Fundamentals Of Combustion (Part 1)

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Lecture - 28
Quasi-steady state and partial equilibrium approximation

So, let us start this lecture with a thought process from great scientist Albert Einstein, who says.

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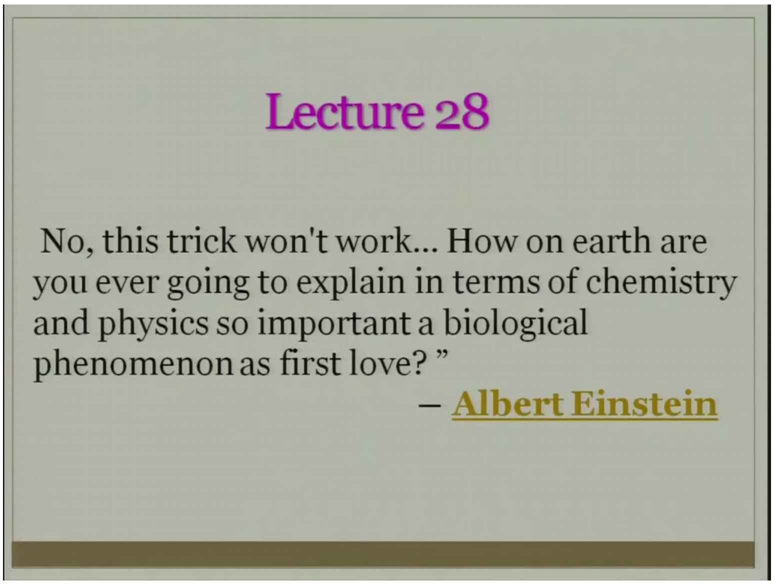

Lecture 28

No, this trick won't work... How on earth are you ever going to explain in terms of chemistry and physics so important a biological phenomenon as first love? ”

– **Albert Einstein**

No, this trick would not work, how on the earth are you ever going to explain in terms of chemistry and physics so important a biological phenomena as first love. You know first love is very important. I like you know very memorable for all of you and all of us rather. So, I mean it cannot be explained through chemistry and physics what Albert Einstein is talking about, but let us recall what we learnt in the last lecture. We are basically looking at types of you know elementary reactions, chain branching, chain initiating, chain carrying, chain terminating.

Then we use those you know chain branching reactions to explain how this chemical explosion will be occurring right. And today what we will do, will basically look at multi step chemistry and later on I will be dealing with how to minimize the number of chemical steps in the multi step chemistry; such that it can be tractable right.

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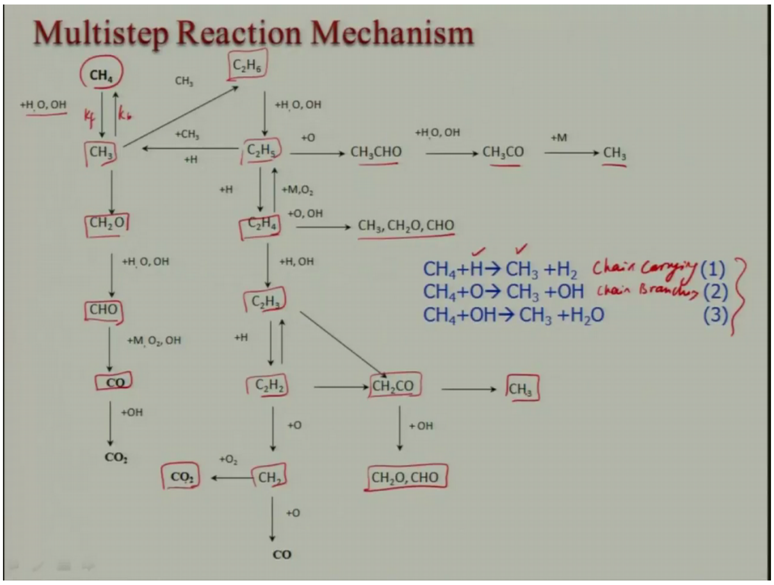

Multistep Reaction Mechanism

$CH_4 + H \rightarrow CH_3 + H_2$ Chain Carrying (1)
$CH_4 + O \rightarrow CH_3 + OH$ Chain Branching (2)
$CH_4 + OH \rightarrow CH_3 + H_2O$ (3)

So, let us look at a multi step chemistry reaction for methane which is a very simple you know hydrocarbons right, and if you look at the methane molecule will be reacting with, let us say there is a radical you know of course, and then what will happen CH 3 plus H 2, and this is what kind of reaction. This is basically chain carrying, because CH 3 is a radical and H is a radical right. So, the ratio is 1, this is a chain carrying reaction yes or no right. And similarly you can say that radical pull is there so that CH 4 is you know reacting with O going to the CH 3 and O H. In this case what will be?

Student: Chain branching.

Chain branching right and CH 4 plus O H getting into CH 3 and water. What is this? This is basically chain, what carrying, is not it only one radical in the product and this thing and the reactant one. So, if you look at, let us say CH 4 is reacting with H O O H, any one of them you know; that means, three reaction I have given, it can go to CH 3 and other thing. These three reactions you know that is the indication and then also it can go backward direction. This is forward if I say kf and this is backward direction CH 3 can be combined with H 2 you know or H and something else and get into that right and C 2 CH 3 will be you know reacting with CH 3 get into C 2 H 6 right, and CA 2 C 2 H 6 can be converted into C 2 H 5 and C 2 H 5 can be converted into C 2 H 4.

It can be getting into C 2 H 3 you know reacting with the what you call H and O H, it can go get into the C 2 H 2, it can get into CH 2 and then from this reacting with it get to the product oxygen. This is a you know some route and there is another CH 3 can be converted into CH 2 O, and then CH 2 can conve[rted]- reacting with H O H getting into CHO and CO right and then CO will be reacting with O H getting into CO 2.

Similarly, there will be several reaction will be taking place here that way in this direction, and then there several product will be formed C 2 H 3 can come into C 2 H 2 plus O H reacting with this products and similarly from here it can C H 3. So, what I was trying, I am trying to show you in this multi step reaction mechanism, you know anything and everything can occur. It is not that this is the thing what is occurring in nature ok.

This is the model what people have device, what exactly is happening god only knows, or maybe in future some of you will do and say look this is the model I am proposing right better model. So, are you getting it is so complicated, but what I am going to show you and this will be containing something, maybe you know around 28 species kind of things and then will be more and maybe something 200 odd reaction or more, but I will not be discussing, that will be you know it will be very difficult, you cant observe also. If you want to look at, then you can look at chemistry of combustion; one book is there by gardener is a one book, chemistry of combustion. Then you can look at that chemistry about that.

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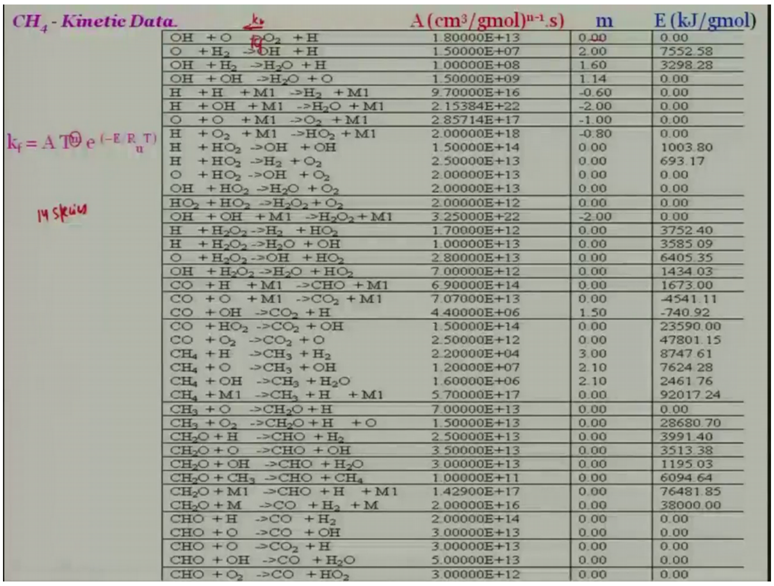

CH_4 - Kinetic Data.

$k_f = A T^{m} e^{(-E/R_u T)}$

14 species

k_f	A $(cm^3/gmol)^{n-1}.s)$	m	E (kJ/gmol)
$OH + O \rightarrow O_2 + H$	1.80000E+13	0.00	0.00
$O + H_2 \rightarrow OH + H$	1.50000E+07	2.00	7552.58
$OH + H_2 \rightarrow H_2O + H$	1.00000E+08	1.60	3298.28
$OH + OH \rightarrow H_2O + O$	1.50000E+09	1.14	0.00
$H + H + M1 \rightarrow H_2 + M1$	9.70000E+16	-0.60	0.00
$H + OH + M1 \rightarrow H_2O + M1$	2.15384E+22	-2.00	0.00
$O + O + M1 \rightarrow O_2 + M1$	2.85714E+17	-1.00	0.00
$H + O_2 + M1 \rightarrow HO_2 + M1$	2.00000E+18	-0.80	0.00
$H + HO_2 \rightarrow OH + OH$	1.50000E+14	0.00	1003.80
$H + HO_2 \rightarrow H_2 + O_2$	2.50000E+13	0.00	693.17
$O + HO_2 \rightarrow OH + O_2$	2.00000E+13	0.00	0.00
$OH + HO_2 \rightarrow H_2O + O_2$	2.00000E+13	0.00	0.00
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	2.00000E+12	0.00	0.00
$OH + OH + M1 \rightarrow H_2O_2 + M1$	3.25000E+22	-2.00	0.00
$H + H_2O_2 \rightarrow H_2 + HO_2$	1.70000E+12	0.00	3752.40
$H + H_2O_2 \rightarrow H_2O + OH$	1.00000E+13	0.00	3585.09
$O + H_2O_2 \rightarrow OH + HO_2$	2.80000E+13	0.00	6405.35
$OH + H_2O_2 \rightarrow H_2O + HO_2$	7.00000E+12	0.00	1434.03
$CO + H + M1 \rightarrow CHO + M1$	6.90000E+14	0.00	1673.00
$CO + O + M1 \rightarrow CO_2 + M1$	7.07000E+13	0.00	-4541.11
$CO + OH \rightarrow CO_2 + H$	4.40000E+06	1.50	-740.92
$CO + HO_2 \rightarrow CO_2 + OH$	1.50000E+14	0.00	23590.00
$CO + O_2 \rightarrow CO_2 + O$	2.50000E+12	0.00	47801.15
$CH_4 + H \rightarrow CH_3 + H_2$	2.20000E+04	3.00	8747.61
$CH_4 + O \rightarrow CH_3 + OH$	1.20000E+07	2.10	7624.28
$CH_4 + OH \rightarrow CH_3 + H_2O$	1.60000E+06	2.10	2461.76
$CH_4 + M1 \rightarrow CH_3 + H + M1$	5.70000E+17	0.00	92017.24
$CH_3 + O \rightarrow CH_2O + H$	7.00000E+13	0.00	0.00
$CH_3 + O_2 \rightarrow CH_2O + H + O$	1.50000E+13	0.00	28680.70
$CH_2O + H \rightarrow CHO + H_2$	2.50000E+13	0.00	3991.40
$CH_2O + O \rightarrow CHO + OH$	3.50000E+13	0.00	3513.38
$CH_2O + OH \rightarrow CHO + H_2O$	3.00000E+13	0.00	1195.03
$CH_2O + CH_3 \rightarrow CHO + CH_4$	1.00000E+11	0.00	6094.64
$CH_2O + M1 \rightarrow CHO + H + M1$	1.42900E+17	0.00	76481.85
$CH_2O + M \rightarrow CO + H_2 + M$	2.00000E+16	0.00	38000.00
$CHO + H \rightarrow CO + H_2$	2.00000E+14	0.00	0.00
$CHO + O \rightarrow CO + OH$	3.00000E+13	0.00	0.00
$CHO + O \rightarrow CO_2 + H$	3.00000E+13	0.00	0.00
$CHO + OH \rightarrow CO + H_2O$	5.00000E+13	0.00	0.00
$CHO + O_2 \rightarrow CO + HO_2$	3.00000E+12	0.00	0.00

So, what I will show you. I will show you kinetics data for methane air system which I had used long time back, 20 years back for my PhD thesis. So, we are showing here. This contains something 14 species and 40 reactions. These are all 40 reactions and keep in mind that here only C 1 chemistry; that means, C 2 H 6 C 2 like you know H 5 H 3 they are not there right, and this is for the forward reaction, you can get the backward reaction, all these coefficients you know. This is your active pre exponential factor A and this is the m coefficient. Here values are given E is the activation energy right and you can calculate the reverse reaction rate by using what this reaction rate, you can calculate.

This is k f and this is kb, you can calculate using the equilibrium at what the way we did, you can calculate right and then use that one and this is giving, this is giving fairly well the about prediction of burning velocity is an ignition delay and other things ok, and this simple one and this can be computed even in your personal you know computers like. So, now, if you look at as I told people are using very you know long, what you call number of reactions being used in chemical reactions for methane air and other higher hydrocarbon, because of course, nowadays CNG being used, which contains methane, but it contains some other higher hydrocarbons also.

But hydrocarbon means more number of species involve more number of reactions, and it will take a lot of time to compute right and unless you are having a parallel computing. And if you are doing a very complicated problem like a internal combustion engine or gas turbine engine or rocket engines you know like, it will be hell of affairs to predict something meaningful using kinetics. So, therefore, there is a need to reduce this mechanism and coming to the global kinetics or maybe two step chemistry, 3 step chemistry or maybe 5 step chemistry there various models are there. So, for that we will be discussing two methodology only.

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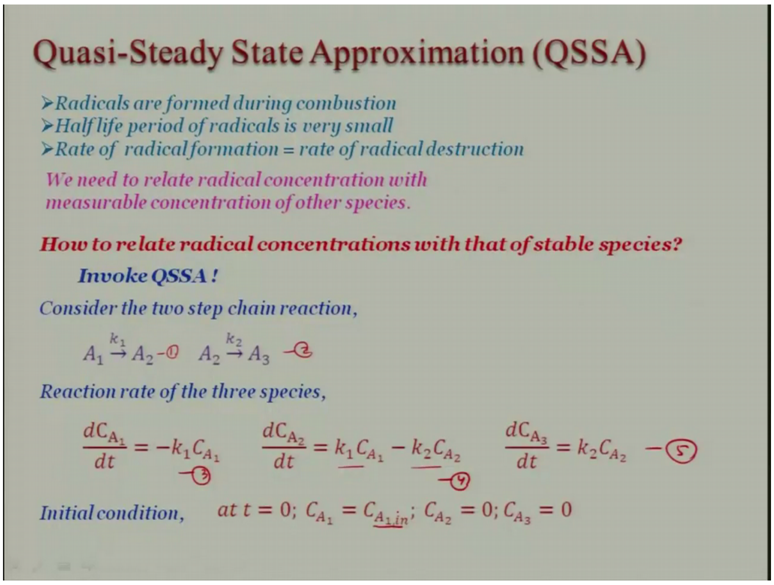

Quasi-Steady State Approximation (QSSA)

- *Radicals are formed during combustion*
- *Half life period of radicals is very small*
- *Rate of radical formation = rate of radical destruction*

We need to relate radical concentration with measurable concentration of other species.

How to relate radical concentrations with that of stable species?

Invoke QSSA !

Consider the two step chain reaction,

$$A_1 \xrightarrow{k_1} A_2 - ① \quad A_2 \xrightarrow{k_2} A_3 - ②$$

Reaction rate of the three species,

$$\frac{dC_{A_1}}{dt} = -k_1 C_{A_1} - ③ \qquad \frac{dC_{A_2}}{dt} = \underline{k_1 C_{A_1}} - \underline{k_2 C_{A_2}} - ④ \qquad \frac{dC_{A_3}}{dt} = k_2 C_{A_2} - ⑤$$

Initial condition, $at\ t = 0;\ C_{A_1} = C_{\underline{A_1,in}};\ C_{A_2} = 0;\ C_{A_3} = 0$

There are several other also; one is quasi steady state approximation method model. In this case what is being assumed that you assume it as reach a steady state and in this case we know that radicals form during combustion right, and radicals life, half life is very very small as compared to stable species ok. So, therefore, I can say the rate of radical formation is equal to rate of radical destruction. I can say that, because they you know in the certain time doing that thing, it will be there, after that it will not be there right.

It is like your if you look at the time scale of the our let us say Indus valley civilization and ours is like a radical will be here, doing something contributing and then go away after that, we will not be there. Similarly radicals you know is the role is that. So, therefore, we can say the rate of radical formation is equal to rate of radical destruction for that region. We need to relate the radical concentration with measurable concentration of other species. Why we are saying, because radical you cannot measure is very difficult to measure radicals ok.

Of course, people are devising very sophisticated instrument, still it will be difficult right, because this will be in the order of femtoseconds, you know not microsecond nano femto right that kind of seconds it will vary. So, therefore, we can you know make this assumption and we want to basic idea of this analysis also to you know relate this concentration of radicals in terms of stable species concentration, which you can measure. So, how to relate this radical concentration with that of the stable species is the question? What will be you know using you know addressing by using this approximation.

So, for that we will have to invoke quasi steady state approximation. Let us consider that A is react you know converted into A 2 with the reaction rate of k 1, and this I can say reaction one and then A 2 is converted into to A 3 is A 2 reaction. So, if you look at this, is basically a series reaction, is not it. A 1 is getting into A 2 then A 2 is getting into A 3.

Now, reaction rate of these three species right if you look at dC A 1 by dt is nothing, but minus k 1 CA 1 right and dC A 2 by dt is nothing, but k 1 CA 1 minus k 2 CA 2 right, because this is coming from reaction 1. This one from reaction 1, this is reaction 2 and dC A 3 is from basically from reaction 1; that is k 2 CA 2 right. So, if I say this is basically what you call this is 3 and this is your 4 and this is your 5 right, equation.

I will have to solve this thing and relate and do some approximation by doing that right. So, what will be the initial condition, initial condition at time t is CA will be C initial and CA 2 will be zero CA 3 will be zero, yes or no. This will be zero. There will be no CA 2 right, concentration will be zero of A 2 molecule and concentration of A 3 will be zero. This is the initial condition which will be using right. Now, I will take this equation 3 right and try to integrate right.

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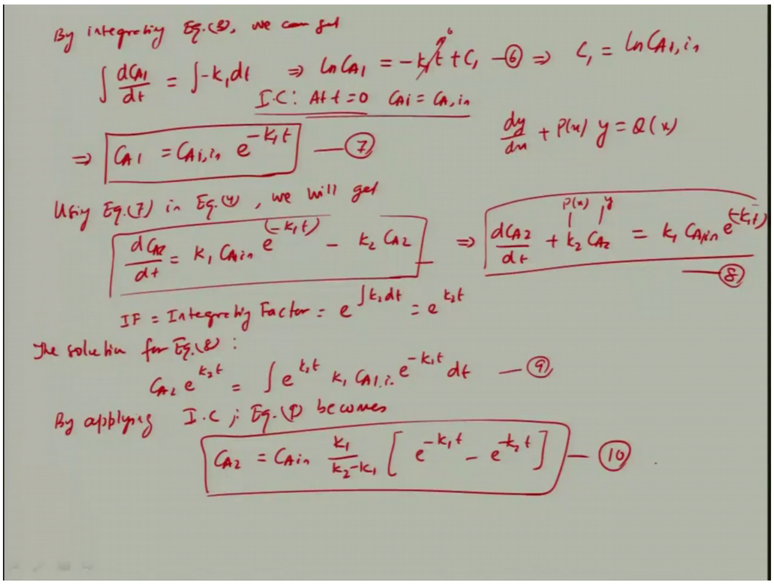

By integrating Eq.(3), we can get

$$\int \frac{dC_{A1}}{dt} = \int -k_1 dt \Rightarrow \ln C_{A1} = -k_1 \overset{0}{\cancel{t}} + C_1 \quad —⑥ \Rightarrow C_1 = \ln C_{A1,in}$$

$\underline{I.C: At\ t = 0 \quad C_{Ai} = C_{A,in}}$

$$\Rightarrow \boxed{C_{A1} = C_{A1,in}\, e^{-k_1 t}} \quad —⑦$$

$$\frac{dy}{dx} + P(x)\, y = Q(x)$$

Using Eq.(7) in Eq.(4), we will get

$$\boxed{\frac{dC_{A2}}{dt} = k_1 C_{Ain}\, e^{(-k_1 t)} - k_2 C_{A2}} \Rightarrow \boxed{\frac{dC_{A2}}{dt} + \overset{P(x)}{k_2}\, \overset{y}{C_{A2}} = k_1 C_{A1in}\, e^{(-k_1 t)}} \quad —⑧$$

$$IF = \text{Integrating Factor} = e^{\int k_2 dt} = e^{k_2 t}$$

The solution for Eq.(8):

$$C_{A2}\, e^{k_2 t} = \int e^{k_2 t}\, k_1 C_{A1,in}\, e^{-k_1 t}\, dt \quad —⑨$$

By applying I.C; Eq.(9) becomes

$$\boxed{C_{A2} = C_{Ain} \frac{k_1}{k_2 - k_1} \left[e^{-k_1 t} - e^{-k_2 t} \right]} \quad —⑩$$

So, by integrating equation 3 we can get basically dC A 1 dt k 1 dt I can write down. This is ln CA 1 is equal to minus k 1 t plus C 1 and what will be C 1. I will have to apply the boundary initial condition right at t is equal to zero, at t is equal to zero, C A 1 will be CA in. Is not it yes or no? so; that means, at t is equal to zero, this will be zero and then what will be C 1, C 1 will be basically ln C A 1 in. So, then I can write down you know from this. I can write down C A 1 is equal to C A 1 in e power to k 1 t.

If I take this is 6 right, this will be 7 and what we will do, we will use this using equation 7 in equation 4 right. Equation 4 we will get dCA 2 by dt is k 1 C A in 1 ok. This is A 1 e power to the minus k 1 t minus k 2 C A 2 right. This we want to solve right. If you look at this equation right is which form is this, is a differential, is a ordinary differential equation of first order right and this is which form are you not getting ok. Let me write down here you will get, catch it very easily right is plus k 2 C A 2 right is equal to k 1 C A i in e k 1 t, this is which form that is if you look at dy by dx plus.

Student: (Refer Time: 15:33).

P x y is equal to Qx form right. This is a first order od inhomogeneous right. So, now, I want to solve I know the solution, solution. What is that solution? We will have to find out basically integrating factor right. In this case what will be integrating factor, integrating factor right, what it would be? It will be e.

Student: (Refer Time: 16:10).

K 2 dt, because this is your.

Student: (Refer Time: 16:16).

P x right, this is your y. So, that is equal to e k 2 t, right. So, then what will happen, I will get this solution. The solution this is ok. Let me write down this is 8, this is 8 ok, 8. The solution for equation 8 ok. What it would be? It will be C A 2 e k 2 t is equal to right e k 2 t k 1 C A 1 in. This is the term I am writing. Now Q x right e power to k 1 t dt right Is not it? So, now, I will not do that, you will have to do this thing by applying this initial condition right. By applying initial condition that already we have discussed, this is your initial condition right.

So, I can get a solution like this right. If I say this is 9 right, equation 9 becomes C A 2 is equal to C A in k 1 by k 2 minus k 1 t minus k 2 t right. This is your equation ok. Now, we will have to basically look at now expression for the CA 3 right, and we will. What we will have to use? This thing, see equation 10 here why? Because if you recall that equation 4 right, is expressed in terms of CA 2 right, because we know CA 3 right, we know that dCA 3 by dt is nothing, but k 2 C A 2.

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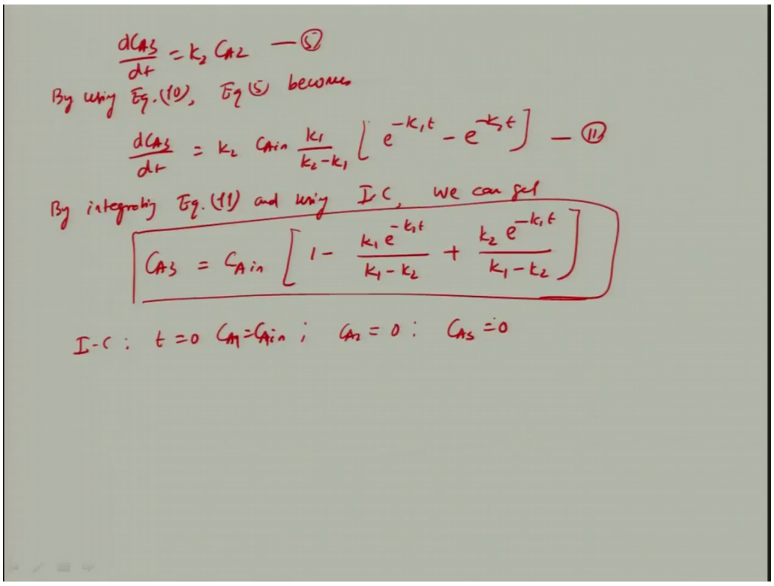

$$\frac{dC_{A3}}{dt} = k_2 C_{A2} \quad — ⑤$$

By using Eq. (10), Eq ⑤ becomes

$$\frac{dC_{A3}}{dt} = k_2 C_{Ain} \frac{k_1}{k_2 - k_1} \left[e^{-k_1 t} - e^{-k_2 t} \right] \quad — ⑪$$

By integrating Eq. (11) and using I.C, we can get

$$\boxed{C_{A3} = C_{Ain} \left[1 - \frac{k_1 e^{-k_2 t}}{k_1 - k_2} + \frac{k_2 e^{-k_1 t}}{k_1 - k_2} \right]}$$

I.C : $t = 0$ $C_{A1} = C_{Ain}$; $C_{A2} = 0$: $C_{A3} = 0$

So, by using equation 10 we can get. This is equation 5. equation 5 becomes d C A 3 by dt is equal to k 2 C A in k 1 k 2 minus k 2 minus k 1 e minus k 1 t minus k 2 t right, and I will have to integrate this equation like this is, let say 11 by integrating equation 11 and using initial condition right, we can get. I am omitting some steps we can get C A 3 is equal to C A in k 1 e k 2 t divided by k 1 minus k 2 plus k 2 e minus k 1 t divided by k 1 minus k 2, this you will get this expression right.

So, you can get and using initial condition. Initial condition here t is equal to zero C A is equal to C A initial 1 initial and CA 2 is zero and C A 3 is zero right. So, you will have to apply that and you will get this. Let us now look at.

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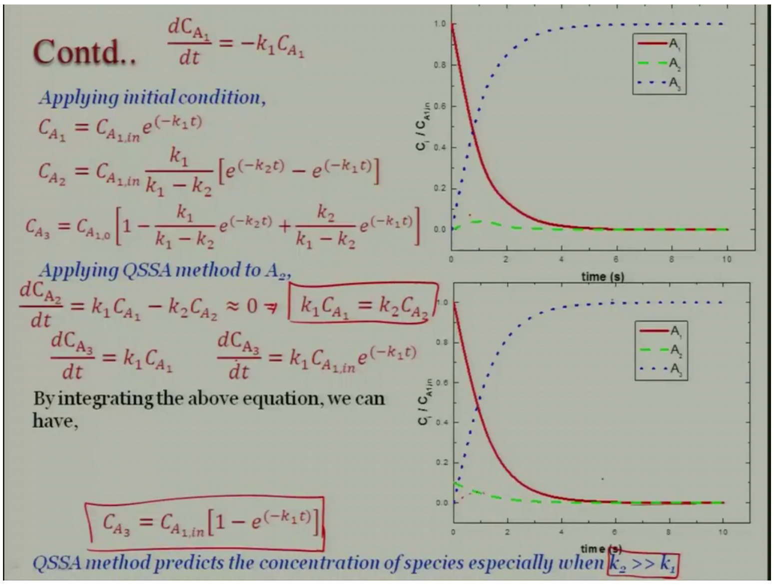

Contd.. $\frac{dC_{A_1}}{dt} = -k_1 C_{A_1}$

Applying initial condition,

$C_{A_1} = C_{A_{1,in}} e^{(-k_1 t)}$

$C_{A_2} = C_{A_{1,in}} \frac{k_1}{k_1 - k_2} \left[e^{(-k_2 t)} - e^{(-k_1 t)}\right]$

$C_{A_3} = C_{A_{1,0}} \left[1 - \frac{k_1}{k_1 - k_2} e^{(-k_2 t)} + \frac{k_2}{k_1 - k_2} e^{(-k_1 t)}\right]$

Applying QSSA method to A_2,

$\frac{dC_{A_2}}{dt} = k_1 C_{A_1} - k_2 C_{A_2} \approx 0 \Rightarrow \boxed{k_1 C_{A_1} = k_2 C_{A_2}}$

$\frac{dC_{A_3}}{dt} = k_1 C_{A_1} \qquad \frac{dC_{A_3}}{dt} = k_1 C_{A_{1,in}} e^{(-k_1 t)}$

By integrating the above equation, we can have,

$\boxed{C_{A_3} = C_{A_{1,in}} \left[1 - e^{(-k_1 t)}\right]}$

QSSA method predicts the concentration of species especially when $\boxed{k_2 >> k_1}$

I mean you can get this thing expression what I have shown. Now what we will do this is the analytical form right, you are getting an analytical form, if I just do that thing with respect to time you will get this is A 1 A 1 is decreasing right and A 3 is increasing; that is you know obvious thing right and A 2 is there is a little peak here, and then after that remaining same with this, these are analytical tools right, but let us say, you know its a very simple one, we are getting analytically, but in the complex one we will not be, we will be doing some approximation that is quasi steady state approximation right and if I look at what I am doing by applying this method, we are saying that C A 2 intermediate that species is C A 2 which will be not remaining.

I am saying it is zero, it is remaining zero kind of things like the change in zero. So, therefore, k 1 CA 1 is equal to k 2 CA 2 right. Then I can write down as is a very simple one right, and so therefore, earlier it was basically CA 3 is equal to k 2 CA 2 right is equal to k 2 CA 2. And then I am saying this is k 1 CO 1 right are you getting. So, CA 3 is if you look at CA 1 right. In place of CA 1 I have already got this result from the beginning right and then I can get this one.

So, by integrating above this equation right we can get that this is basically CA 3 is equal to say 1 in 1 minus k 1 t, and this is very easy, you can do that right. So, now, I got these values you know C A 3 in terms of C 1 and C A 2 right, and then I can plot these values.

This will be possible only when k 2 is greater than k 1, k 2 is very fast reaction as compared to the k 1; otherwise you cannot apply this kind of you know approximation.

If you do that what you will get, you will get basically the similar values for the CA 1 right concentration and keep in mind this is concentration of i-th species with respect to initial species right of A 1 and respected, but and also you will get similar prediction for the A 3, there is no problem, but problem is here right. It is having some finite value at zero which is not true right, because in the beginning it was supposed to be like that zero right I have shown, but it is not true; that means, this is violating, it is not possible to have that, but; however, later on it is same. So, if I am considering in this region, then it will be fine, it is predicting well.

So, therefore, this is the limitation of this approximation method, but; however, we can simplify the reactions and we can also express in terms of that.

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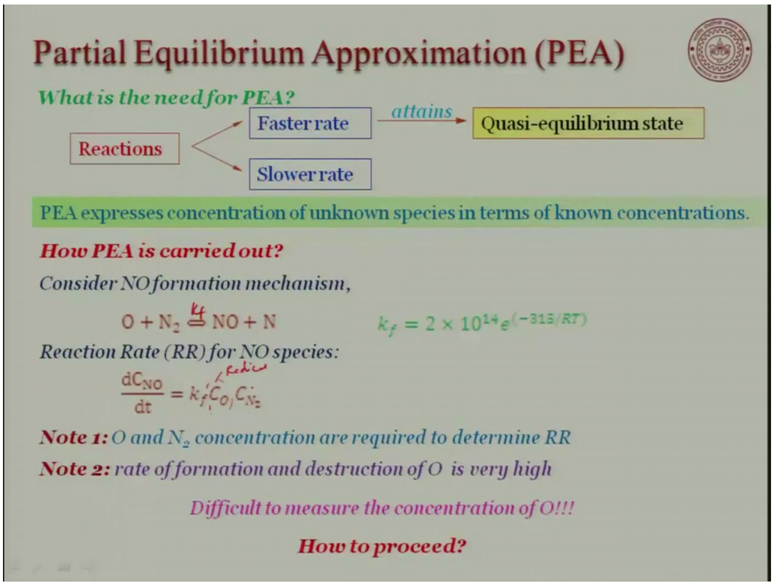

Partial Equilibrium Approximation (PEA)

What is the need for PEA?

PEA expresses concentration of unknown species in terms of known concentrations.

How PEA is carried out?

Consider NO formation mechanism,

$$O + N_2 \overset{k_f}{\rightleftharpoons} NO + N \qquad k_f = 2 \times 10^{14} e^{(-315/RT)}$$

Reaction Rate (RR) for NO species:

$$\frac{dC_{NO}}{dt} = k_f \overset{\text{Radical}}{C_O} C_{N_2}$$

Note 1: *O and N_2 concentration are required to determine RR*

Note 2: *rate of formation and destruction of O is very high*

Difficult to measure the concentration of O!!!

How to proceed?

Let us look at the partial equilibrium approximation right, there is a quasi steady state; that means, something is you know attaining the steady state, but here we are saying partially equilibrium approximation and why it is required, because the reaction you know, certain reaction will be having faster rate certain the action will be slower rate. And if it is faster rate then we can say it is quickly attaining the equilibrium are you getting, it is quickly attending, because it is very fast. So, therefore, we call it as a quasi equilibrium state or partial equilibrium like kind of thing the partially equilibrium expresses concentration of unknown species in terms of known concentration.

So, how is pea is carried out, let us consider a no formation mechanism like O is react with N 2 is getting into N O plus N right, and let us say this kf value is given to you right the some coefficients is known to you and reaction rate of a no species I can write down d C NO divided by dt is equal to kf CO N 2. Keep in mind that C O is a radical the concentration of O is difficult to measure right, this is the radical right and N 2 is a stable species.

So, you can very easily measure right and; however, you need both concentration of O and N 2 to determine the reaction rate of the N O. Now how to go about it and what we can say the rate of formation destruction O is very high; that is the assumption right, because it is a very fast, slow will be and with this as a result of course, it is very difficult to measure the concentration of O that I have already. Now, how will handle it, basically what we will have to do. We will have to invoke the equilibrium ok, and step one assume the partial equilibrium O 2 molecules, right.

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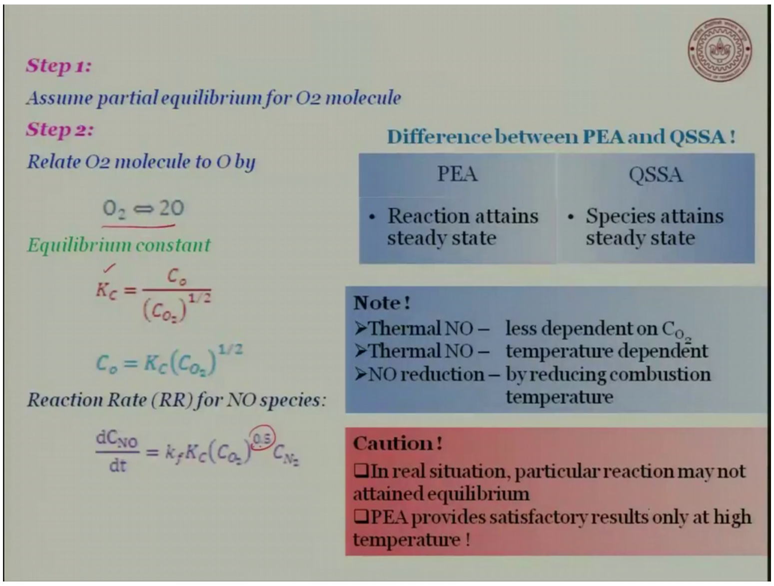

Step 1:

Assume partial equilibrium for O2 molecule

Step 2:

Relate O2 molecule to O by

$$\underline{O_2 \Leftrightarrow 2O}$$

Equilibrium constant

$$\checkmark K_C = \frac{C_O}{(C_{O_2})^{1/2}}$$

$$C_O = K_C(C_{O_2})^{1/2}$$

Reaction Rate (RR) for NO species:

$$\frac{dC_{NO}}{dt} = k_f K_C (C_{O_2})^{\textcircled{0.5}} C_{N_2}$$

Difference between PEA and QSSA !

PEA	QSSA
• Reaction attains steady state	• Species attains steady state

Note !

- ➢Thermal NO – less dependent on C_{O_2}
- ➢Thermal NO – temperature dependent
- ➢NO reduction – by reducing combustion temperature

Caution !

❑In real situation, particular reaction may not attained equilibrium

❑PEA provides satisfactory results only at high temperature !

That means, I will take consider that and then try to relate O 2 with the molecule with the O right, and I will consider O 2 is getting into 2 O, and then it has attained equilibrium right. From that I will find out equilibrium constant KC is equal to C O concentration of O 2 half right. If I know this KC at certain temperature; of course, right, then I can very easily substitute this CO by concentration of O 2 and then I will get co is nothing, but K C concentration of O 2 power to the half and reaction rate or species become kf KC concentration of O 2 half into point 5 CN right. This is basically the reaction rate N O is a function of concentration of O 2 and CN 2. Of course, KC is there and kf is there, but concentration wise the CN 2 will be playing a major role, not the oxygen right.

So, what is the difference between pea and quasi static state approximation? Pea is the partial equilibrium approximation right reaction attends a steady state; that means, this reaction attending a steady state, but in this case, species attain the steady state. There is a difference, are you getting. And as I told this is the part of this reaction whatever, with example you have considered is a thermal N O, though thermal N O or the N O formation due to temperature in less dependent on concentration of O 2, because this is power half. So, therefore, it is less dependent and it is dependent on the temperature.

Therefore, we call it as a temp you know thermal N O and a N O reduction by reducing the combustion temperature you can get, you know you can reduce the N of formation due to, of course, the thermal mechanism by reducing the temperature. So, keep in mind that in real situation particular reaction may not attain equilibrium ok. Therefore, you will have to apply it cautiously and pea partial equilibrium provides satisfactory results only at the high temperature. It will not give you know good approximation at the low temperature for example, we will consider that.

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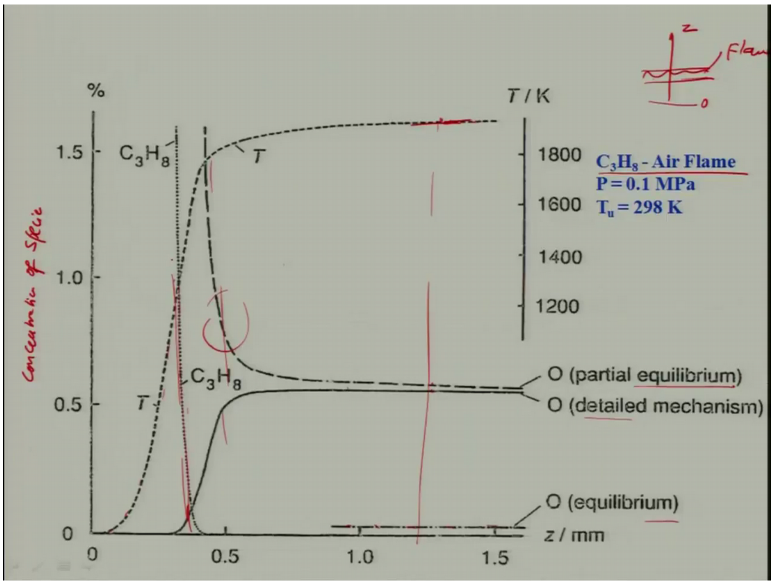

Let us say that I am having a C 3 H 8 air flame at point 1 mega Pascal and 298 and then I am plotting what you call concentration profiles right. These are concentration or species versus the what you call flame. Flame means across the flame, if there is a flame here let us say right, I am going by the z direction, this is my flame, one dimensional flame and this is z direction, I am plotting z. Now what will happen; of course, this is your temperature right, this side is scale is temperature and this is your propane, propane is given.

So, therefore, my you know like kind of things and what will happen to the O right, if I say detailed mechanism this is a solid line, but if I take partial equilibrium mechanism O will be like this; that means, and if I take only equilibrium which you have done, this is the data is here is remaining constant, its not changing are you getting. So, therefore, at this equilibrium at the high temperature zone, because if you look at, if I am saying this is your z this zero my flame is here somewhere nearby. So, therefore, the temperature here will be higher and this temperature will be very low in this region right, because this is a temperature [FL] in this region, temperature is very high.

So, at the high temperature, this both are partial, equilibrium detailed mechanism is approximately same or almost same and this is possible only in the high temperature, but if I consider here in this region, it will be diametrical, it is not wrong, it is not right, because here temperature is not that high as compared to this, and if I consider here in somewhere, where low temperature is there, so it will be quite different. So, therefore, partial equilibrium method has to be applied at the high temperature only global kinetics. Why you will go for global kinetics, why not multi step chemistry.

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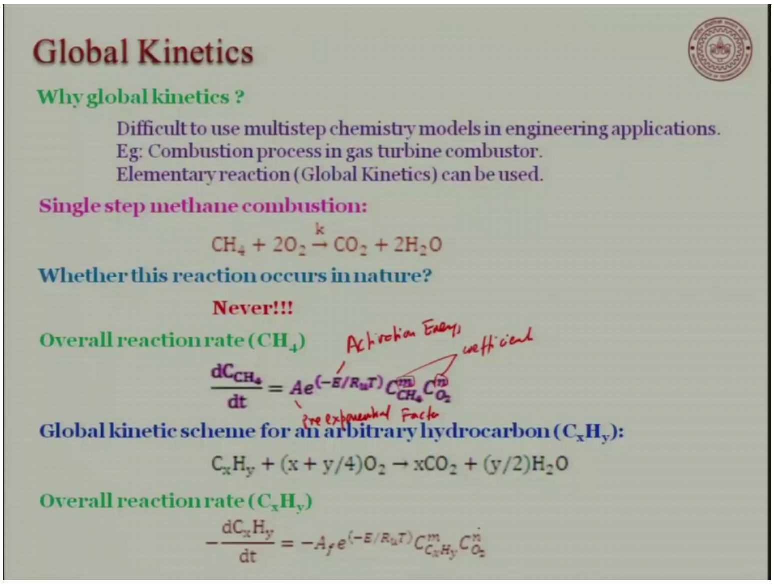

Global Kinetics

Why global kinetics ?

Difficult to use multistep chemistry models in engineering applications.
Eg: Combustion process in gas turbine combustor.
Elementary reaction (Global Kinetics) can be used.

Single step methane combustion:

$$CH_4 + 2O_2 \xrightarrow{k} CO_2 + 2H_2O$$

Whether this reaction occurs in nature?

Never!!!

Overall reaction rate (CH_4)

Activation Energy

coefficient

$$\frac{dC_{CH_4}}{dt} = Ae^{(-E/R_uT)} C_{CH_4}^{\boxed{m}} C_{O_2}^{\boxed{n}}$$

Pre exponential Factor

Global kinetic scheme for an arbitrary hydrocarbon (C_xH_y):

$$C_xH_y + (x + y/4)O_2 \rightarrow xCO_2 + (y/2)H_2O$$

Overall reaction rate (C_xH_y)

$$-\frac{dC_xH_y}{dt} = -A_f e^{(-E/R_uT)} C_{C_xH_y}^{m} C_{O_2}^{n}$$

Because, you know there are several reaction mechanism, we would like to involve, we would like to consider to get a predictions. And if we will do that the computationally, it will be very difficult and analytically impossible. You cannot have anything analytical. Analytical means if you write equation and do that impossible, even computationally it will be very very what you call costly. So, therefore, we always go for a global kinetics, particularly if the flow problem is complex or the engineering problem like your IC engine gas turbine engine other thing.

Therefore, there is a need to go for global kinetics. What is that? That is basically single step you know combustion, you can say people are talking about what to call reduce mechanism 2 steps or 3 steps, but I will consider as a single step, as a global kinetics. Let us say methane 1 mole of methane reacting with 2 oxygen moles of oxygen getting into carbon dioxide and 2 moles of water right.

And whether the reaction occur in nature, certainly no, it is just a model right and overall reaction. I can write down CH 4 dt is equal to a e exponential factor of you know like this you explain as a activation energy. This is your activation energy right and R u is a universal gas constant, T is temperature and this is the concentration of methane and oxygen, and these are coefficients, these are coefficients that has to be obtained, and this is generally obtained by matching the heat release propane right.

And this A values is the pre exponential factors type, and which has to be obtained you know the some values. So, and you can get a kinetic scheme for arbitrary hydrocarbons right, and this is the things you can, you know it is a similar I can instead of methane I am just writing Cx Hy m n right, are you getting. This is just a generalizing. Now, I can get this you know in terms of a tabular data, and then or the data will be there in the table, and you can use that or you can conduct experiment and do keep in mind.

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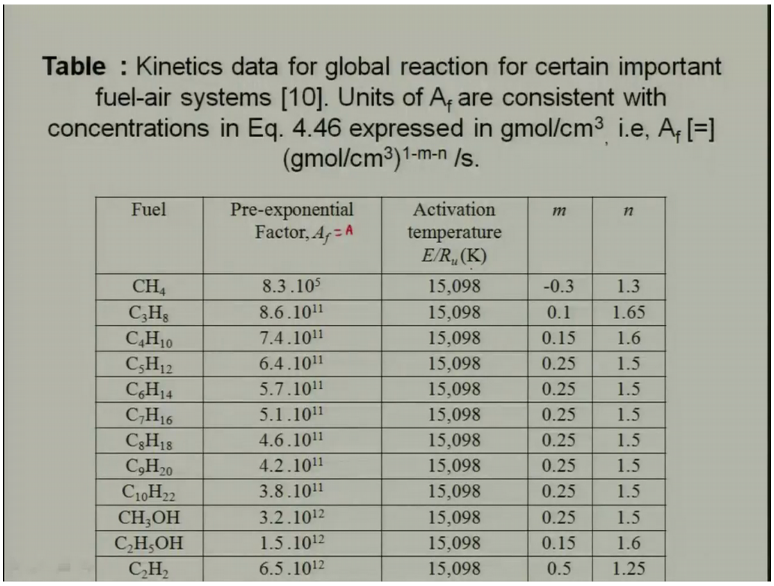

Table : Kinetics data for global reaction for certain important fuel-air systems [10]. Units of A_f are consistent with concentrations in Eq. 4.46 expressed in gmol/cm^3, i.e, A_f [=] (gmol/cm^3)$^{1-m-n}$ /s.

Fuel	Pre-exponential Factor, $A_f = A$	Activation temperature E/R_u(K)	m	n
CH_4	$8.3 . 10^5$	15,098	-0.3	1.3
C_3H_8	$8.6 . 10^{11}$	15,098	0.1	1.65
C_4H_{10}	$7.4 . 10^{11}$	15,098	0.15	1.6
C_5H_{12}	$6.4 . 10^{11}$	15,098	0.25	1.5
C_6H_{14}	$5.7 . 10^{11}$	15,098	0.25	1.5
C_7H_{16}	$5.1 . 10^{11}$	15,098	0.25	1.5
C_8H_{18}	$4.6 . 10^{11}$	15,098	0.25	1.5
C_9H_{20}	$4.2 . 10^{11}$	15,098	0.25	1.5
$C_{10}H_{22}$	$3.8 . 10^{11}$	15,098	0.25	1.5
CH_3OH	$3.2 . 10^{12}$	15,098	0.25	1.5
C_2H_5OH	$1.5 . 10^{12}$	15,098	0.15	1.6
C_2H_2	$6.5 . 10^{12}$	15,098	0.5	1.25

That this data what I am going to show you, is basically for various you know fuel and this is the pre exponential factor A f or a whatever you call, is the same as a what I am using and activation temperature, basically E by R u is nothing, but your activation temperature right and this given and m is our coefficients right. Keep in mind that these values will be varying from various resources you know like or various sources, rather its not that it will be same that is why I was telling this.

A values will be you know quite different and then, so also activation energy here. He has taken all activation, same need not to be this from the just a kind of things people have done modeling and then use it. It need not do the same ok, are you getting my point? This number will be very different from you know various sources if we will use.

So, generally we use this thing and I will stop over with this. And in the next lecture will be discussing about physics of the combustion part.

Thank you very much.