Combustion in Air Breathing Aero Engines

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Lecture - 09
Oxidation Mechanism of Fuels II

Hello everybody. Welcome back now before we go in to this just let us recapitulate from previous class this different kind of reactions ok.

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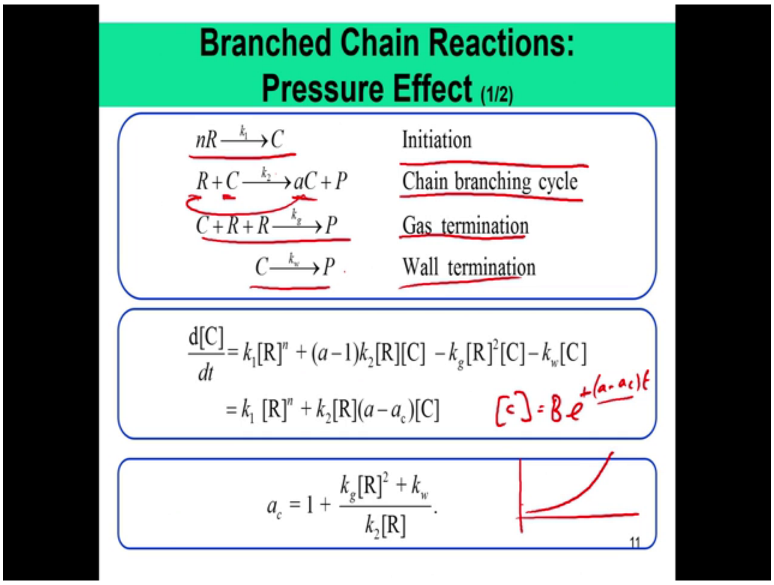

Branched Chain Reactions: Pressure Effect (1/2)

$nR \xrightarrow{k_1} C$ Initiation

$R + C \xrightarrow{k_2} aC + P$ Chain branching cycle

$C + R + R \xrightarrow{k_g} P$ Gas termination

$C \xrightarrow{k_w} P$ Wall termination

$$\frac{d[C]}{dt} = k_1[R]^n + (a-1)k_2[R][C] - k_g[R]^2[C] - k_w[C]$$

$$= k_1 [R]^n + k_2[R](a - a_c)[C]$$

$[c] = B e^{+(a-a_c)t}$

$$a_c = 1 + \frac{k_g[R]^2 + k_w}{k_2[R]}.$$

So, this n R, R is a kind of a generalized hydrocarbon. So, we said that yes first what happens is that there must be an initiation reaction. So, this C H 3, C H 3, C H, C H 3, C H 2, C H 3 which is represented by this n R or this C H 3, C H 3 which is an ethane goes to basically this form this first intermediate that is C c is nothing but change carrier or a radical an active radical.

So, then first step is production of this chain carrier; so in our bricks it reacts with something a third body collision like that or a second body collision as such here and then it gives up this makes this this intermediate C. So, R then can again react with C and form this a C a and a C here is it in a generalized sense. So, this C as I said before the C can be H and this this C can be H or H etcetera so, but this essential means if there is a multiplication of these chain carriers and then it forms a P, and then there can be gas termination and wall termination.

So, what we were trying to say is that, that these chain branching is a very critical step. So, whether a mixture is explosive; that means, whether this this start from a given initial temperature and pressure whether and you keep it at a at an that initial temperature and pressure whether that mixture will spontaneously react and the temperature will continue to raise quickly and because of quick generation of energy because of fast generation of energy that is that is the explosiveness.

Now, whether that is going to happen or not that is governed by this chain branching cycle at this one chain branching means once it gives rise to more than one C a k is a greater than one number it can be 2 typically it is 2 or something like that. So, then, but then the thing is that it is competing with this termination reaction also, once you produce C this it is not guaranteed that C will go and attack R to form subsequent reactions C might be vendured inactive by this R species by gas termination or by wall termination. So, essentially we need to find out what are the conditions under which these reaction can compete with these reactions and which can lead to effective chain branchings.

So, then we did this thing we find out the concentration rate of change of concentration of C and using this we found out that that that we can arrive at a generalized expression for dC dt, and then we arrived found that this dc dt can ask is expected a kind of a can give out some kind of an exponential type of behavior with there C can have a behavior like this in time is equal to something some constant k or some constant which is less than (Refer Time: 03:39) constant B times e to the power of plus a minus ac times t.

Now, so then this a minus ac you determine whether this you whether this if this is a minus ac is positive then of course, then C can rapidly raise because we know that exponentials are lead to lead to a rapid increase whereas, if a minus ac is positive then C will really decay.

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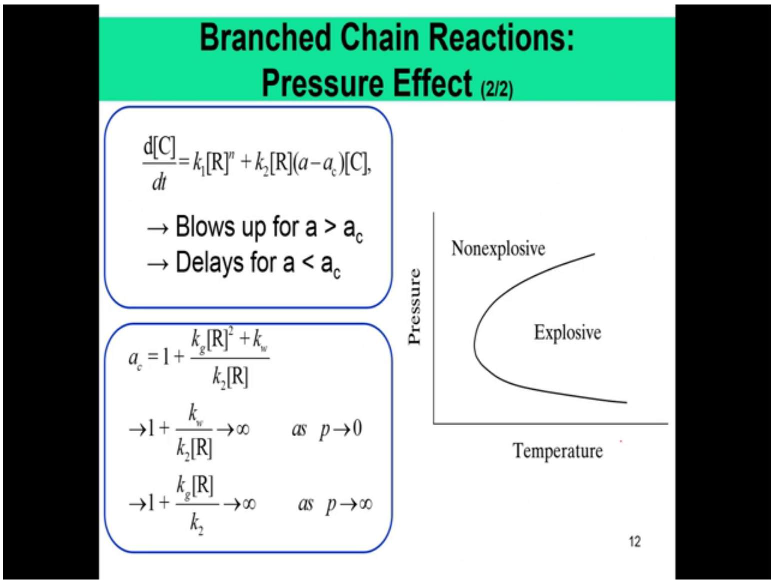

Branched Chain Reactions: Pressure Effect (2/2)

$$\frac{d[C]}{dt} = k_1[R]^n + k_2[R](a-a_c)[C],$$

→ Blows up for a > a_c

→ Delays for a < a_c

$$a_c = 1 + \frac{k_g[R]^2 + k_w}{k_2[R]}$$

$$\to 1 + \frac{k_w}{k_2[R]} \to \infty \quad as \ p \to 0$$

$$\to 1 + \frac{k_g[R]}{k_2} \to \infty \quad as \ p \to \infty$$

So, that criteria as you remember was given by a with a minus ac and we found that that a minus ac is greater than 0 when the temperature and pressure when the temperature is large and the of course, but when the pressure is attain intermediate level or that is very large pressure or very small pressure is not conducive for explosion.

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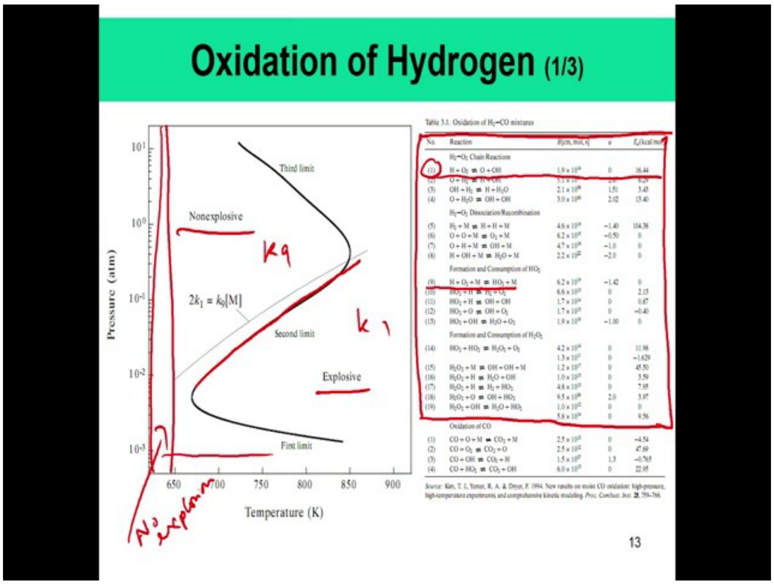

Oxidation of Hydrogen (1/3)

So, this is what we did for a generalized case, now we go in to the oxidation of hydrogen. We find we consider a hydrogen air mixture and we see we try to understand under what conditions hydrogen is explosive no as you understand this is very important because of course, in a hydrogen because it is a very small molecule, it can diffuse very very quickly and then it has got a very large range over which it can basically form quick reactions it carries combustible.

So, under what conditions hydrogen is explosive that is very very important for practical point of view also no I feel do the detailed analysis or if you do an experiment we will find that the it is not even what we previously said for a given hydrocarbon, it is not that simple instead of this 2 branch behavior it shows a 3 kind of behavior which is call the zee curve or the z curve.

So, nearly see that the most interesting behavior of hydrogen explosion is that hydrogen in your hydrogen oxidation of the hydrogen air explosion limit is that. There if you start the given temperature say 750 kelvin, first up to certain pressure at and you start from the low pressure of course, at low pressure it is are well understood that this mixture is non explosive because whatever you there is simply not enough collisions happen all right.

So, then after that if you go then it becomes explosive in this regions then it becomes non explosive again and then it becomes explosive again; so it is strongly non monotonic behavior that you see all right. So, what controls it is behavior, for that we need to go into under to understand the oxidation the reaction mechanism of hydrogen here mixtures. So, these up to this is essentially the mechanism the reaction mechanism of hydrogen oxygen oxidation, and as you have as we have discussed in last class that it essentially involves 9 species and 19 reactions.

So, these are all the reactions. So, we will study this in details to understand what controls this explosive behavior, this z curve of these limits of explosion and non explosion.

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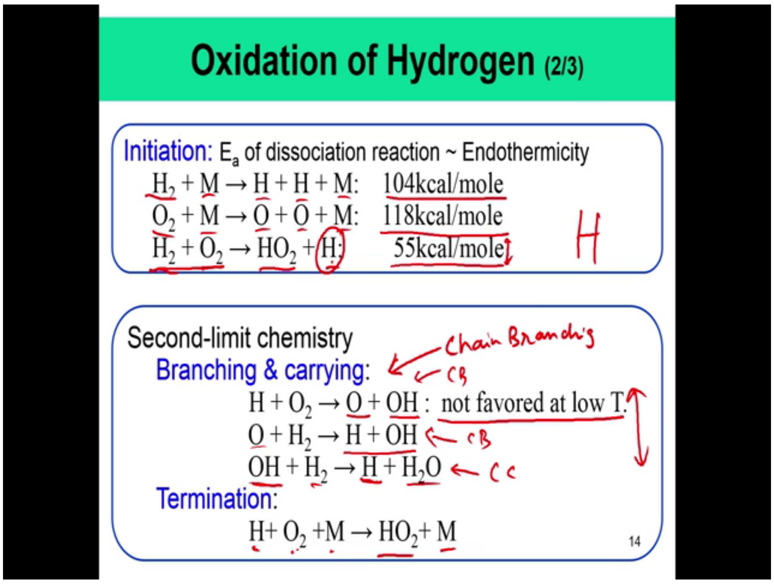

Oxidation of Hydrogen (2/3)

Initiation: E_a of dissociation reaction ~ Endothermicity

$H_2 + M \rightarrow H + H + M$: 104kcal/mole

$O_2 + M \rightarrow O + O + M$: 118kcal/mole

$H_2 + O_2 \rightarrow HO_2 + H$: 55kcal/mole

H

Second-limit chemistry

Branching & carrying: ← Chain Branching ← CB

$H + O_2 \rightarrow O + OH$: not favored at low T.

$O + H_2 \rightarrow H + OH$ ← CB

$OH + H_2 \rightarrow H + H_2O$ ← CC

Termination:

$H + O_2 + M \rightarrow HO_2 + M$

So, first thing you have to understand is that, how is hydrogen oxygen reaction initiated. There are 3 possibilities, hydrogen as you see that hydrogen can be attacked by a third body and it can split up into H radicals plus M of course, H radicals are very active oxygen can be split up by a third body and it can split up in to oxygen oxygen atoms and then the M, and then third possibility is that the hydrogen oxygen itself can collide and form H O 2 and H. Now we have to understand that the activation energy of dissociation reaction these are all dissociation reaction where hydrogen oxygen etcetera are dissociating, this is essentially proportional to the endothermicity.

Then now the endothermicity for these 3 reactions if you try to understand, this is for the first reaction it is 1 0 4 kilo calorie per mole, for the second one is one 1 8 kilo calorie per mole and for the third one is 55 kilo calorie per mole of course, because the endothermicity is small here the barrior to be crossed is the minimum and as a result of which this and the activation energy is a essentially the minimum because these endothermicities are smallest. So, as a result this is typically the reaction by which hydrogen oxygen combustion is initiated; so by the formation of H O 2.

Now, then the most important thing to note here is that in the initiation reaction is that before we go in to this is that when H 2 and O 2 react it forms H O 2 and forms the H this is the key here, H is the key vary key radical in both hydrogen as well as in hydrocarbon combustion. So, we will see that the next step what H does is nothing but H does H contributes to this branching reaction.

So, H now once H is formed through the initiation reaction H reacts with O 2. So, H reacts with O 2 to form O and OH, but these reaction is endothermic and requires large energy to be initiated and is not favored at low temperature, but it needs as a result it needs high temperature. So, as a result you see that at low temperature in this curve in this hydrogen oxygen explosion curve at when there is at these low temperatures there is no explosion. The reason is that for explosion to happen we need to have this branching reactions happening, and these branching reactions does not happen at low temperatures.

Because you can see here clearly from this thing itself the H plus O 2, H plus O the activation energy 16.44 kilo calorie per mole. So, it needs sufficient energy in the in the system for this activation energy barrior to be crossed from the H O O and O H. So, thus as a result of this there is no explosion at low temperature and of course, there is no explosion at low pressure because there is not sufficient because these things are also, but this initiation also does not happen because whenever H is formed it can just because it is just if the if the pressure is low it is. So, dilute it does not this is are also short lived radicals it does not find another oxygen molecule to attack and it can just go and hit the wall and diffuse.

So, there is essentially no reaction at low pressure now this can be we have seen from the previous generalized discussion of the of explosion limits. So, when we discuss this n R goes to C etcetera this chain propagation reaction etcetera. So, this as a result at very low temperature and low pressure there is no reaction that is present, and then the other branching reactions are O and H 2 goes to H and O H and OH pus H 2 goes to H plus H 2 O and also there is this termination reaction which is very important this H plus O 2 plus M goes to H O 2 plus M.

So, you see that while H that is formed from the initiation reaction can attack O 2 and give it to this chain branching step this is the key chain branching step, there is also something happening parallely that is H plus O 2 in presence if the third body, in the presence of a third body M can become this inactive body H O 2 plus M, and as a result it can also reactions can also terminate.

And you will see that is the essentially the competition of these 3 chain branching reactions and or change branching or chain carrying this is also this is chain branching, this is chain branching this is chain carrying because 1 O H 1 O H give rise to one radical H if these 3 reactions this branching and carrying reactions, essentially compete with the termination reaction H plus O 2 plus M and that will determine whether the system is explosive or not how do we do the analysis.

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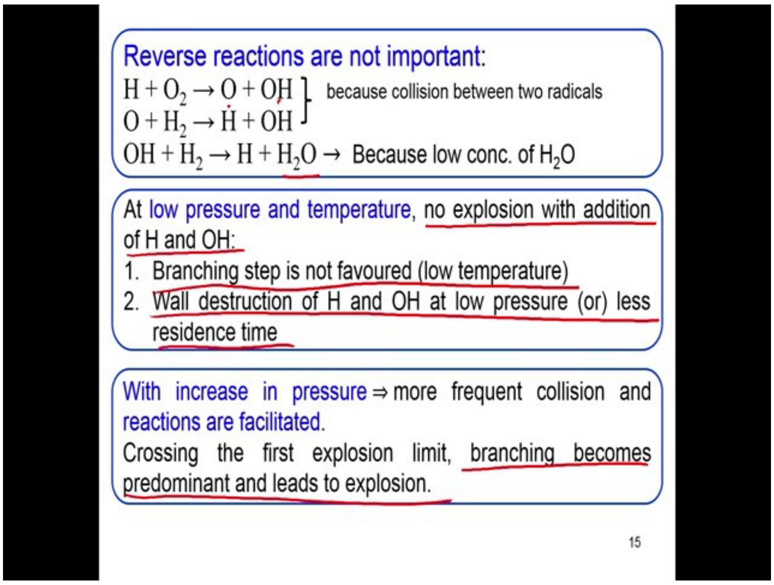

Reverse reactions are not important:

$H + O_2 \rightarrow O + OH$ } because collision between two radicals
$O + H_2 \rightarrow H + OH$
$OH + H_2 \rightarrow H + H_2O \rightarrow$ Because low conc. of H_2O

At low pressure and temperature, no explosion with addition of H and OH:

1. Branching step is not favoured (low temperature)
2. Wall destruction of H and OH at low pressure (or) less residence time

With increase in pressure ⇒ more frequent collision and reactions are facilitated.

Crossing the first explosion limit, branching becomes predominant and leads to explosion.

So, another point to notice that this reverse reactions in this between 2 radicals there you see that we have given only forwarded signs that H plus O 2 goes to O H and O, but the reverse reaction that is OH plus O go in to H plus H plus O 2 is not really favored because between moles collision between 2 radicals and this because of radicals itself are present in a very low concentration; so there and there also very energetic also. So, their colli their collisions does not really result in the backward reaction.

And also this where the reverse reaction of this is this one is not favored because at beginning at the time of ignition there is very low concentration of this product water, which is formed during the latest (Refer Time: 13:21) oxidation which concentration of H (Refer Time: 13:22) relative low oxidation. So, what we see is here is that to summarize just what we discussed that at lower pressure and temperature there is no explosion with addition of H and O H, because of we have said that the branching step is not favored at low temperature, and wall distraction of H and O H at low pressure or less residence time.

So, this is what we discussed that this branching step is not favored at low temperature and H and O H they can be formed at wall at low pressure they can just go to the wall and get destroyed. Now what happens with increase in pressure physically means that, it means that there is more frequent collision and more reactions are facilitated it. So, as a result of this the first explosion limit branching reaction becomes prominent as the same reason why at low pressure reactions are not favored are as you increase the temperature reactions are favored that branching reactions become prominent and lead to explosion, but remember that we have the termination reaction also.

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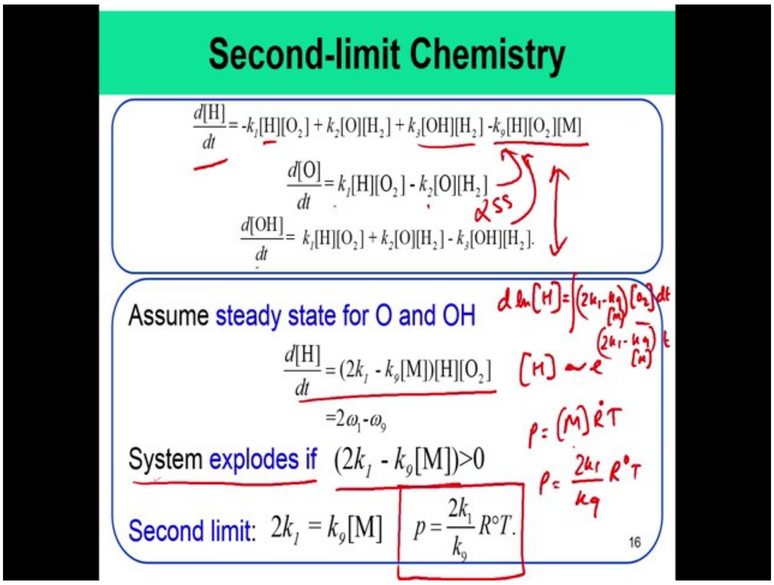

Second-limit Chemistry

$$\frac{d[\mathrm{H}]}{dt} = -k_1[\mathrm{H}][\mathrm{O_2}] + k_2[\mathrm{O}][\mathrm{H_2}] + k_3[\mathrm{OH}][\mathrm{H_2}] - k_9[\mathrm{H}][\mathrm{O_2}][\mathrm{M}]$$

$$\frac{d[\mathrm{O}]}{dt} = k_1[\mathrm{H}][\mathrm{O_2}] - k_2[\mathrm{O}][\mathrm{H_2}]$$

$$\frac{d[\mathrm{OH}]}{dt} = k_1[\mathrm{H}][\mathrm{O_2}] + k_2[\mathrm{O}][\mathrm{H_2}] - k_3[\mathrm{OH}][\mathrm{H_2}].$$

αSS

Assume steady state for O and OH

$$\frac{d[\mathrm{H}]}{dt} = (2k_1 - k_9[\mathrm{M}])[\mathrm{H}][\mathrm{O_2}]$$

$$= 2\omega_1 - \omega_9$$

System explodes if $(2k_1 - k_9[\mathrm{M}]) > 0$

Second limit: $2k_1 = k_9[\mathrm{M}]$ $\boxed{p = \frac{2k_1}{k_9} R^\circ T.}$

$d \ln[H] = \int (2k_1 - k_9[M])[O_2]\, dt$

$[H] \sim e^{(2k_1 - k_9[M])t}$

$p = [M] R^\circ T$

$p = \frac{2k_1}{k_9} R^\circ T$

16

So, it is essentially it is branching reactions has to compete with the termination reaction to determine the explosive is or not.

So, whom (Refer Time: 14:30) under what we have to basically this explosive or non explosive this tells us that is in the second limit is essentially the competition between the termination and the branching reactions and when it is explosive, it is essentially the branching reaction is winning and when it is non explosive essentially this termination reaction is winning all right. So, for that we are analyze the concentration the rate of change of concentration of H, and as you know that H we have seen that these are the reactions that contribute all of these reactions involve H 1, 2, 3 and 4. So, here you see that all this reactions k 1 is a first reaction, k 2 is a third reaction, k 3 is the third reaction and k 2 is the second reaction, k 3 is a third reaction, k 9 is the your termination reaction. So, all this you can write this dH dt.

As a in terms of this things because all this reactions are contributing to this H to the constringe of concentration of H, and also we analyze the rate of change of concentration of O because that is another important radical and that is contributed by 2 reactions k 1 and k 2 and this this is the third reaction where we try to analyze the rate of change of concentration of O H and which is contributed by essentially 3 reactions ok.

And now we assume that the second 2 species O and O H they are in steady state that is the q s assumption that we learnt in last class this is also another very important thing we learnt. So, when you do that and when you basically substitute this things in to this after applying for QSS you can find that what you find is that you can write dH dt as 2 k 1 that is a reaction rate constant of the first reaction, minus k 9 that is reaction rate constant of the ninth reaction which is the termination reaction you can validate from here the this is this is the first reaction which is the chain branching reaction H plus O 2 give rise to O H plus O and this is the termination reaction H plus O 2 plus M give rise to OH O 2 plus M and. So, the dH dt is essentially a concent is given by 2 k 1 minus k 9, times M times the concentration of the third body itself which comes from the termination reaction times H and O 2 ok.

Now, let us just we can this is also essentially means that it is 2 omega 1, minus omega 9 which is are at (Refer Time: 17:10) reaction rate of the first reaction minus reaction rate of ninth reaction. So, we see that what this is exactly the similar form of dC dt is equal to something some constant a minus ac times C times some other things that we saw previously in the generalized discussion. So, here this this thing dH dt is equal to once again some constant v times H and O 2 this will give have an exponential form and the sign of the exponent of the expo of e to the power of something, the sign of that something will tell you whether this system will explode or not. So, that is why the sign of B is very important. So, what is B? B is nothing but 2 k 1 minus k 9 ok.

And we can say that the system explodes if 2 k 1 minus k 9 times n is greater than 0, you understand where it comes from, but if you just remove this. If we solve for this what we will get is that d lon H if you solve for this this thing now, we will get is that is equal to all right. So, it has a it will show kind of an explosive behavior of course, there will be some there will be this function of O 2 also coming in, but let us not consider that we can say that this this thing becomes explosive H will be essentially some you can write it as something like e to the power of 2 k 1 minus k 9 times t.

There will be some other things and also that the there will be change of rate of change of oxygen, but on average this is the thing, but the system will explode if 2 k 1 minus k 9 times M sorry here M is there. So, 2 k 1 minus k 9 times say M is greater than 0, now M is essentially a third body and the concentration of M depends on the essentially the pressure. So, we can say that we can replace we can write the ideal gas equation of state P is equal to essentially M R T and under the limit end condition we can just substitute this M, we can substitute e by R 0 T into here and we find is that we essentially find that P is equal to 2 k 1 by k 9 times R 0 T which is this thing.

And we find that P is essentially a linear function of temperature and the as a result of and because of this linearity you get this the second exposure limit to be nearly linear. So, this is the reason, why it is linear like this why pressure and temperature are proportional.

It essentially means you see what it means is that it essentially means that when twice of the first chain branching reaction is equal to k 9 times M. So, it is essentially a competition between the most important chain branching reaction and the termination reaction. So, when this 2 are at essentially equal rate, that gives if on this side essentially k 9 is winning and on this side is k 1 is winning and as a result of which this this this side is non explosive and this side is explosive.

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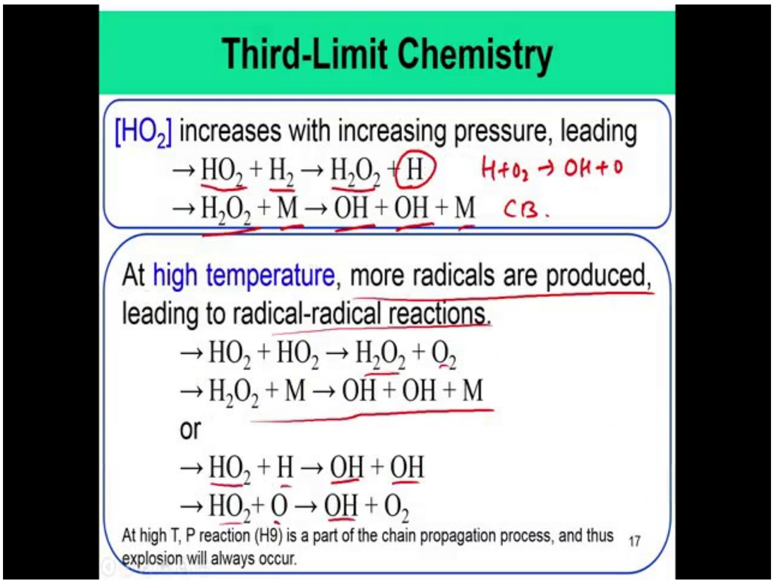

Third-Limit Chemistry

$[HO_2]$ increases with increasing pressure, leading

$\rightarrow HO_2 + H_2 \rightarrow H_2O_2 + \boxed{H}$ $H + O_2 \rightarrow OH + O$

$\rightarrow H_2O_2 + M \rightarrow OH + OH + M$ CB.

At high temperature, more radicals are produced, leading to radical-radical reactions.

$\rightarrow HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

$\rightarrow H_2O_2 + M \rightarrow OH + OH + M$

or

$\rightarrow HO_2 + H \rightarrow OH + OH$

$\rightarrow HO_2 + O \rightarrow OH + O_2$

At high T, P reaction (H9) is a part of the chain propagation process, and thus explosion will always occur.

17

So, this is the clearly the second limit explosive ex it explains the second limit, the third limit is that as we have seen that H O 2 the formation of H O 2 here is we call it termination because when the when the temperature in for example, we have seen that H O 2 is here in the termination reaction H O 2 is essentially formed. So, this is the formed and H O 2 is essentially rather in active radical, under low temperature and pressure conditions because it can it does not do much and it essentially defuse it is to the walls and becomes inactive.

But when you raise the pressure what can happen is that as the concentration of H O 2 increases the H O 2 can essentially react with H 2 and then it can form H 2 O 2 plus H. So, once again you whens as soon as you form H which is a very very active radical it can go to the chain branching step, where H plus O 2 once again goes to O H plus O and also of course, this H 2 O 2 the hydrogen peroxide can react with M to form O H OH and M this is a chain branch reaction.

So, these chain branching reactions can now take over and as a result of this as the concentration of as you increase the pressure, you once again from explosive it becomes from in explosive it becomes explosive. So, that is why even with increase in pressure even with the promotion of this termination reaction it becomes explosive because now the H O 2 radical is formed as soon as this is crossed. Now this H O 2 radical essentially gives rise to chain branching reactions. So, this chain branching reactions that would be informed actually makes the system explosive again. So, watt (Refer Time: 22:59) explains this is a very unique shape of this z curve here. So, and as a result and also has high temperature more and more radicals are produced, and leading to radical radical reactions as you see that H O 2 plus H O 2 can also become H 2 O 2 plus O 2 and H O 2 plus M goes to OH plus OH plus M. So, this is the thing ok.

And also that H O 2 plus H goes can become O H plus O H and H O 2 can also react with O it to become O H at. Now, what the means is that at high temperature and pressure H 9 is part of a reaction chain propagation process, and thus explosion is always will always occur.

To summarize if I can let me just summarize this thing in terms of what we have learnt that is this was the thing we were discussing about; so this explosion of hydrogen and oxygen. So, here what happens here is that at low temperature and pressure when the key reactions or of course, the initiation reaction.

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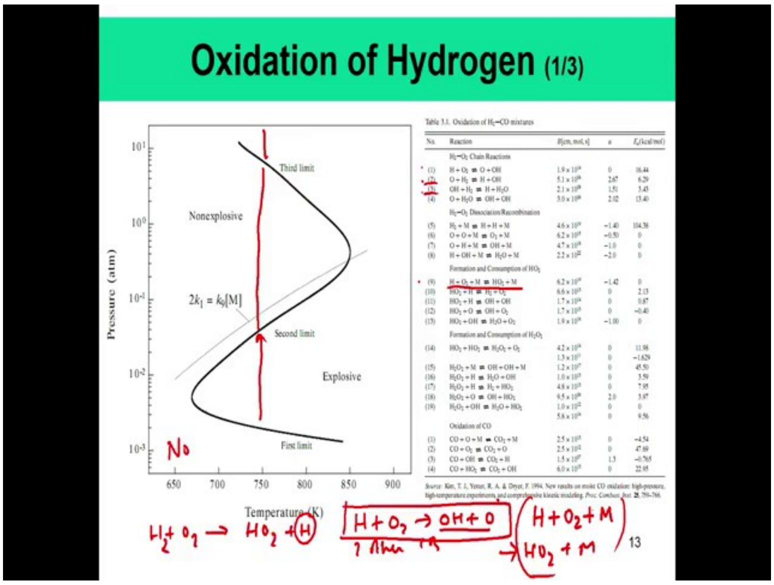

Oxidation of Hydrogen (1/3)

Table 3.1. Oxidation of H_2–CO mixtures

No.	Reaction	A(cm, mol, s)	n	E_a(kcal/mol)
	H_2–O_2 Chain Reactions			
(1)	$H + O_2 \rightleftharpoons O + OH$	1.9 × 10[illegible]	0	16.44
(2)	$O + H_2 \rightleftharpoons H + OH$	5.1 × 10[illegible]	2.67	6.29
(3)	$OH + H_2 \rightleftharpoons H + H_2O$	2.1 × 10[illegible]	1.51	3.43
(4)	$O + H_2O \rightleftharpoons OH + OH$	3.0 × 10[illegible]	2.02	13.40
	H_2–O_2 Dissociation/Recombination			
(5)	$H_2 + M \rightleftharpoons H + H + M$	4.6 × 10[illegible]	−1.40	104.38
(6)	$O + O + M \rightleftharpoons O_2 + M$	6.2 × 10[illegible]	−0.50	0
(7)	$O + H + M \rightleftharpoons OH + M$	4.7 × 10[illegible]	−1.0	0
(8)	$H + OH + M \rightleftharpoons H_2O + M$	2.2 × 10[illegible]	−2.0	0
	Formation and Consumption of HO_2			
(9)	$H + O_2 + M \rightleftharpoons HO_2 + M$	6.2 × 10[illegible]	−1.42	0
(10)	$HO_2 + H \rightleftharpoons H_2 + O_2$	6.6 × 10[illegible]	0	2.13
(11)	$HO_2 + H \rightleftharpoons OH + OH$	1.7 × 10[illegible]	0	0.87
(12)	$HO_2 + O \rightleftharpoons OH + O_2$	1.7 × 10[illegible]	0	−0.40
(13)	$HO_2 + OH \rightleftharpoons H_2O + O_2$	1.9 × 10[illegible]	−1.00	0
	Formation and Consumption of H_2O_2			
(14)	$HO_2 + HO_2 \rightleftharpoons H_2O_2 + O_2$	4.2 × 10[illegible]	0	11.98
		1.3 × 10[illegible]	0	−1.629
(15)	$H_2O_2 + M \rightleftharpoons OH + OH + M$	1.2 × 10[illegible]	0	45.50
(16)	$H_2O_2 + H \rightleftharpoons H_2O + OH$	1.0 × 10[illegible]	0	3.59
(17)	$H_2O_2 + H \rightleftharpoons H_2 + HO_2$	4.8 × 10[illegible]	0	7.95
(18)	$H_2O_2 + O \rightleftharpoons OH + HO_2$	9.5 × 10[illegible]	2.0	3.97
(19)	$H_2O_2 + OH \rightleftharpoons H_2O + HO_2$	1.0 × 10[illegible]	0	0
		5.8 × 10[illegible]	0	9.56
	Oxidation of CO			
(1)	$CO + O + M \rightleftharpoons CO_2 + M$	2.5 × 10[illegible]	0	−4.54
(2)	$CO + O_2 \rightleftharpoons CO_2 + O$	2.5 × 10[illegible]	0	47.69
(3)	$CO + OH \rightleftharpoons CO_2 + H$	1.5 × 10[illegible]	1.3	−0.765
(4)	$CO + HO_2 \rightleftharpoons CO_2 + OH$	6.0 × 10[illegible]	0	22.95

Source: Kim, T. J., Yetter, R. A. & Dryer, F. 1994. New results on moist CO oxidation: high-pressure, high-temperature experiments and comprehensive kinetic modeling. *Proc. Combust. Inst.* 25, 759–766.

$H_2 + O_2 \rightarrow HO_2 + \textcircled{H}$

$\boxed{H + O_2 \rightarrow \underline{OH + O}}$

$\left(H + O_2 + M \rightarrow HO_2 + M \right)$

That is when H 2 plus O 2 becomes H O 2 plus H as we have seen here, H 2 plus O 2 becomes OH H 2 plus h. So, I am just summarizing here. So, this is the most important initiation reaction because of it is low endothermicity.

Now, once H is formed we can have chain branching reactions where H plus O 2 goes to O H plus O, and there can be other 2 other chain branching also which you see that.

These are the other chain branching this this one and this one these are the different chain branching reactions this curve which you can have, but also there is simultaneously there is competition from the termination reaction. H plus O 2 plus M becomes H O 2 plus M termination become termination means the chain carrier becomes in activated.

So, in the when the temperature and pressure is when the temperature is low that is in this regime there is no reaction happening, because even if there is initiation reaction these reaction which is the most important reaction in combustion H plus O 2 go in to H plus O these does not happen because this needs high temperature. So, in these reactions it is there is no reaction that is happening if this is non-explosive.

But now as we increase and of course, where at low pressure there is also no reaction because you see the wall destruction of H and O H at low pressure or at low residence times. So, when there will pressure is low as we have discussed that that there is too less number of collisions happening, and this H radical which is being formed from the initiation reaction just flies away into the walls before it hits another like an oxygen molecule and it is can just deactivate.

So, in this case there is it is there is no explosion. Now as you increase the pressure of course, this now this H can now attack O 2 and this can leads to chain branching and reaction can happen, but once happens is that as you increase it the pressure then this termination reaction H plus O 2 plus M become go into H O 2 plus M of this starts and these basically instead of H going in to this chain branching step H plus O 2 go into OH plus O these takes away the H atom and it makes this deactivated H O 2. I just write it more clearly it makes this small deactivated H O 2 instead of this chain branching step.

So, and we see that then and it is between the competition of this 3 chain branching reaction 1 2 and 3 these competes with this k 9 which is H O 2 plus H plus O 2 plus M going to H O 2 plus M, and that basically deactivates the makes as makes a whole system non explosive. So, as a result of this at high pressure because of the dominants of this reaction at higher pressure this becomes non explosive. So, we grow to this limit, but then again what happens is that at even higher pressure this deactivated H O 2 can now basically react with a third body and or it can react with the other things and that can lead to chain branching reactions; so at very high pressure that in this limit you see that this again becomes explosive.

So, these can explains the summarizes the different the 3 different limits of hydrogen oxygen oxidation and the z curve of hydrogen oxygen explosion, but this is very important as you see because it determines that under which condition hydrogen oxygen mixture can be explosive, under which condition it will become in explosive. And it is this explosive in explosive state of. Once again as you see that one can never predict this using the global one step reaction mechanisms or global one step reactions, you need the details of this chain initiation chain branching chain termination and the competition between the chain branching and the chain termination to understand when it is explosive and when it is non-explosive ok.

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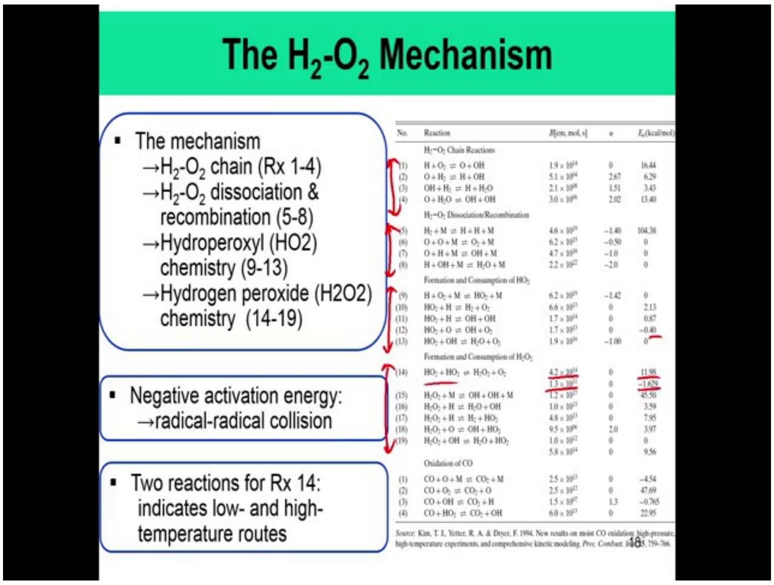

The H_2-O_2 Mechanism

- The mechanism
  - →H_2-O_2 chain (Rx 1-4)
  - →H_2-O_2 dissociation & recombination (5-8)
  - →Hydroperoxyl (HO2) chemistry (9-13)
  - →Hydrogen peroxide (H2O2) chemistry (14-19)
- Negative activation energy:
  - →radical-radical collision
- Two reactions for Rx 14: indicates low- and high-temperature routes

No.	Reaction	A[cm, mol, s]	b	E_a(kcal/mol)
	H_2-O_2 Chain Reactions			
(1)	$H + O_2 \rightleftharpoons O + OH$	1.9×10^{14}	0	16.44
(2)	$O + H_2 \rightleftharpoons H + OH$	5.1×10^{4}	2.67	6.29
(3)	$OH + H_2 \rightleftharpoons H + H_2O$	2.1×10^{8}	1.51	3.43
(4)	$O + H_2O \rightleftharpoons OH + OH$	3.0×10^{6}	2.02	13.40
	H_2-O_2 Dissociation/Recombination			
(5)	$H_2 + M \rightleftharpoons H + H + M$	4.6×10^{19}	−1.40	104.38
(6)	$O + O + M \rightleftharpoons O_2 + M$	6.2×10^{15}	−0.50	0
(7)	$O + H + M \rightleftharpoons OH + M$	4.7×10^{18}	−1.0	0
(8)	$H + OH + M \rightleftharpoons H_2O + M$	2.2×10^{22}	−2.0	0
	Formation and Consumption of HO_2			
(9)	$H + O_2 + M \rightleftharpoons HO_2 + M$	6.2×10^{19}	−1.42	0
(10)	$HO_2 + H \rightleftharpoons H_2 + O_2$	6.6×10^{13}	0	2.13
(11)	$HO_2 + H \rightleftharpoons OH + OH$	1.7×10^{14}	0	0.87
(12)	$HO_2 + O \rightleftharpoons OH + O_2$	1.7×10^{13}	0	−0.40
(13)	$HO_2 + OH \rightleftharpoons H_2O + O_2$	1.9×10^{16}	−1.00	0
	Formation and Consumption of H_2O_2			
(14)	$HO_2 + HO_2 \rightleftharpoons H_2O_2 + O_2$	4.2×10^{14}	0	11.98
		1.3×10^{11}	0	−1.629
(15)	$H_2O_2 + M \rightleftharpoons OH + OH + M$	1.2×10^{17}	0	45.50
(16)	$H_2O_2 + H \rightleftharpoons H_2O + OH$	1.0×10^{13}	0	3.59
(17)	$H_2O_2 + H \rightleftharpoons H_2 + HO_2$	4.8×10^{13}	0	7.95
(18)	$H_2O_2 + O \rightleftharpoons OH + HO_2$	9.5×10^{6}	2.0	3.97
(19)	$H_2O_2 + OH \rightleftharpoons H_2O + HO_2$	1.0×10^{12}	0	0
		5.8×10^{14}	0	9.56
	Oxidation of CO			
(1)	$CO + O + M \rightleftharpoons CO_2 + M$	2.5×10^{13}	0	−4.54
(2)	$CO + O_2 \rightleftharpoons CO_2 + O$	2.5×10^{12}	0	47.69
(3)	$CO + OH \rightleftharpoons CO_2 + H$	1.5×10^{7}	1.3	−0.765
(4)	$CO + HO_2 \rightleftharpoons CO_2 + OH$	6.0×10^{13}	0	22.95

Source: Kim, T. J., Yetter, R. A. & Dryer, F. 1994. New results on moist CO oxidation: high-pressure, high-temperature experiments, and comprehensive kinetic modeling. *Proc. Combust. Inst.* 25, 759-766.

So, and to discuss a little bit about the about this hydrogen oxygen mechanisms, you see that this hydrogen oxygen mechanism is done in a very organized manner where the first 4four reactions essentially represents the chain branching reactions, and the from 5 to 8 it represents the hydrogen oxygen dissociation reactions, and then from 9 to 13 it essentially introduces the hydroperoxyl chemistry and then it introduces from 14 to 19 we have this hydrogen peroxide chemistry the rest is C oxidation which will come in a short (Refer Time: 29:58).

Now, one important thing is that you see that in certain cases you have got negative activation energy this one like this one etcetera. So, it means that radical this involves essentially this this this is essentially this one is involves is essentially the radical collision. So, it means that the radical collision is promoted in a low temperature state, but this you do not have a need more energy if you provide more energy the reactions are not promoted rather prohibited because radicals itself contain lot of energy.

So, when you even you energize them to or they did the reactions simply does not happen because they are 2 an energetic when they collide they just simply fly away, without any reactions or change of electronic structure happening. So, that is that what explains negative activation energy and it is the radical collision. Also there will 2 for example, in 14you have this 2 2 different values of this pre exponential factor B and this and this activation energy which means there are 2 temperature or 2 roots for low and high temperatures ok.

So, if a in the following we will go in to the oxidation of carbon monoxide and as you have seen that that in carbon monoxide oxidation is involve is actually included in the oxidation in the reaction of the reaction mechanism of hydrogen oxygen combustion.

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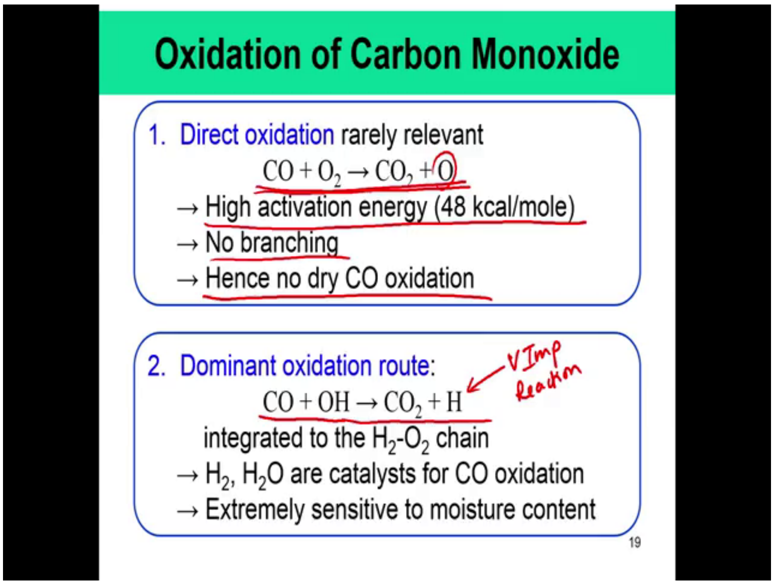

Oxidation of Carbon Monoxide

1. Direct oxidation rarely relevant

$$CO + O_2 \rightarrow CO_2 + O$$

→ High activation energy (48 kcal/mole)

→ No branching

→ Hence no dry CO oxidation

2. Dominant oxidation route:

$$CO + OH \rightarrow CO_2 + H$$

V Imp Reaction

integrated to the H_2-O_2 chain

→ H_2, H_2O are catalysts for CO oxidation

→ Extremely sensitive to moisture content

So, now what we need to understand is that this direct oxidation of carbon monoxide to carbon dioxide that is C O plus O 2 going to C O 2 plus O, this is really relevant this does not happen. Now because the reason is that there is a very high activation energy of 48 8 kilo calory per mole involved and this oxygen atom that is formed does not really go in to form any branching reaction, the chain branching reaction is does not happen and if chain branching is does not happen you see that there is no very rapid reaction happening and then this is as a result this dry oxidation that is which is this oxidation of carbon monoxide in absence of moisture is not really, promoted this does not happen. The dominant oxidation route is essentially this C O plus O H go into C O 2 plus H.

And this is also this another very very important reaction in hydrocarbon combustion and you will see that these reactions that H plus O 2 go in to O H plus O, and this C O plus O H go into CO 2 plus H these 2 are the 2 most important reactions involving hydrocarbon combustion, and in later what the fuel is you will see that this is come up or very often and essentially they come and always form the major chain branching step and these essentially forms a major heat release step of this C O plus O H going to C O 2 plus H.

And here as you see the this is integrated into the hydrogen oxygen chain and the reason is that whenever there is little bit of hydrogen present in the system these hydrogen can form this O H be (Refer Time: 33:21) chain branching step the H plus O 2 go into O H plus O and these OH essentially reacts with C O and forms this C O 2 plus H. And as a result and also water whenever there is water also then this reaction comes and as a result this C O oxidation becomes very very sensitive to moisture contents because this C O oxidation does not happen in a dry state through this reaction rather it happens in through this O H is here through this O H in to this C O plus O H go in to C O 2 plus H ok.

So, this is the most important reaction involving a C O 2, and you can see here that this is the reaction this C O 3 this C O plus O H go into to C O 2 plus H and which is actually and which happens in a very spontaneous manner you see that activation energy is also nearly zero almost ok.

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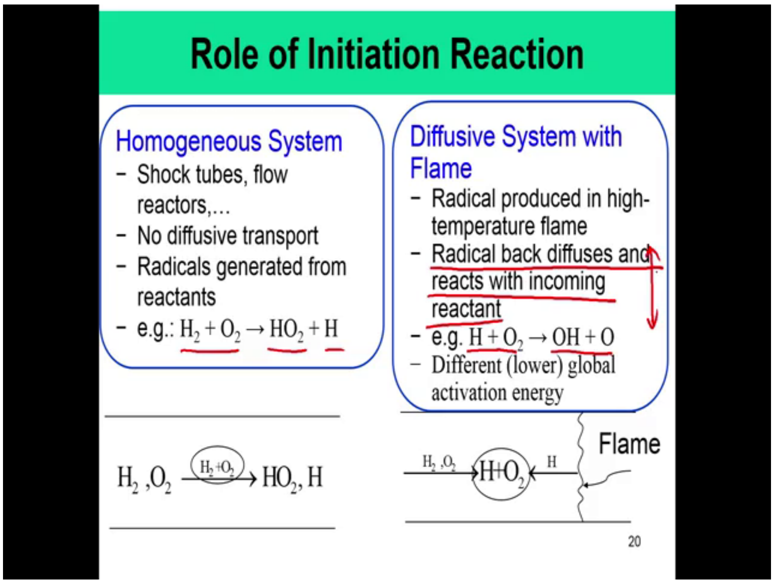

Role of Initiation Reaction

Homogeneous System

- Shock tubes, flow reactors,…
- No diffusive transport
- Radicals generated from reactants
- e.g.: $H_2 + O_2 \rightarrow HO_2 + H$

Diffusive System with Flame

- Radical produced in high-temperature flame
- Radical back diffuses and reacts with incoming reactant
- e.g. $H + O_2 \rightarrow OH + O$
- Different (lower) global activation energy

So, now the initiation reactions we have to understand one thing that is in the homogeneous system whatever we have described so far, I already told you a little bit about the difference between homogeneous systems and the like in actual systems like flames etcetera, in a shock tube flow reactor or a this ignition delay calcula designation delays experimental setups there is no diffusive transport. So, any mirror ignition delay actually there is no diffusive transport that is a very very important thing. So, only you have a balance of this only this dc dt is essentially equal to your the stoichiometric coefficient times a reaction rate ok.

So, there is no diffusion involved. So, when there is no diffusion involved it is only progresses in one direction of that is in the direction of time. So, the radicals that are generated when there consume there are no way of coming back, now this might some strange there is. So, the initiation reaction in this one is H plus H 2 plus O 2 is H O 2 plus H; however, in a flame say for example, in a practical combustion we have a flame the radical are as producing high temperature regimes, but this because of diffusion the radicals can back diffuse with and react with the incoming reactants and as a result the initiation reaction for a of course, after splitting a fuel the initiation reactions in a actual flames is essentially H plus O 2 go into O H plus O.

And as a result it is a different global activation energy for if you consider homogeneous system versus a diffusive system. So, this is the initiation reaction of choice H plus O 2 go into a H plus O in a flame whereas, this is a reaction for H 2 plus O 2 giving rise H O 2 plus H in a flame (Refer Time: 36:02) of course, the detailed reaction mechanisms are same, but the we say that the chemistry is different for homogeneous system versus the chemistry is different for diffusive system in that, the relative importance of the reactions in this kinds of things like initiation etcetera these becomes different when you have this radicals back diffusing and reacting with the species of the incoming reactants.

So, this is what is the major difference between a homogeneous system when you calculate the or which involves like ignition delay what happens in a shock tubes etcetera versus what you have in a flame. So, that is the thing here and we will take a short break and when we join we are go into oxidation of methane.

Thank you.