Fundamentals of Aerospace Propulsion
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Lecture - 20

We start this lecture 20, with simple thought process a mighty flame emanates from a tiny spark, if we look at we are here basically discussing about the chemistry of combustion. And in the process we looked at law of mass action, then we moved into the collision theory to find out reaction rate, if you recall reaction rate is proportional to not only the concentration of the spaces, participating spaces.

And also it will be dependent on the activation energy, and also the pre-exponential factor, which comes from the collision theory. And that reaction rate co efficient, which is determined from the collision theory is based on what you call is known as the Arrhenius law, and what will do we well taken example today, how to use this Arrhenius law. And also whether we can determine the activation energy by conducting experiment or not, that we will illustrate through this example.

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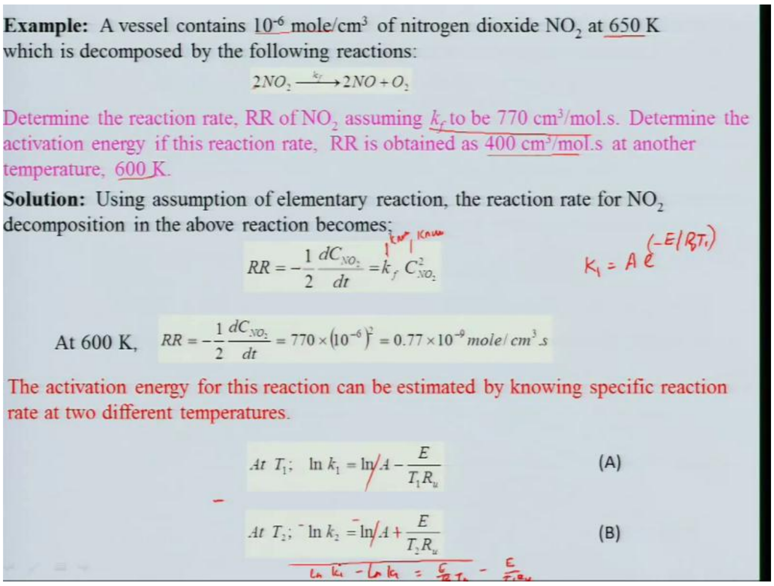

Example: A vessel contains 10^{-6} mole/cm^3 of nitrogen dioxide NO_2 at 650 K which is decomposed by the following reactions:

$$2NO_2 \xrightarrow{k_f} 2NO + O_2$$

Determine the reaction rate, RR of NO_2 assuming k_f to be 770 cm^3/mol.s. Determine the activation energy if this reaction rate, RR is obtained as 400 cm^3/mol.s at another temperature, 600 K.

Solution: Using assumption of elementary reaction, the reaction rate for NO_2 decomposition in the above reaction becomes;

kf, know

$$RR = -\frac{1}{2}\frac{dC_{NO_2}}{dt} = k_f\, C^2_{NO_2}$$

$$K_1 = A\, e^{(-E/RT_1)}$$

At 600 K, $RR = -\frac{1}{2}\frac{dC_{NO_2}}{dt} = 770 \times (10^{-6})^2 = 0.77 \times 10^{-9}\ mole/cm^3.s$

The activation energy for this reaction can be estimated by knowing specific reaction rate at two different temperatures.

$$At\ T_1;\quad \ln k_1 = \ln A - \frac{E}{T_1 R_u} \qquad \text{(A)}$$

$$At\ T_2;\quad \ln k_2 = \ln A + \frac{E}{T_2 R_u} \qquad \text{(B)}$$

$$\ln k_1 - \ln k_2 = \frac{E}{RT_2} - \frac{E}{T_1 R_u}$$

And this example is basically a vessel you know, which contains 10 to the power to minus 6 mole per centimeter cube of nitrogen dioxide at 650 Kelvin, if you look at it is basically isothermal reaction, which is decomposed in to the following reaction. That is 2 N O 2 goes to 2 N O plus O 2, keep in mind that, this is in one direction the reaction can also come in the backward direction as well, this is a forward direction backward direction, but we are considering at this moment only the forward direction.

We need to determine the reaction rate of N O 2, assuming k f to be 770 centimeter cube per mole second. And we need to also determine the activation energy, if this reaction rate is obtained as the 400 centimeter cube per mole at another temperature, that is 600 Kelvin. So, these are 2 parts, one is that we need to determine the reaction rate of N O 2, where k f is given, if k f is given then is it possible, we can find it out, we will have to basically applied the law of mass action, k f is known to you.

And then we can determine, what is the reaction, let us do that is the simple part, and of course here we are assuming the reaction to be elementary in nature. What is the meaning of elementary reaction, that we will try to discuss maybe after this example, but keep in mind, that the law of what you call the Arrhenius form of equation is valid only for the elementary reaction. But, however, we will be using for the global reaction as well, and law of mass action also right, is also valid for the elementary reaction only.

So, therefore, whenever we are applying for the law of mass action, we should keep in mind that reaction must be elementary, but you must know what is elementary action, and how it is different from other reaction. And how many kinds of elementary reaction one can think of those things we learn, but before that let us look at this problem, so reaction rate is equal to minus half d C N O 2 divide by d t.

What it is saying, this is the rate of concentration of N O 2 with respect to you know, time of course the rate when I saying it means it is time, and of course the minus sign is there, because it is been decomposed, therefore it is minus. And half, of course I have taken because 2 N O 2 is participating, which is equal to k f that is reaction coefficient, reaction rate co-efficient, and C N O 2 square.

Why this square comes into picture, because the coefficient in this reaction is 2, and it is an elementary reaction that, so that is queue coefficient. So, therefore, it comes to the square, and then what we will do the because concentration is given, this is your concentration of N O 2 and this is known this is known, you just substitute those values and get the answer, which is very simple.

That is x you know 650 Kelvin, that is reaction rate is equal to minus half d C N O 2 divided by d t, and you just substitute this values for k f from here, and then C N O 2 square get this value 0.77 into 10 power to minus 9 mole per centimeter cube. It is very, very small quantities if you look at, and activation energy for this reaction can be estimated by knowing the specific reaction rate or the reaction rate coefficient you know both are same at 2 different temperature.

So, one is 650 other is of course, the 600 Kelvin, so we must know those values, and k f is known, so you can determine, that is at T 1 it will be ln k 1 is equal to ln A minus E by T 1 R u. How it is coming, because we know that k 1 is equal to A E by R T 1, of course this is R v, so if I take both the side log the natural will get ln k 1 is equal to ln A minus E divided T 1 R u. Similarly, I will do for the at the temperature t 2, that is ln k 2 is equal to ln A minus E divided by T 2 R u, R u is the universal gas constant.

What I will do, I will just say like equation 1 minus equation, like equation A minus equation B will give what, if I just say this is minus, and it cancel it out, what will happen, so this become minus, this become minus, this become plus. So, this will cancel it off, what I will get, I will get ln A 1 minus ln k 2 is equal 2 E by R T 2 minus E by T 1 R E, I can get that and will simplify these and get those expression.

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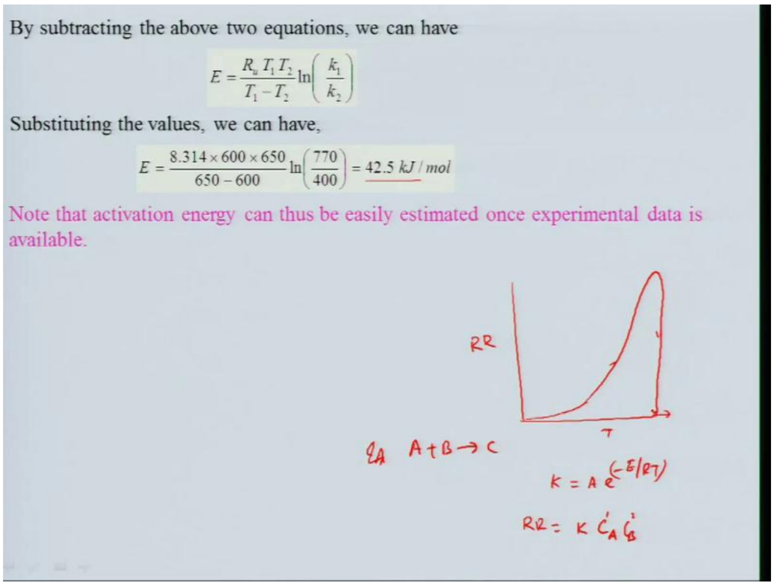

By subtracting the above two equations, we can have

$$E = \frac{R_u T_1 T_2}{T_1 - T_2} \ln\left(\frac{k_1}{k_2}\right)$$

Substituting the values, we can have,

$$E = \frac{8.314 \times 600 \times 650}{650 - 600} \ln\left(\frac{770}{400}\right) = \underline{42.5\ kJ/mol}$$

Note that activation energy can thus be easily estimated once experimental data is available.

eg $A + B \rightarrow C$

$k = A e^{(-E/RT)}$

$RR = k C_A^1 C_B^2$

Because, now E is both are same, so we need to determine E from this equation, and I know k 1 is known, k 2 is known, and T 1 is known, T 2 is known, R u is of course the same, so you can very easily determine what will be E.

Let us look at that is E becomes R u T 1 T 2 divided by T 1 minus T 2 ln k 1 by k 2, so all these are know k 1 k 2 T 1 T 2 R u, so you just substitute those values, and you will get that is 42.5 kilo joule per mole. Keep in mind that you need to this is very important, otherwise you know it will be landing some different values. So, what we have learned from here, we have learned that activation energy can be easily estimated once experimental data is available, of course most of the experiment are conducted under isothermal condition, because where you can maintain temperature.

We have seen that it is the reaction rate is you know strongly dependent on the temperature, so, therefore you know it is a very minor change in this example it is only the 50 Kelvin difference. And it is if you look at the reaction rate has been change, if you look at the specific reaction rate is changing from 770 to 400, only 50 Kelvin difference.

So, therefore, it is very important to conduct in the reaction in the isothermal condition, generally most of the data whatever you get the we use isothermal unless otherwise stated, and of course in some small reaction why it is. So, sensitive this k f or k in the specific reaction rate constant to temperature in this example, why or is it true only for this example or it is different for different reaction, because it goes exponential.

And if you remember I have shown you how this reaction rate will be changing with respect to the temperature. For example, if I plot it here the reaction rate with the temperature, if you look at in the beginning, it will be the reaction rate will be going like these, and then it will be coming like that. Now, it increases you know at very rapid rate, whenever it will be going towards high temperature, but why it is going down here, do you think about it last time I had discussed this, but I did not discuss about you know in detail.

But, I thought you will be thinking and ask me a question why it is. So, can anybody tell me.

Student: disassociation

Always will be occurring some reaction always will be occurring, but why it is going up, because it is exponential we have seen that k you know is equal to A power to E by R T, and why there would not be any reaction, which will there in this system. Because, the activation energy you know like may not be having that high, so it will be remaining I have exaggerated a little bit it will be remaining always constant, and in the low temperature.

Then it will be suddenly going off, but why it will be going up, because it is having activisms energy it will go up, but why it will go down, because whatever the participating space is there it will get consumed. And if concentration is not there, if you look at the reaction rate will be k into C A C B or may be 1 or 2 something, if I look at C A plus B is going to the d, you know or if I am saying that A is reacting is going to the C.

So, this will be C A C B, so therefore this reaction rate if C A is coming to 0, what will happen to the reaction rate, then it will be coming to the 0 here even though temperature is higher I did not get even point. Similarly, if C B is 0 or C B is very, very small or one of them is 0, then you will come to this, even though temperature is very high, I was thinking you will think about it, and if you would not get the way you can ask me.

So, let us now get into elementary reaction, so if you look at what do you call it elementary, if the reaction occurs successfully at molecular level, the reaction is termed as elementary. In this example if O H is reacting with hydrogen molecule, it is going to water and the H, if you look at water is a stable molecule, hydrogen is also a stable molecule, what about O H is it stable, what do you mean by stable.

And this O H or the H, what do we call is the radical, these are very reactive in nature, there life time will be very small, and it will be going and reacting you know. As you we have discussed about the molecules being collided, as resolved there will be breaking of bonds old bonds and forming of new bonds. So, therefore, these reaction, where there will be molecules or even atoms are involved in that, and some of the you know the radicals are formed, we call those as the elementary reactions.

And these elementary reactions will be depended on what, it will be depend on molecularity, but what is the molecularity then; that means, number of molecules will be participating in a reaction, will determine the molecularity of a reaction. That means, as I told number of molecules or atoms participating in the reaction in each reaction leading to a product, in this example O H is reacting with hydrogen going to the water and H.

So, if you look at the molecules are participating here and it is going to a product, product means it need not to be stable a long, it can be any other thing; that means, there is a change.

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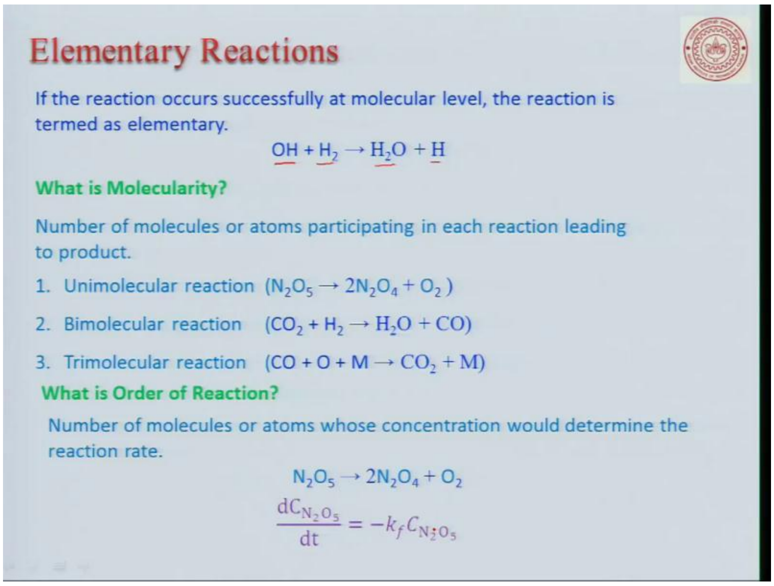

Elementary Reactions

If the reaction occurs successfully at molecular level, the reaction is termed as elementary.

$$\underline{OH} + \underline{H_2} \rightarrow \underline{H_2O} + \underline{H}$$

What is Molecularity?

Number of molecules or atoms participating in each reaction leading to product.

1. Unimolecular reaction ($N_2O_5 \rightarrow 2N_2O_4 + O_2$)
2. Bimolecular reaction ($CO_2 + H_2 \rightarrow H_2O + CO$)
3. Trimolecular reaction ($CO + O + M \rightarrow CO_2 + M$)

What is Order of Reaction?

Number of molecules or atoms whose concentration would determine the reaction rate.

$$N_2O_5 \rightarrow 2N_2O_4 + O_2$$

$$\frac{dC_{N_2O_5}}{dt} = -k_f C_{N_2O_5}$$

So, based on this molecularity, in this reaction if you look at the 2 are participating, O H and hydrogen, therefore we call it a bimolecular reaction, similarly if it is a single molecule and it is decomposed, then we call it as a uni molecular reaction. So, the reaction can be broadly divided into 3 categories, it need not to be 3 even 4 also, but they are 4 molecules coming together, and reacting you know less likely to happen in nature therefore, that is not been considered; however, nobody can rule it out.

So, therefore, the reaction can be you know based on these moleculate will be divided into 3 categories, uni-molecular reaction N 2 O 5 is decomposed into 2 N 2 O 5 O 2 plus O 2, because 1 molecule nitrogen pent oxide is being decomposed. So, therefore, it is a uni-molecular reaction, but if I consider a backward reaction, can it be un-imolecular backward reaction means N 2 O 4 is reacting with oxygen is going to the N 2 O 5, we have seen anything can happen either reaction can be forward, reaction can be backward as well.

So, at the time that is not uni-molecular, only for the forward reaction in this example is known as uni-molecular reaction, bi molecular reaction you know where 2 molecules are participating or rather 2 reactants like C O 2 and hydrogen. It is going to the water, and carbon monoxide and that is known bimolecular, fortunately both the forward and the backward are bimolecular in this example.

Similarly, tri molecular reactions is where 3 molecules are been part are being participated, like C O 2 plus M is going to the C O 2 plus M, M is known as a third body reaction. Third body reaction means it will be not participating actively in the reaction, but his presence will be required, for example referee you know in the games. Of course, referee role is different, but he must be there to any, you know games to be conducted, but he would not play in the games, but his presence is required.

And what is this M can be in real example, M can be anything it is a stable, it is basically stable spaces, like water oxygen, hydrogen or carbon dioxide, those are basically stable spaces. That means, which would not be unless otherwise you know large amount of energy will be available, which is beyond the activation energy to decompose, but you keep in mind each reaction will be having certain activation energy.

Unless otherwise the reaction or the participating spacing that amount of energy, you know beyond this threshold value of activation is reaction would not occur, so therefore those are stable spaces. Of course, one may be stable space is for one reaction, but it need not be the stable space for the other reaction, it may be participating, so therefore these are third body reaction.

And third body reaction will be more important in case of higher pressure, when the reaction is occurring at higher pressure, third body reaction is very important. So, now, when you talk about the molecularity, but there is a another one we talk about order of reaction, the question is that what do you mean by order of reaction. You know the order of mathematical equation like algebraic equation, PDE partial differential equation, OD's like you know order of a equation you know, but similarly we need to understand what is the order of reaction, which you must be knowing.

I guess so; that means, it will dictate basically how many you know spaces are being participated, and not only, that is of course, you can say that you know number of moleculate. But, it will be depending on the number of molecule's atom, whose concentration would determine the reaction rate; that means, it basically comes from the law of mass action, if I take this example of N 2 O 5, it is decomposed to 2 N 2 O 4 plus O 2.

If I look at this forward reaction alone, then what would will be the reaction rate, reaction rate will be d C N 2 O 5 d t is equal to minus k f C N 2 O 5, in this case what will be the order of reaction, can anybody tell me it will be only fast order of reaction, it is a decomposed reaction.

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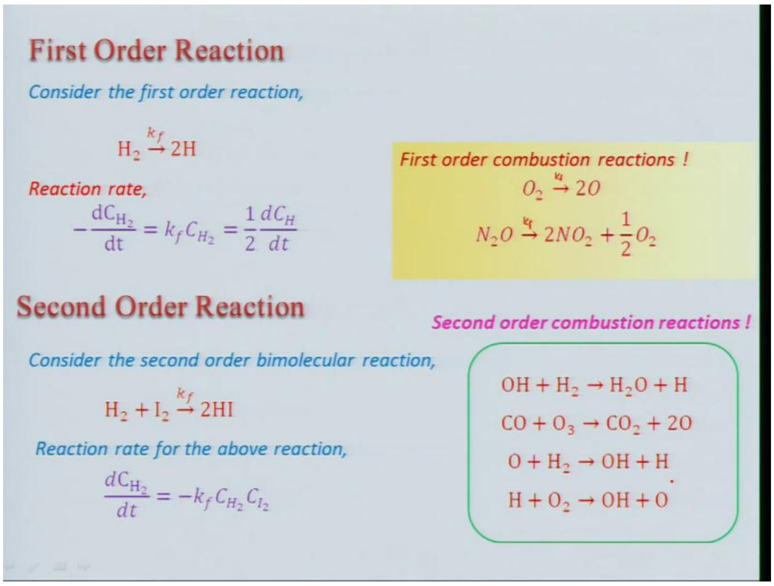

First Order Reaction

Consider the first order reaction,

$$H_2 \xrightarrow{k_f} 2H$$

Reaction rate,

$$-\frac{dC_{H_2}}{dt} = k_f C_{H_2} = \frac{1}{2}\frac{dC_H}{dt}$$

First order combustion reactions !

$$O_2 \xrightarrow{k_f} 2O$$

$$N_2O \xrightarrow{k_f} 2NO_2 + \frac{1}{2}O_2$$

Second Order Reaction

Consider the second order bimolecular reaction,

$$H_2 + I_2 \xrightarrow{k_f} 2HI$$

Reaction rate for the above reaction,

$$\frac{dC_{H_2}}{dt} = -k_f C_{H_2} C_{I_2}$$

Second order combustion reactions !

$$OH + H_2 \rightarrow H_2O + H$$

$$CO + O_3 \rightarrow CO_2 + 2O$$

$$O + H_2 \rightarrow OH + H$$

$$H + O_2 \rightarrow OH + O^{\cdot}$$

So, therefore, it will be fast, but if I consider the backward reaction, then what it would be, it will be 3 basically, not 2, so we will take some examples to enforce this ideas of order of reaction. As, I told that whenever the first order reaction will be there, then it will be 1 H 2 consider only 1, you know concentration kind of things in terms of participating co efficient will be 1. In the example of hydrogen going to the 2 H, in this case reaction rate is basically d C H 2 d t is equal to k f C H 2, keep in mind that this minus negative sign, because it will decompose it will be half d C H y d t.

I can this I have put other way wrong, because C H, so there for 1 have comes in the picture, and if you look at I can write k f C H 2. This is from the basically law of mass of fraction, you can say and the examples of first order reactions of course, any decompose reactions like O 2 is going to 2 O, and N 2 O is going to 2 N O 2 plus half O 2 is basically first order reaction.

Provided you are considering only the forward reaction; that means, in this direction, I can say this is forward first order reaction, k f backward reaction of course, it need not to be, it would not be. In this example, similarly second order reaction let us consider the order you know second order bio molecular reaction, hydrogen reacting with I 2 Iodine going to 2 H I.

So, the reaction rate you can write down d C H 2 d t minus k f C H 2 C I 2, in this case there are two concentration, who will be determining what will be the reaction rate one is the hydrogen, other is I 2 Iodine in there for it will be second order reaction. And there are several laws that lot of reactions which are involved in combustion, but equally second order reaction some of the example I have given.

And O H plus hydrogen is going to be water plus H, O plus H 2 going to the O H plus H and H plus O 2 going to be a O H plus O. So, there is several reaction which is to be occurring, even in hydrocarbons hydrogen oxygen systems all those are importance, these are second order reactions.

So, and let us look at third order reaction, tri molecular reaction 2 N O plus O 2 is going to the 2 N O 2, we are considering only forward reaction this example, there for the reaction rate will be d C N O 2 will be d t is k f C N O 2 square and C O 2. And if you look at here, there is no negative sign, because N O 2 being formed and we are considering other way around.

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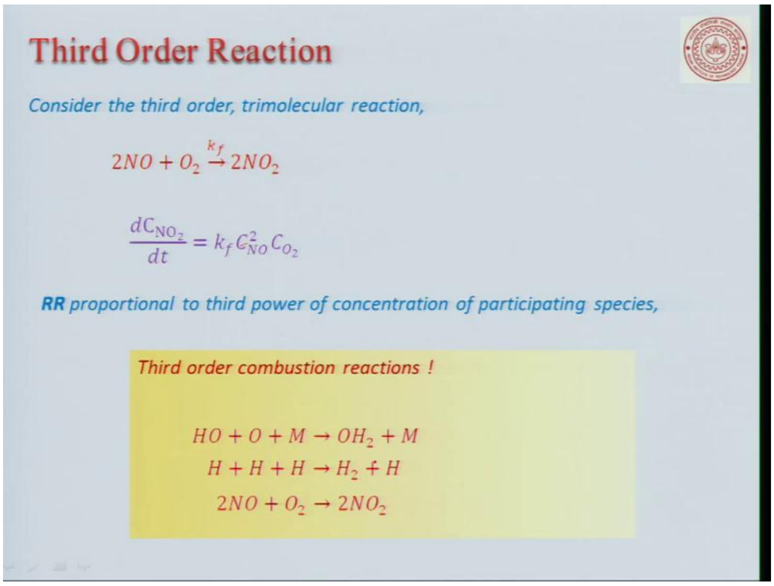

Third Order Reaction

Consider the third order, trimolecular reaction,

$$2NO + O_2 \xrightarrow{k_f} 2NO_2$$

$$\frac{dC_{NO_2}}{dt} = k_f C_{NO}^2 C_{O_2}$$

***RR** proportional to third power of concentration of participating species,*

Third order combustion reactions !

$$HO + O + M \rightarrow OH_2 + M$$
$$H + H + H \rightarrow H_2 + H$$
$$2NO + O_2 \rightarrow 2NO_2$$

So, there for if you look at this is basically the what to call the third order reaction, because it is coming from N O and O 2, so therefore there is no negative sign, so reaction rate is proportional to third power of the concentration of the participating species, therefore we call it a third reaction. Some of the example which you know third order reaction, which occur in combustion, I have shown here H O plus O, and third body M is going to be O H 2 plus M H plus H plus H, you know it is very less likely to occur, but always people say that it occurring.

That means, H at atom has to come through together and collide it, and form an hydrogen gauge and 2 N O plus O 2 into the 2 N O 2, and if you look at this you know forward reaction are hard the nature, where as the reverse reaction need not to. So, these are basically the reaction you know kind of reaction rates, which is govern by the forward reaction, and which I am not going to discuss further, but their concentration with respect to time can be very differently for different order of reactions.

If some of your interested refer standard book and combustion, and of course you can refer my book fundamental of combustion. So, now let us look at the chain reaction you know which is very important, like what do you mean by chain reaction, is it really in combustion chain reaction occur. Certainly, yes because if you look at the all the reaction are occurring in chain manner, chain in the sense you will initiate something, and then and something will be propagating.

Like for example, if you look at you know, like you know if you look at family, suppose a father and a mother will produce a kid, and then that kid will be producing another kids, you now it will be go on. So, it will be terminated of course, one person will die terminated of the this thing, so it goes on that is how the chain. So, whole nature is a chain of actions, similarly chemical reaction is a part of nature, there for it is you know chain of action of rule will be taking place, so there for chain reaction will be there.

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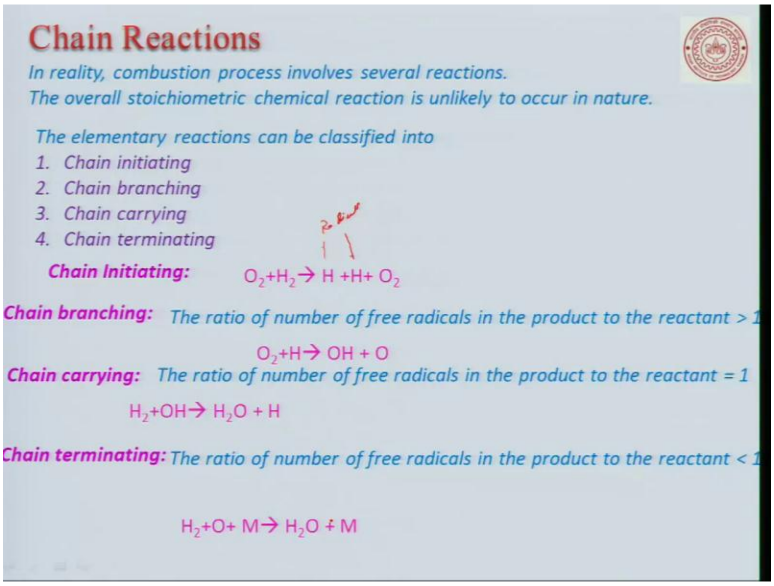

Chain Reactions

In reality, combustion process involves several reactions.
The overall stoichiometric chemical reaction is unlikely to occur in nature.

The elementary reactions can be classified into

1. *Chain initiating*
2. *Chain branching*
3. *Chain carrying*
4. *Chain terminating*

Chain Initiating: $O_2+H_2 \rightarrow H + H + O_2$

Chain branching: *The ratio of number of free radicals in the product to the reactant > 1*

$O_2+H \rightarrow OH + O$

Chain carrying: *The ratio of number of free radicals in the product to the reactant = 1*

$H_2+OH \rightarrow H_2O + H$

Chain terminating: *The ratio of number of free radicals in the product to the reactant < 1*

$H_2+O+ M \rightarrow H_2O + M$

So, in reality combustion passes involves several reactions as I have told, and it is not that meeting the reactions with oxygen in to the carbon di oxide, and water in enormous or numerous you know reactions will be taking place between this step, which is global in nature. So, overall stoichiometric chemical reaction is unlikely to occur in nature, I have told several times, because you know lot of people believe from their childhood from there earlier studies, that this is the reaction, which occur.

In order to eliminate, in order to remove that bogus idea that is occurring, I am repeating l several time, so that is nature never occurs just a model. And elementary reactions can be classified into elementary means basically chain reactions you know, which will be occurring into 4 categories. One is chain initiating; that means, you know initiation will occur, initiation is very important we do like you people may not be knowing in earlier our systems, insisters' were students are been initiated.

How they are initiated, they initiated by the teacher to start their life, to learn and they start learning, again teaching then it goes on, so chain branching up to of course, they will go up to start another school, you know thought of schools. And chain carrying some of them ideas they carry forward in their life, and terminating some of the chain will be terminated, so that will take 1 by 1 like chain initiating.

If you look at, if I consider the whole oxygen O, reacting with hydrogen molecule, and both are you know stable species keep it in mind. And in this what is happening; that means, one oxygen molecule is coming and colliding with another hydrogen molecule, as resolve hydrogen is broken, but oxygen remains. Of course, other way around it can occur depending on the prevailing situation, because all are probabilities you know all are depend upon the what temperature, what pressure, and what is the concentration all those arrival available.

So, in this case what is happening, these are radicals, you know radicals which are very important carry forward the reactions, because these are very energetic, you know atoms molecules, so there for these will be chain carrying, so going to the oxygen. So, this is basically an initiation the stable, and you make the stable to unstable and converting into the lot of energy, so that is chain initiate, chain reaction, and chain branching, where you know ratio of number of free radicals in the product to the reactant.

Then only we call it as a chain branching, for example O 2 is reacting with the age is another radical going to be O H plus O, the product how many radials are there 2, and in the reactant side it is 1. So, 2 divide by 1 you know there for this ratio is better than 1, kind of thing we just 2 is to 1 is 2, so is greater than 1, therefore this chain branching reaction, the chain carrying the ratio of number of free radicals in the product to the reactant is equal to 1.

That means, there nothings is happening, but the passes is going on like, it is again give an example son you know, suppose he is taken over the business of a person he is just managing, whatever the profit he was having, but he is not increasing. That means, he is carrying forward, but he is not branching you know, in this examples so; that means, in this example hydrogen react with O H going to the water.

And H if you look at the right hand side H is one radical, the left hand side only one radicals, and both are of course, other two are stable spices. So, there for this is known as carrying reaction, and chain terminating where the ratio of number of free radicals in the product, to the reactant is less than 1; that means, you are basically, you know reducing the number of radicals.

When we were doing that you call chill terminating, because it cannot carry forward the successful reaction, because radicals are one which make the you know reaction to carry forward, so is basically terminated. Hydrogen is reacting with O with plus another third body is going to water plus M, of course third body means the stable for that particular reaction, and what is solid table no radical in this case.

Of course, in those example, but there in some example may be, there might be a radical in the product, but those number of radicals will be less than that of the number of radicals in the reactant. So, there for that can be consider as the chain terminating reaction, so these reactions will be going on and on, and no need of you know verities of things will be happening.

So, now, what we have seen is the basically elemental reactions which we be occurring in nature, but we will be more interested in global kinetics. The global reactions, because it is not easy to really handle, so many chemical reactions, particularly when we are trying to model something, because those as I go along, I will tell show you.

Even second order reaction third order reaction and other things those are the non-linear in nature, you might have looked at reaction rates, it is dependent on temperature, it is also dependent on concentration. If I look at equation you need to solve both the concentration and temperature, both are dependent to each other both arenon-linearin nature, so there for to solve those is quite difficult.

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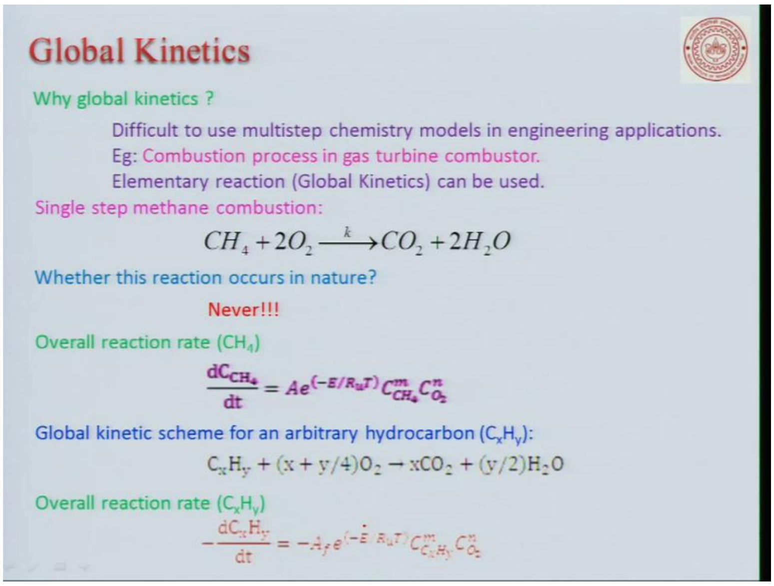

Global Kinetics

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)

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

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)

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

So, and in practical situation is difficult to use multistep chemistry models in engineering applications, for example like combustion process in gas turbine or you can think of in rocket engines or any other engine even in internal combustion ((Refer Time: 32:40)) is quite difficult, because in several number of you know spaces which will be participating. So, there for we need to look at elementary reaction are gold global kinetics, where will look at the one mole of you know methane this reacting the 2 moles of oxygen going to be C O 2 and water.

So, very simple global reaction in nature is not occurring, we are assuming it as a model and looking at it, so when you look at this whether of course, I have already emphasized these things, whether these reaction occurs I nature or not certainly no. It can never occur, but how ever will be interest in over all reaction rate that is d C H by d t is A e power to the minus E by R u T, of course C C H 4 m and C N O 2 n.

So, this m and n these are co efficient which are to be determined, by some mathematical tools, and so also the active energy E and pre exponential character A. So, those values will be available by doing some kind of a mathematical models, does it can replicate the heat realize profile, because we are interested in how much heat be released. And if we managed to do that this global you will be happy, but how ever there is lot of problems associated with it as we know.

So, there for it is having limitations and may be when more computers and other things will be developed, may be some other means may be some other elementary action in modeling, even people have started using the brute course of computers. So, this is about methane, but we look at global kinetic scheme of arbitrary hydrocarbon C x H y, which we have already discussed earlier, it can be you know C 1 H 4 it is methane. If x is 1, y is 4, similarly if the x is 2 H is 6 it will be ethane, propane, butane like that you can go on.

So, if I take this reaction arbitrary hydro carbon C x H y plus x plus y by 4, in the bracket moles of oxygen reacting giving rise to that of x C O 2 plus y by 2, water. For that reaction you can write down a basically C x H y d t, and minus A f e power to C H m and n. Of course, these values you know m and n and e, all those values must be known to you to use it.

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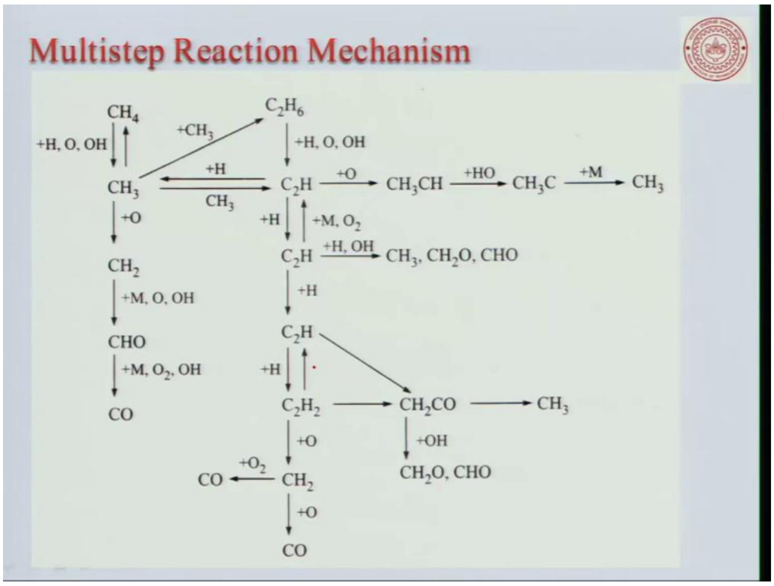

Multistep Reaction Mechanism

So, those values I have I am not going to discuss they are there in my book, so you can use those values. So, let us look at a multistep reaction mechanism, because I felt that what do we mean by that, and because you may not have feel what it is I will just show you a very simple model. And which looks to be like complex in nature, but if you look at this is only may be 14 spices kind of things, and 40 reactions you can think of it.

But; however, these not adequate to you know model meet an air chemistry you know simplest hydro carbon, for example, I will just give for example, C H 4 is can react with A H or O or O H can go to C H 3 and several other products. Similarly, C H 3 can react with O and it can go to C H 2, C H 2 can be you know colloidal with stable spices M O O H go to C H O, several others you know several products am not saying. What will be C H O again may be react with M O 2 O H going to C O and C s 3 can be colliding with C H 3 going to C 2 H 6, there is a possibilities.

Similarly, C H 3 can react with H you know like C H 3, it can go to 2 H and some others, similarly C 2 H can go back react with H going to C H 3. There are permutation combination will be goes on, and similarly C 2 H is reacting with A H going to O H and some other molecule, C 2 H can react with H and O H going to C H 3, C H 2 O, C H O, so and, so forth. So, if you look at time in it is goes on and you can get C O, and you can C O get from an some other channel, there are several channels, which will be going on, the way our society works.

You know like, because we do work in a similar fashion, for example, an engineer take interest in family, may take interest in some other thing, may be literature you know doing interacting lot of things, because of natural way. So, the reaction what I am showing you is a very simple thing, and what it is, it is having a 14 spices, and 40 forward reactions, and 40 backward reactions.

I am going to show you that 40 reactions for a ((Refer Time: 38:17)), and if you look at that the kinetic data, and k f and for A f, A f is your pre exponential factor, this is your A f. And T m these are the co efficient m, and this is E your active x energy, these let us r obtained, to be obtained from barriers reaction, barriers experiment, because what are the error involved in it, and what are those things. So, and this has to be solved; that means, if you look at like number of spices is 14 in this case.

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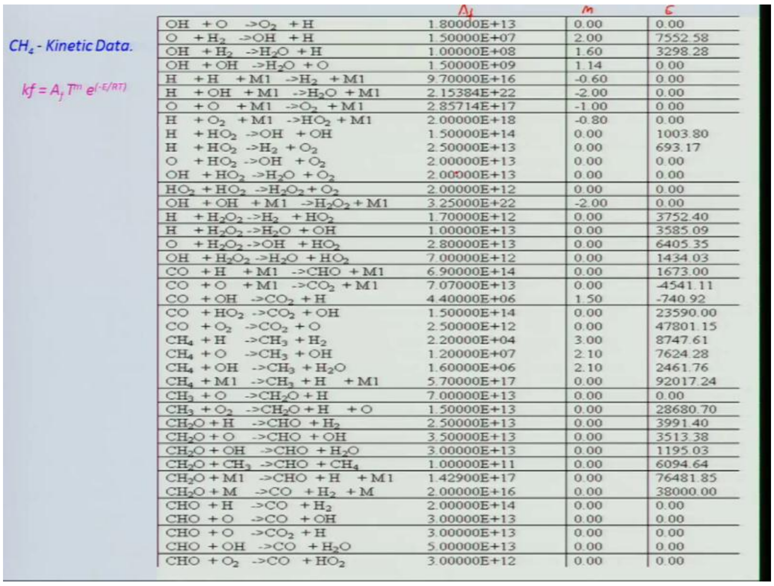

CH_4 - Kinetic Data.

$kf = A_f T^m e^{(-E/RT)}$

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

And number of reaction is 40, and backward reaction is also to be considered, that is being considered from the equilibrium chemistry, which I do not want to you know discuss about, because it is quite complex. And this is being used in what you call combustion model, and this chemistry cannot work for the you know these mixtures, for example you know if you can involve for the lean mixture like.

When fuel layer ratio is less than stroke gramatic ratio, but it cannot work further this thing, so for that we need to go for the you know more number of spices, may be you know 33 32 spices are required minimum barrier required. And go for something may be

400, 500 reactions, then only you can get something meaningful otherwise no, so what we have seen till now is about kinetics and other things, but what are the modes of combustion, which will be taking place in a combustion system.

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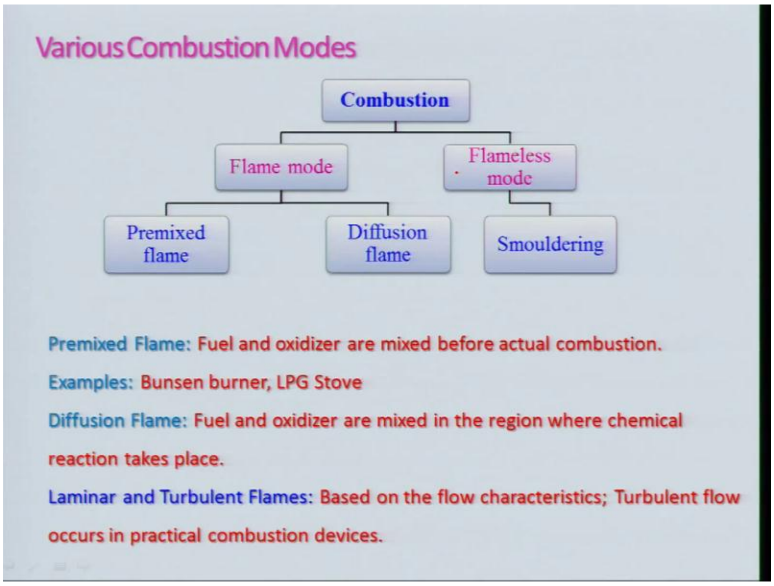

Various Combustion Modes

Combustion

Flame mode

Flameless mode

Premixed flame

Diffusion flame

Smouldering

Premixed Flame: Fuel and oxidizer are mixed before actual combustion.

Examples: Bunsen burner, LPG Stove

Diffusion Flame: Fuel and oxidizer are mixed in the region where chemical reaction takes place.

Laminar and Turbulent Flames: Based on the flow characteristics; Turbulent flow occurs in practical combustion devices.

What are the things, let us look at this it is basically a very ((Refer Time: 40:18)) I am giving one is flame mode, flame means you must have seen, flame is part of our life, you have seen flame, yes or no. There are various kinds of flame you might have seen, but whether you identify or not, but flame can be broadly divided into premixed flame, and diffusion flame.

And there is of course, people now does talking about another flame known as partially pre mixed flame, which I have not included here, but; however, it is on the research state people are talking about flameless mode, one of them is smoldering. You know what is smoldering like you know some of you might be, might not be smoking as well or smoking, but you know when you burn that cigarette, get something red color you can see, which is propagating.

So, that is nothing but, smoldering you might have seen some kind of a dry leave been burn there is no flame, but it is still burning that is known as moldering combustion. I would not be discussing much about that, because all that is quite complex in nature of course, similar thing is might be occurring in a solid combustion as well, but we will be not discussing it. And what we will be discussing premixed flame, diffusion flame, now what do you mean by premixed flame, where fuel and oxidizer are mixed before actual combustion takes place, we call premixed flame and examples you people are aware.

That is a Bunsen burner and of course, LPG stove that you use in your kitchen for cooking food is an example of premixed flame, and similarly for the diffusion flame can be defined as fuel and oxidizer are mixed in the region, where chemical reaction takes place. That is a diffusion flame example, basically your candle flame you know your weak flame, and any natural flame is basically diffusion flame, un natural flame man made flame is basically premixed flame that I can say very lean manner concept.

So, the this flame even the combustion can be divided into 2 categories, that is one is laminar flame and turbulent flame, based on the flow characteristics. And keep in mind we will be the strict in our discussion to laminar flame only, and laminar based combustion although the practical flame are turbulent in nature. How will go and do that of course, a not easy task, but how ever there is a way to talk about turbulent flame in terms of laminal flame characteristics, if you look at the what we have done is basically, you know simplified and try to understand fundamentals involve in that.

But, why flame we need to look at is a question, why it is important, without flame there will be combustion as well, why you need to look at it, and what is the flame by the way. We are talking about flame, but what is the flame can anybody define it, you can think of a special domain in which rapid, you know chemical reaction of course, ex thermic in nature over away taking in place while emitting light.

Of course, there is a some kind of flame, which need not to emit light, do you know any example, the combustion will be taking place and flame will be there, but it is not visible. Is it possible, what is that, then if it is possible can you give an example, actually it is possible, but you know that depends upon the kind of fuel in oxygen, that you are using particularly hydrogen and air. Of course, clean air you know, it can be turns out to be very, very front color is not really seen unless it is dark, in the day time you really cannot see.

And premixed flame as I told earlier the fuel and oxidized mixed well at the molecular level before combustion takes place, but question is, is it premix flame possible you know only when the constituent fuel, and oxidizer are in gaseous state or in possible in the liquid state or is it possible premix flame in the solid state. I just leave that question for you people to think about, as you go along will see, and examples of premix flame we have already given Bunsen burner LPG domestic burner and what about your aerospace application.

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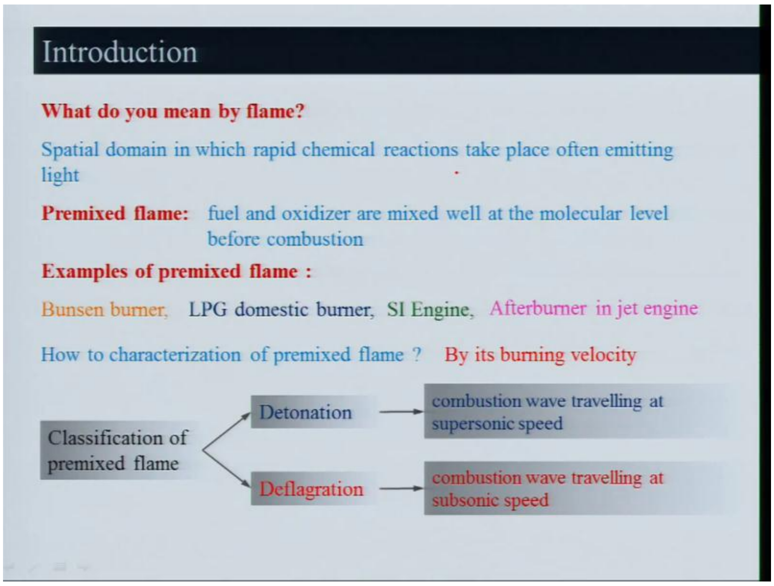

Introduction

What do you mean by flame?

Spatial domain in which rapid chemical reactions take place often emitting light

Premixed flame: fuel and oxidizer are mixed well at the molecular level before combustion

Examples of premixed flame :

Bunsen burner, LPG domestic burner, SI Engine, Afterburner in jet engine

How to characterization of premixed flame ? By its burning velocity

Classification of premixed flame

Detonation → combustion wave travelling at supersonic speed

Deflagration → combustion wave travelling at subsonic speed

We can model as a basically, what you call the SI engines the part ignition engine kind of things, where you can consider as a premix, and the after burner engine people consider as to be a premix flame. Although, need not to be unless otherwise this flame are quiet fine, but generally it is been modeled as a you know a premix flame, you know whenever they want to model after one, but where are the actual combustors are the main combustors, you cannot really model with the premix flame.

Unless otherwise you have designed a premix combustor, which is being going on today, nowadays in order to overcome the problem of emission. How to characterize a premix flame, is a very important question, how to characterize it, and which will be discussing about that is basically, you would need to look at the burning velocities.

What do you mean by burning velocity, we will be learning about it and so, classification of premixed flame can be broadly into 2 categories, based on the you know what is the speed of burning velocity. It can be you know speed of, it can be more than the speed of sound, it can be less than the speed of sound, and if it is more than the speed of sound we call it as a detonation, and if it is less than that of the speed of sound, we call it a deflagration.

So, therefore, detonation in case of detonation combustion wave travelling at a supersonic speed, that is detonation and whereas, deflagration like where the combustion wave will be travelling at a subsonic speed. So, we will be basically concentrating on the deflagration; however, may be in the next lecture, will be discussing and finding out what is the difference between the detonation and deflagration.

And look at the combustion wave, because like your shock wave, the combustion is also considered it is like a wave. So, how to analyze that, and what are the reason when will be talking about detonation, deflagration other things, then I will moved into the premix flame, so with this I will stop over, do have any question to be asked or any doubts, you are having.

Thank you.