So, we have seen how to do that for elementary reactions.

Now, we will see how the global reaction rate is calculated. Now, for elementary reactions what we have told is there is a kinetic theory basis for arriving at the way the reaction rate is written like the Arrhenius form, A, pre-exponential factor into exponent of $-E_a/R_uT$ or if you want to add a third temperature factor T^m also is multiplied there.

But, for a global reaction there is no basis because these are molar based reactions. So, only by careful experiments we will be able to get the reaction rate for this.

So, normally this particular global reaction it is useful for doing bigger problems where the dimensions or the chambers are higher, it may be 2-dimensional 3-dimensional simulations and so on.

In that case, using a detailed mechanism will be very tough. So, in several cases you can use a global single step mechanism like this and basically for each of this we have determined the rate coefficient.

For example, if you want to do ignition delay calculation or flame extinction characteristic of a particular burner etcetera, then a single step reaction involving that can be tested and the rate coefficient can be determined and that can be used for doing parametric studies.

So, let us consider the reaction of methane and air. For this reaction the rate of change of concentration of methane is given by again same type of Arrhenius rate coefficient, pre-exponential factor and activation energy.

$$d[CH_4]/dt = A \exp(-E_a/R_uT)\,[CH_4]^m\,[O_2]^n$$

So, Aexp($-E_a/R_uT$), this is the K_G. So, global rate coefficient K_G is a strong function of temperature as you see here. If you want you can also add T^m that is also possible.

Here you can also add this and multiply this to this. Then concentration of methane to the power m, and concentration of oxygen to the power n; now, this m is not 1 or n is not 2×4.76. It is not stoichiometric coefficients.

m and n are determined by the curve fit in which you conduct the experiment in several isothermal conditions and measure the concentration of CH_4 as a function of time and then fit this curve to get this values of m, n, A, E_a etcetera. So, the values of A, E_a, m and n are obtained from careful experimental data.

So, m and n are not stoichiometric coefficients and they need not be integers also. For example, m can be 0.25 and n can be 1.5. So, that the total order of the reaction can be m + n = 1.75. So, similar values you will get. There is no need that we have to fit only integers here, it can be 0.25, 1.5 etcetera.

So, the overall order of the global reaction. So, this is where we are now defining the order of the reaction; order of the reaction for elementary reaction is same as the molecularity. So, number of molecules participating, but here there is no molecule business here. So, there is no molecular definition here for global reaction.

However, you can see that the order can be defined from the rate equation. What is the order? The powers of the concentration of reactant which have raised to those powers they are added up that will give the order. So, in this case m + n will be the overall order of the reaction and for hydrocarbon fuels, the m + n lies in between 1.7 to 2.2.

So, again indicating that the order is second order, second order reactions. So, global reaction rate is obtained only from experimental data and it is actually done for several purposes. See if you have a elementary reaction based mechanism detailed mechanism with several steps that can be used to obtain anything.

Say for example, ignition delay flame extinction accurate temperature etcetera. So, structure of the flame. So, that elementary based reaction schemes which are several reactions and several species are involved in that that can be used for getting all type of oxidation features of any particular fuel.

However, when you try to construct a single step reaction like this we have to get the coefficient for a particular type of problem. For example, if ignition delay, the coefficient can be a different way of expression like A and E_a it be can be different if you want to predict flame extinction the A and E_a value can be different.

So, even m and n values also can be different. So, for a particular condition we try to do experiments and try to correlate, this called experimental correlation.

So, empirical correlations are got for the overall reaction rates. This is called overall reaction rate, the rate at which the main fuel species is consumed. So, you can see that this is the rate at which the oxygen also will be consumed and the rate at which this CO_2 is formed and so on.

So, based upon the mass you can also write. For example, if 1 kg of methane is consumed, how much oxygen it takes? Say s kg of oxygen. If 1 kg of methane is consumed then s kg of oxygen will be consumed.

Similarly, the products; 1+s kg of total product should be formed, so, that will be formed. So, this is the way we write the overall reaction rate for a global reaction.

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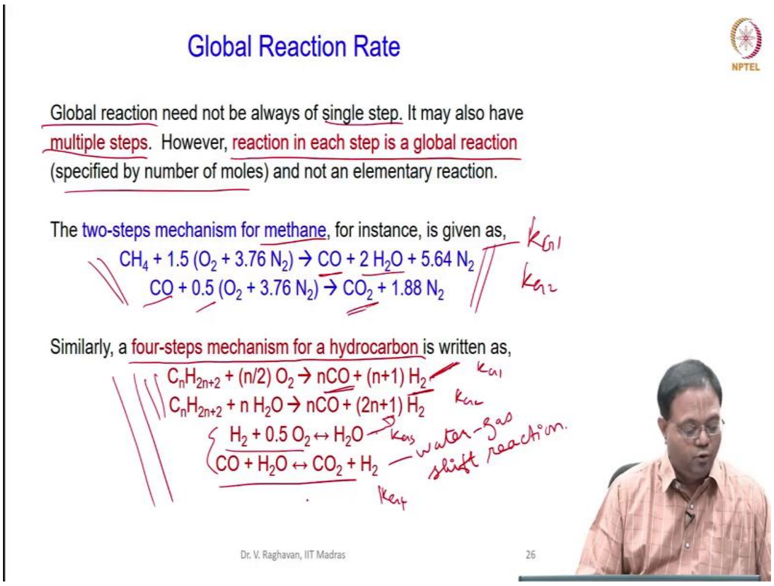

Global Reaction Rate

Global reaction need not be always of single step. It may also have multiple steps. However, reaction in each step is a global reaction (specified by number of moles) and not an elementary reaction.

The two-steps mechanism for methane, for instance, is given as,

$$CH_4 + 1.5\,(O_2 + 3.76\,N_2) \rightarrow CO + 2\,H_2O + 5.64\,N_2 \quad k_{G1}$$
$$CO + 0.5\,(O_2 + 3.76\,N_2) \rightarrow CO_2 + 1.88\,N_2 \quad k_{G2}$$

Similarly, a four-steps mechanism for a hydrocarbon is written as,

$$C_nH_{2n+2} + (n/2)\,O_2 \rightarrow nCO + (n+1)\,H_2 \quad k_{G1}$$
$$C_nH_{2n+2} + n\,H_2O \rightarrow nCO + (2n+1)\,H_2 \quad k_{G2}$$
$$H_2 + 0.5\,O_2 \leftrightarrow H_2O \quad k_{G3}$$
$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad k_{G4}$$

water-gas shift reaction.

Now, the global reaction need not be always single steps. Say a single step if you write you have only major products CO_2 and H_2O only you have in this but if you want to include say a few more species like CO, H_2 etcetera which will be more accurate. So, the calculation will be more accurate when you involve CO, H_2 etcetera in the reaction scheme.

So, you can also have multiple steps for the global reaction. When I say multiple steps what is the difference between a mechanism involving elementary reactions and a mechanism involving global reactions, here you can see that the reaction in each step is only of global reaction; that means, they cannot take place in one step and they are not molecular level reactions. They are again specified by the number of moles only.

So, multiple step reactions are there for example, two-step reaction mechanism for methane in which what we do is CH_4 it will not burn with 2 times air, it will be 1.5 times oxygen. First step will produce only CO, but please see that all the H_2O will be produced in the first step. But only CO will be produced.

The second step the CO will be oxidized with the remaining oxygen and CO_2 will be finally formed.

So, again please understand this is only one-way reaction these two are only one-way reactions and they are going to occur in several steps again. So, these are all global reactions.

Again, by experiments we can get the values of k_1 and k_2 this is the first reaction. So, say k_{G1} and this is k_{G2}. This k_{G1} is nothing, but the rate coefficient for the reaction 1 which produces CO and H_2O. k_{G2} is the rate coefficient for the second reaction which consumes CO to produce CO_2.

So, these two reactions are global reactions. Similarly, researchers have come out with four-step mechanism for any hydrocarbon say here C_nH_{2n+2}, the first step produces CO + H_2.

$$C_nH_{2n+2} + (n/2)\,O_2 \rightarrow nCO + (n+1)\,H_2$$

$$C_nH_{2n+2} + n\,H_2O \rightarrow nCO + (2n+1)\,H_2$$

$$H_2 + 0.5\,O_2 \leftrightarrow H_2O$$

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

So, now please see this in the single step global reaction. We do not have CO at all we have only CO_2 and H_2O. In the two-step H_2O dissociation is not taken into account. So, H_2O is not there, but CO is included because CO consumption is very important for several cases. So, this heat release due to CO oxidation is very important. So, that is taken care by this.

But, in several scenarios if H_2 also is required, then the four-step mechanism is formulated in which the first step we will take some amount of O_2. When I say O_2 you can also write plus 3.76 N_2 and write the N_2 in the right hand side also.

So, it is not only oxygen based, it is also air based. So, wherever I put O_2 in the reactant side here you can also put $O_2 + 3.76 N_2$. So that the nitrogen treated as inert will come to the product side.

Here, the first step produces CO and H_2; second step produces H_2O. See for example, H_2O will react with this to form CO and H_2O again, but how H_2O is formed? H_2O is formed by reaction between H_2 and O_2 and this is formed. So, this will go to this now and react with this alkane to form CO and further CO and H_2O are formed then. So, coupled equations, they are all coupled.

Then finally, we already discussed this water gas shift reaction $CO + H_2O \leftrightarrow CO_2 + H_2$. So, it is called water-gas shift reaction. So, these are all global reactions. All are global reactions. You can wonder these two can be elementary reactions, but these two are global reactions in this. So, you can see basically this calculation of formation of CO and here this plus H_2O alkane plus H_2O giving CO plus H_2 etcetera should be carefully determined by experiments and the rates are formulated. So, k_{G1} here k_{G2}, this is k_{G3} and this is k_{G4}.

So, now this set of equations can be solved to get the detailed, it is not as detailed as the elementary reactions will do, but this will give you additional species like CO and H_2 to be participated in the reaction. So that I will get better prediction of temperatures and other features extinction and ignition etcetera. So, this is about the global reaction rate.