Advanced Thermodynamics and Combustion

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Module - VI
Chemical Kinetics
Lecture - 25
Reaction Mechanism (Part II)

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

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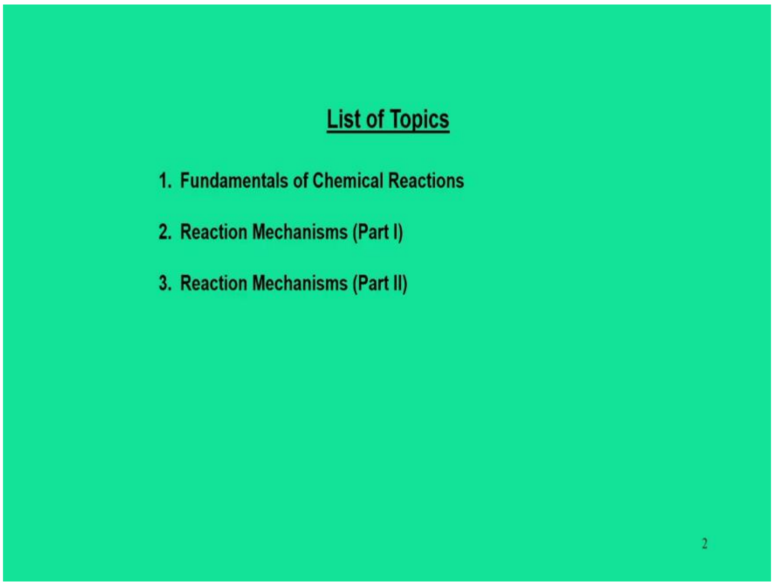

List of Topics

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

In this module, we have 3 lectures. One is a fundamental of chemical reactions, where you have covered the basics of chemical kinetics. Second one is the reaction mechanisms, here also if we have seen what are the different possible reactions, global reaction, elementary reactions, how they need to be addressed. And, also, we elaborated the concept of chemical time scale.

And, in today's lecture, we will be considering Reaction Mechanisms and it is part II of this reactant mechanism, it is mainly dealt with the practical considerations of some reaction systems. So, this is the summary of this today's lecture.

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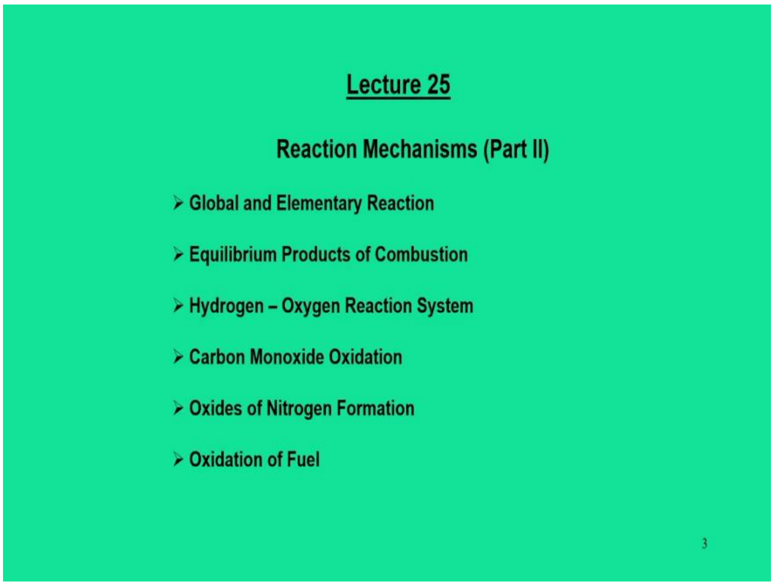

Lecture 25

Reaction Mechanisms (Part II)

- Global and Elementary Reaction
- Equilibrium Products of Combustion
- Hydrogen – Oxygen Reaction System
- Carbon Monoxide Oxidation
- Oxides of Nitrogen Formation
- Oxidation of Fuel

And, here in this lecture number 25, that is reaction mechanism part II, first we will introduce the concept of chemical kinetics with global and elementary reactions. And, then we will look into the equilibrium products of combustion which we have discussed earlier. Now, in this lecture we will try to focus on very specific chemical mechanisms that are of interest for combustion.

First one is the very common phenomena which is used in the rocket propulsion systems and it is called as hydrogen oxygen reaction systems. Then, another one is carbon monoxide formations in the IC engines when the fuels are not burnt completely. Then, there are also issues of formation of nitric oxide, NOx formations when we do not run the engines at its appropriate fuel ratio or equivalence ratio.

Then, for all these three cases, we will see that what type of reactions are very important and for which it leads to this formation like CO or NOx. Another important concept that, we are also going to introduce that when fuel gets oxidized, how all the molecules of the fuel gets burnt and the way how they have been formed. And, when you say oxidation of the fuel and our main concern is the fuel nothing, but your hydrocarbon fuel.

So, basically speaking till this point of time whatever we have covered, we will try to look into the practical glimpses that which are normally the conventional issues nowadays to look into the reaction mechanism of practical systems.

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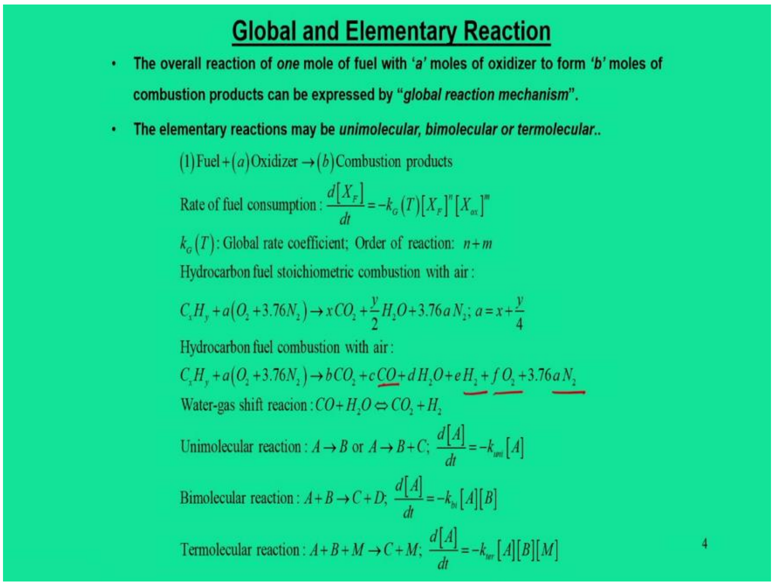

Global and Elementary Reaction

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

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

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

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

Hydrocarbon fuel stoichiometric combustion with air:

$$C_xH_y+a(O_2+3.76N_2)\rightarrow xCO_2+\frac{y}{2}H_2O+3.76aN_2;\ a=x+\frac{y}{4}$$

Hydrocarbon fuel combustion with air:

$$C_xH_y+a(O_2+3.76N_2)\rightarrow bCO_2+c\underline{CO}+dH_2O+e\underline{H_2}+f\underline{O_2}+3.76a\underline{N_2}$$

$$\text{Water-gas shift reacion}: CO+H_2O\Leftrightarrow CO_2+H_2$$

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

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

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

Just to give preliminary introductions, we all know that we have global and elementary reactions. And, when a global reaction we see fuel and oxidizer as a whole and it give combustion products. And, this rate at which the fuel gets consumed is a function of the global rate coefficients and concentrations of fuels and oxidizer. So, based on which we can define the order of reactions.

Now, when you look into the elementary reactions. So, the elementary reactions if you see fuel gets dissociated, oxidizer also gets dissociated and they form some kind of elementary reactions. They categorized as unimolecular, bimolecular, termolecular reactions. And in fact, these reactions are nothing, but the chain initiation reactions, chain propagation reactions and also chain termination reactions.

So, through this process they are not seen as a globally, but they are formed during the reactions and they are also destroyed after the products have been formed. So, they are called as elementary reactions. So, our tendency is to find out in this lecture that what are the elementary reactions that are being formed in various reaction mechanisms. And, in particular we will be discussing about H_2 - O_2 systems, carbon monoxide oxidation, nitric oxide formations. These three are important.

And, in particular when you look at hydrocarbon fuel combustion with air, we will have two cases. One is stoichiometric cases, where CO_2 formation and H_2 formation is quite natural. But when we will deal with the non-stoichiometric situations either the fuel can be rich or lean. So, based on that the formation of CO, CO, O2, H_2 and N_2 also becomes predominant. And, to some extent when the temperature is very high, this N_2 can also break and they can take part the formation of NO. So, this is the background of these today's discussions.

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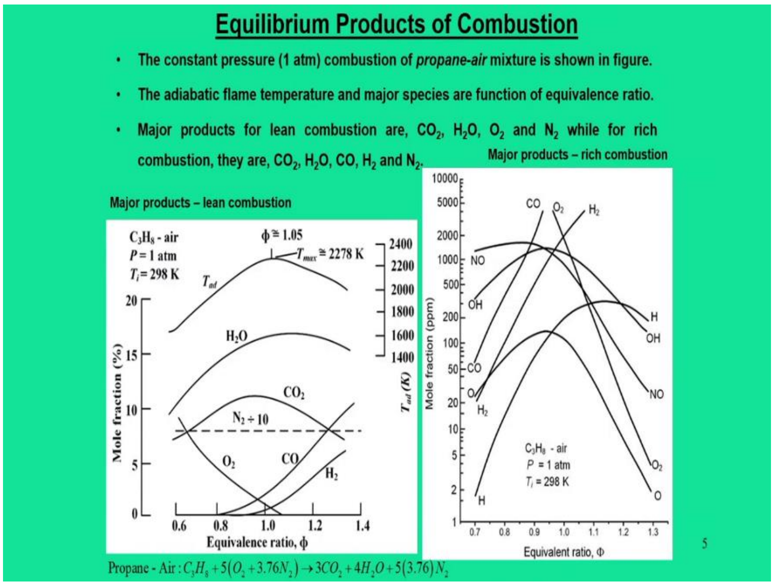

Equilibrium Products of Combustion

- The constant pressure (1 atm) combustion of *propane-air* mixture is shown in figure.
- The adiabatic flame temperature and major species are function of equivalence ratio.
- Major products for lean combustion are, CO_2, H_2O, O_2 and N_2 while for rich combustion, they are, CO_2, H_2O, CO, H_2 and N_2.

Major products – lean combustion

Major products – rich combustion

Propane - Air : $C_3H_8 + 5(O_2 + 3.76N_2) \rightarrow 3CO_2 + 4H_2O + 5(3.76)N_2$

Now, even if you look at the discussion points of earlier like one case where propane air mixture gives the major products of products of combustion are CO_2, H_2O, O_2 and N_2. So, those things are formed during lean combustion and you can see these concentrations of all the components or species, they vary with equivalence ratio. And, also their mole fractions sometimes increase, sometimes decreases, at one point of time there is a maximum.

And, in addition to that when we have lean combustion, we can plot the adiabatic flame temperatures where we can ensure what is the maximum temperature that we can achieve during this methane air combustion process. Now, when you move on to rich combustion process, the same mole fractions are also important and they are also formed.

Apart from this, when you have rich combustion you can see the formation of O, CO, OH, NO and then oxygen and all these things are form and their concentration varies when we increase the equivalence ratio. Now, the question arises why these are formed? What is the mechanism? And, when these are formed, I mean from where they started arising?

And in fact, all these are radicals, they sometimes come out as a product and sometimes they do not. So, our point of discussion today will be that how formation of these components during a combustion process, what are the elementary reactions that accelerates this formations.

And, if at all they are formed, what is the condition of the fuel in terms of its equivalence ratio, whether it is a rich or lean first thing. Second thing is that effect of temperature, because when the reactions and the products are formed when the temperature is increased then effect of temperature has to be taken into accounts. So, these two things are very basics for the reaction mechanisms.

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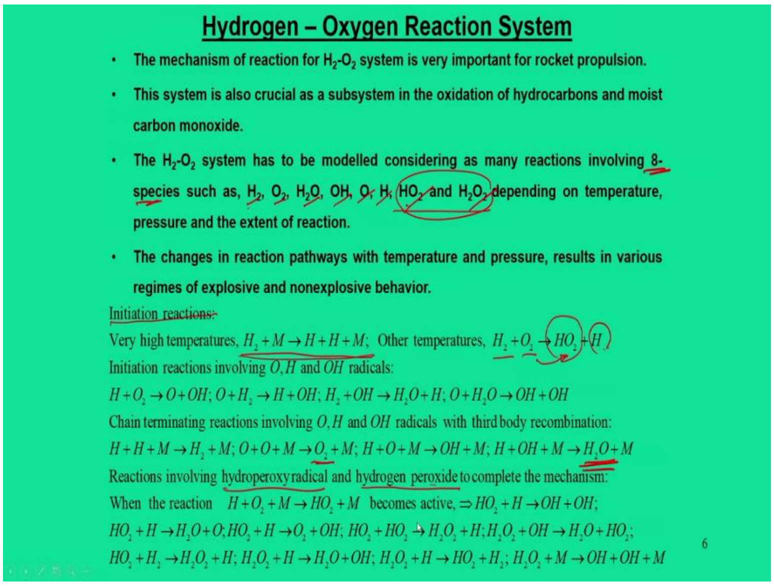

Hydrogen – Oxygen Reaction System

- The mechanism of reaction for H_2-O_2 system is very important for rocket propulsion.
- This system is also crucial as a subsystem in the oxidation of hydrocarbons and moist carbon monoxide.
- The H_2-O_2 system has to be modelled considering as many reactions involving 8-species such as, H_2, O_2, H_2O, OH, O, H, HO_2 and H_2O_2 depending on temperature, pressure and the extent of reaction.
- The changes in reaction pathways with temperature and pressure, results in various regimes of explosive and nonexplosive behavior.

Initiation reactions:

Very high temperatures, $H_2 + M \rightarrow H + H + M$; Other temperatures, $H_2 + O_2 \rightarrow HO_2 + H$

Initiation reactions involving O, H and OH radicals:

$H + O_2 \rightarrow O + OH$; $O + H_2 \rightarrow H + OH$; $H_2 + OH \rightarrow H_2O + H$; $O + H_2O \rightarrow OH + OH$

Chain terminating reactions involving O, H and OH radicals with third body recombination:

$H + H + M \rightarrow H_2 + M$; $O + O + M \rightarrow O_2 + M$; $H + O + M \rightarrow OH + M$; $H + OH + M \rightarrow H_2O + M$

Reactions involving hydroperoxy radical and hydrogen peroxide to complete the mechanism:

When the reaction $H + O_2 + M \rightarrow HO_2 + M$ becomes active, $\Rightarrow HO_2 + H \rightarrow OH + OH$;

$HO_2 + H \rightarrow H_2O + O$; $HO_2 + H \rightarrow O_2 + OH$; $HO_2 + HO_2 \rightarrow H_2O_2 + H$; $H_2O_2 + OH \rightarrow H_2O + HO_2$;

$HO_2 + H_2 \rightarrow H_2O_2 + H$; $H_2O_2 + H \rightarrow H_2O + OH$; $H_2O_2 + H \rightarrow HO_2 + H_2$; $H_2O_2 + M \rightarrow OH + OH + M$

Now, first reaction that we are going to discuss and it is very common that hydrogen and oxygen reaction systems. We all know that hydrogen is a fuel nowadays and also it is a green fuel and also and oxygen is oxidizer. And, when they mix, they also form water which is a friendly liquid and its used for day to day life. And, also in some situations when these hydrogen and oxygen they mix, they can behave in explosive manner.

So, the control of hydrogen and oxygen is very vital, because it is mainly used in the rocket propulsion systems. In a rocket propulsion system, usually oxygen tanks is being carried out and hydrogen tank also is being carried out and they are kept in a liquefied form; so, that we can have a higher density. Now, if at all they need to be stored combinedly then under what circumstances they behave in a friendly manner and other circumstances they behave in an explosive manner.

So, this is the very basic bottom line of this H_2 O_2 systems. So, if you look at closely this system, many reaction species and in particular there are about 8 important species. And, these 8 species are hydrogen, oxygen, water, OH radical, oxygen atom, hydrogen atom, HO_2 is another compound and H_2O_2, the combination system.

Now, out of this HO_2 and H_2O_2, it is very friendly. But, these radicals when they form OH and they are actually chain initiation or chain propagating reactions. And, they keeps on spreading as and when they get a very good environment, I mean that is required pressure and temperature if they get, they make their chain in a growing manner.

So, the reaction during this phase, the changes of reaction pathways which is a function of temperature and pressure, it can result in various regimes of explosive and non-explosive behavior. So, let us understand how it can form, I mean in H_2O_2 system what may happen. There are two important case happens during the initiation process, if the temperature is very high then we may have this kind of interactions. $H_2 + M \rightarrow H + H + M$ with high temperature collision.

But, if temperature is not too high then H_2 and O_2 they will not break rather $H_2 + O_2 \rightarrow HO_2 + H, HO_2$ is a friendly, but H is not. So, what it does is, this H and depending on the temperatures, OH and OH radical they keeps on increasing the chain and in this manner, that mean in particular $H + O_2 \rightarrow O + OH$. And, even in some cases you can find out $H_2 + OH \rightarrow H_2O + H$ and $O + H_2O \rightarrow OH + OH$.

So, these are chain in chain reactions that keeps on happening, if the pressure and temperatures are friendly. And, these things keeps on happening till entire fuel or entire H_2 is consumed and at one point of time we will have a chain terminating reactions. And, this chain terminating reaction when we see either you can get in the form of water formations or we may have oxygen again directly. And, there is also formation of hydroperoxy radicals and hydrogen peroxide.

And in fact, this HO_2 and H_2O_2; these are nothing but hydroperoxy radical and hydrogen peroxide. When they form, they try to stop the chain. I mean we can say that reaction is complete and they are not in active. So, when such a situation arrives; so, we can say the HO_2 formation is active.

And, again this HO_2 sometimes if you get a very friendly environment, it again can start other radicals as well. So, what I am trying to say all these reactions are dependent on pressure and temperatures

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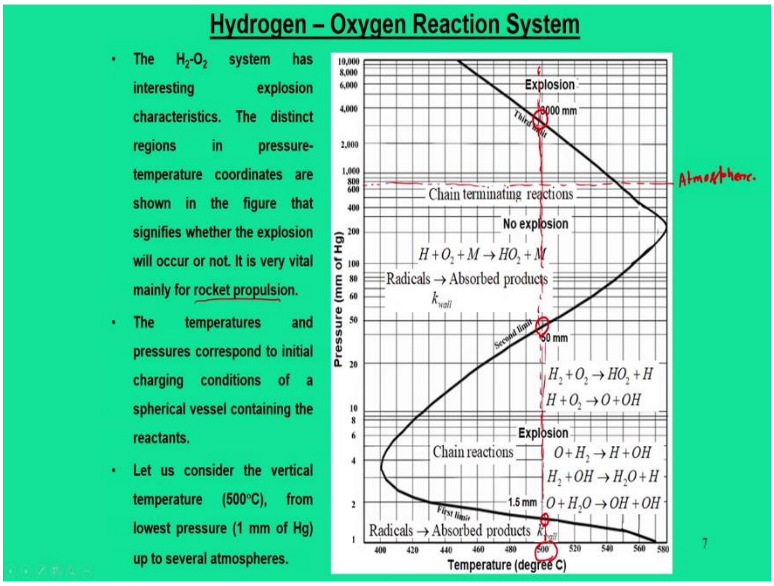

Hydrogen – Oxygen Reaction System

- The H_2-O_2 system has interesting explosion characteristics. The distinct regions in pressure-temperature coordinates are shown in the figure that signifies whether the explosion will occur or not. It is very vital mainly for rocket propulsion.
- The temperatures and pressures correspond to initial charging conditions of a spherical vessel containing the reactants.
- Let us consider the vertical temperature (500°C), from lowest pressure (1 mm of Hg) up to several atmospheres.

Now, let us see what is the effect of pressure and temperature. And, this particular figure talks about the pressure and temperature plot in a H_2O_2 systems. I mentioned earlier that in some environment of pressure and temperature conditions H_2 and O_2 can stay together and in other situation they can behave in an explosive manner. So, we will categorize in two philosophy; one is no explosion, other is the explosions.

And, we will try to see under what conditions we will have explosion, under what conditions will have no explosion. Now, if there are explosion which reactions are predominant, if there is no explosion why there is no explosion. So, such things need to be answered in this plot. So, what has been plotted? In y axis, we have pressure in mm of Hg.

And, the pressure can starts from 1 mm of Hg means which is almost a vacuum conditions and you can go up to 10000 mm of Hg. And, somewhere you have 750 mm of Hg, we can draw this line. So, which is normally called as atmospheric. So, if you draw this is your atmospheric line. Now, in this atmospheric line, we can say this we are mostly in the no explosion zone.

And, let us see what is effect of temperature. Now, when we look at temperatures, typically the behavior of H_2O_2 system comes when the temperatures range is between 400 to close to 580 C. And, at 1 mm of Hg, we can store the hydrogen and oxygen systems at 580 degree centigrade.

Now, let us see how you look at this graph or how you interpret this graph so that we can understand the chain reactions and the chain terminating reactions. Why this chain reaction happens, how it initiates, how it propagates and finally, how it terminates. So, normally when it terminates, it forms which HO_2 or H_2O_2 and when it have chain reactions, it tries to form OH or O, all these things.

And, why this system is important? Because, it is mainly required for rocket propulsion systems. What we are looking at the temperature and pressure corresponding to initial charging conditions of in a spherical vessel which contains reactants. Like in a spherical vessel, we are putting hydrogen and oxygen and try to see the thermodynamic behavior in terms of pressure temperature plot.

Now, imagine a particular case like we are looking at 500 C; and and I am just drawing a vertical line. What it means is that if I go along this line we can have different pressures.

And, and we can see a curve which typically a sinusoidal curve and if you draw a vertical line at 500, it cuts this pressure axis or I mean cuts this curve at different pressure values. So, let us start the first line; that means, we are looking at a vertical temperature at 500 C with lowest pressure of 1 mm and we are going up.

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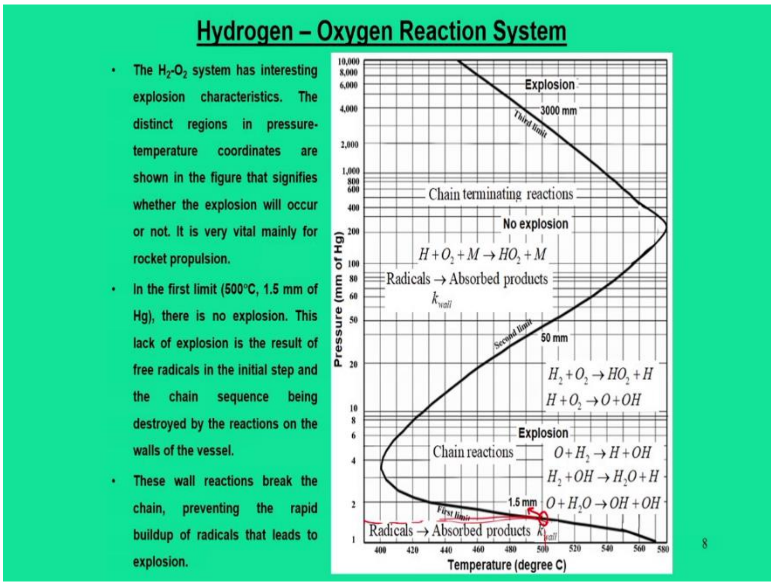

Hydrogen – Oxygen Reaction System

- The H_2-O_2 system has interesting explosion characteristics. The distinct regions in pressure-temperature coordinates are shown in the figure that signifies whether the explosion will occur or not. It is very vital mainly for rocket propulsion.
- In the first limit (500°C, 1.5 mm of Hg), there is no explosion. This lack of explosion is the result of free radicals in the initial step and the chain sequence being destroyed by the reactions on the walls of the vessel.
- These wall reactions break the chain, preventing the rapid buildup of radicals that leads to explosion.

So, what we see? So, it meets the first curve close to somewhere 1.5 mm of Hg; Now, in this zone if you look at the hydrogen and oxygen systems, we see there is no explosion.

So, what it means, why there is no explosion? Because, in the initial step, the radicals are about to form, but they have not started the chain sequence. And, if at all they are formed and these reactions when they keep on propagating and finally, they get destroyed in the walls of the vessels. So, what it means that when these radicals whatever form, they are absorbed as products in the vessel wall or geometrical vessel wall.

So, why is a spherical? Because, it all depends on the geometry, how you are storing. So, these wall reactions break the chain; that means, when the reactants goes and hits this wall, they normally break the chain. I mean they are basically the culprits of the breaking the chain. So that means, the reaction is not further in initiated and also the reaction do not get a good environment to proceed further. So, that is the reason there is no explosion till this point.

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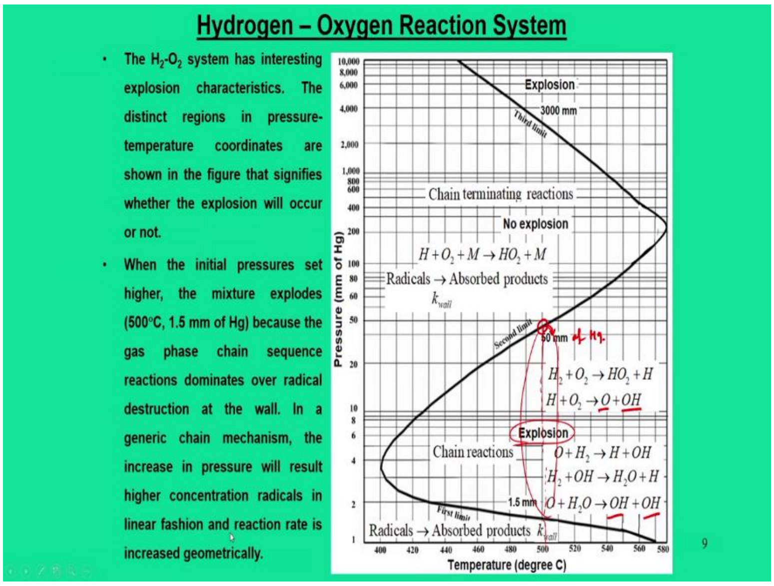

Hydrogen – Oxygen Reaction System

- The H_2-O_2 system has interesting explosion characteristics. The distinct regions in pressure-temperature coordinates are shown in the figure that signifies whether the explosion will occur or not.
- When the initial pressures set higher, the mixture explodes (500°C, 1.5 mm of Hg) because the gas phase chain sequence reactions dominates over radical destruction at the wall. In a generic chain mechanism, the increase in pressure will result higher concentration radicals in linear fashion and reaction rate is increased geometrically.

Now, moving further in same line, if you go vertically, you will find the second limit of the curve and this refers to as 50 mm of Hg. And, during this particular phase we can see that there is a big explosion. And, why there is a big explosion? You can see that is mainly because the formation of O atom, OH atom and this chain keeps on propagating. And, when they keeps on propagating, the walls of the spherical vessel is not sufficient to withstand or stop their propagation.

And, these reactions dominate over the wall reactions and mean; that means, wall cannot absorb further. So, because the wall cannot absorb further it try to explodes. So, it means that when your storage medium is at 500 C, any point above from 1.5 mm to 50 mm of Hg there will be an explosion; that means, we cannot store H_2 O_2 simultaneously in a spherical vessel.

And, here in a generic chain mechanism, the increase in the pressure will result in higher concentration radicals in a linear fashion and the reaction rate is increased geometrically.

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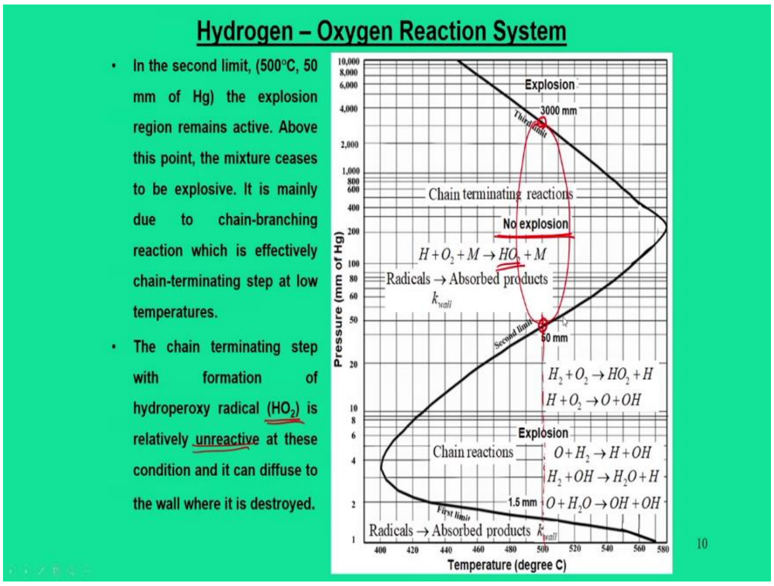

Hydrogen – Oxygen Reaction System

- In the second limit, (500°C, 50 mm of Hg) the explosion region remains active. Above this point, the mixture ceases to be explosive. It is mainly due to chain-branching reaction which is effectively chain-terminating step at low temperatures.
- The chain terminating step with formation of hydroperoxy radical (HO_2) is relatively unreactive at these condition and it can diffuse to the wall where it is destroyed.

Now, moving further in same 500 degree line, if you go vertically till above 50 mm of Hg up to close to 3000 mm of Hg. So, during this point you can see there is no explosion. So, what it means? So, during this phase, during this region we can store them without any explosion because, during this phase the chain mechanisms try to terminate.

Why it try to terminate? Because, it gets suitable pressure and temperature regime for which the formation of HO_2 or H_2O_2 becomes possible. And, when they form, they are typically relatively unreactive. And, we say that the chain reactions are almost terminated and the further branching is not possible and because of this reason there is no explosion.

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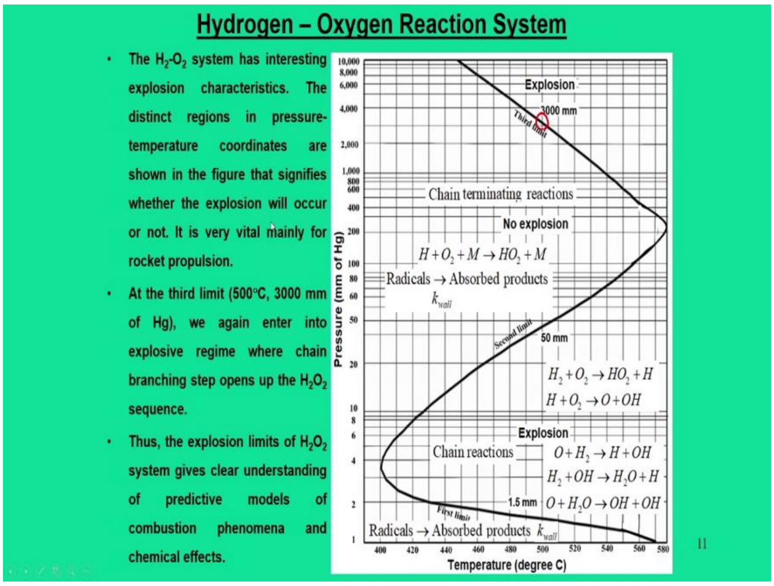

Hydrogen – Oxygen Reaction System

- The H_2-O_2 system has interesting explosion characteristics. The distinct regions in pressure-temperature coordinates are shown in the figure that signifies whether the explosion will occur or not. It is very vital mainly for rocket propulsion.
- At the third limit (500°C, 3000 mm of Hg), we again enter into explosive regime where chain branching step opens up the H_2O_2 sequence.
- Thus, the explosion limits of H_2O_2 system gives clear understanding of predictive models of combustion phenomena and chemical effects.

And, this will go on till we reach the 3000 mm of Hg. So, we say there are three limit and all are on 500 C line. One limit is 1.5 mm of Hg, second limit is the 50 mm of Hg, third limit is 3000 mm of Hg. But, again beyond 3000 of mm of Hg, in the same temperature line, if you go there will be further explosion.

So, what we can say that when the formation of HO_2 or H_2O_2 is predominant, then the radicals effect is no longer severe and the reaction tried to settle down and there is no explosions. So, this is the complete philosophy of hydrogen oxygen reaction systems. And in fact, the models needs to be developed to study the combustion phenomena. And, experimentally it is very vital that you should know that what pressure and temperature we should store H_2 and O_2; so, that it will not explode.

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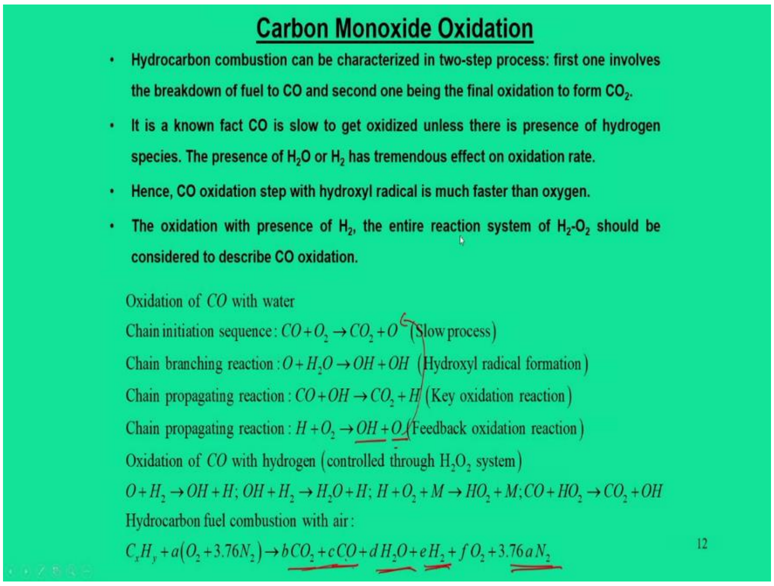

Carbon Monoxide Oxidation

- Hydrocarbon combustion can be characterized in two-step process: first one involves the breakdown of fuel to CO and second one being the final oxidation to form CO_2.
- It is a known fact CO is slow to get oxidized unless there is presence of hydrogen species. The presence of H_2O or H_2 has tremendous effect on oxidation rate.
- Hence, CO oxidation step with hydroxyl radical is much faster than oxygen.
- The oxidation with presence of H_2, the entire reaction system of H_2-O_2 should be considered to describe CO oxidation.

Oxidation of CO with water

Chain initiation sequence: $CO+O_2 \rightarrow CO_2+O$ (Slow process)

Chain branching reaction : $O+H_2O \rightarrow OH+OH$ (Hydroxyl radical formation)

Chain propagating reaction : $CO+OH \rightarrow CO_2+H$ (Key oxidation reaction)

Chain propagating reaction : $H+O_2 \rightarrow \underline{OH}+\underline{O}$ (Feedback oxidation reaction)

Oxidation of CO with hydrogen (controlled through H_2O_2 system)

$O+H_2 \rightarrow OH+H;\ OH+H_2 \rightarrow H_2O+H;\ H+O_2+M \rightarrow HO_2+M; CO+HO_2 \rightarrow CO_2+OH$

Hydrocarbon fuel combustion with air:

$C_xH_y+a(O_2+3.76N_2) \rightarrow \underline{bCO_2+cCO}+d\underline{H_2O}+e\underline{H_2}+fO_2+3.\underline{76aN_2}$

The next reaction mechanism is carbon monoxide oxidations. Carbon monoxide normally forms when we do not have the stoichiometric hydrocarbon fuel oxidation with air. You can see that when there is in a non-stoichiometric case, we will have CO_2 and CO formation simultaneously. And, if at all this has to be and again we have hydrogen also and nitrogen also.

Now, also we have water. So, if you look at closely hydro carbon monoxide emissions, when you see $CO + O_2 \rightarrow CO_2 + O$, but it is a very slow process, but it gives an oxygen atom.

And, we can say it is a radical, but this radical will create a hydroxyl radical. And, and that is where the chain branching starts and when it forms$CO + OH \rightarrow CO_2 + H$. So, it is a key oxidation reaction because that is the oxidation process. So, what we see is that directly with CO_2 this is a slow process.

But, through a route of hydroxyl radicals, it is a fast process. And, again during this chain propagation reactions, there is also another a feedback oxidation reactions where $H + O_2 \rightarrow OH + O$. OH and O_2 will initiate this hydroxyl reactions, O will initiate this chain initiation reactions. So, this process keeps on happening. So, the combined effect is that the how you are going to do the oxidation of carbon monoxide. Either to do that, we must do through the HO_2 or H_2 root, because they have tremendous effect in enhancing the oxidation rate.

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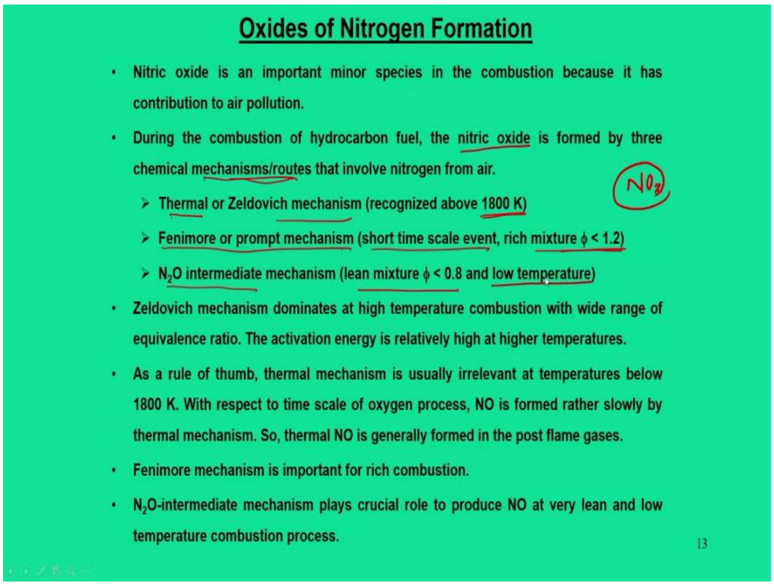

Oxides of Nitrogen Formation

- Nitric oxide is an important minor species in the combustion because it has contribution to air pollution.
- During the combustion of hydrocarbon fuel, the nitric oxide is formed by three chemical mechanisms/routes that involve nitrogen from air.

NO_2

  - Thermal or Zeldovich mechanism (recognized above 1800 K)
  - Fenimore or prompt mechanism (short time scale event, rich mixture $\phi < 1.2$)
  - N_2O intermediate mechanism (lean mixture $\phi < 0.8$ and low temperature)
- Zeldovich mechanism dominates at high temperature combustion with wide range of equivalence ratio. The activation energy is relatively high at higher temperatures.
- As a rule of thumb, thermal mechanism is usually irrelevant at temperatures below 1800 K. With respect to time scale of oxygen process, NO is formed rather slowly by thermal mechanism. So, thermal NO is generally formed in the post flame gases.
- Fenimore mechanism is important for rich combustion.
- N_2O-intermediate mechanism plays crucial role to produce NO at very lean and low temperature combustion process.

The next important mechanism is oxides of nitrogen formation. Typically, we call this as NOx. Now, this NOx formation is also equally important in a combustion process both in rich combustion and lean combustion. And, why it is more important? Because, this NO formation has a important contribution to air pollution and mostly we should avoid this NO formation. So, if you look at the combustion process of hydrocarbon fuels, the nitric oxides or NO_2 is formed by three chemical important mechanisms or routes.

So, we can say the NO, the NOx formation comes by three important mechanisms. First one is a thermal mechanism or in a scientific way we call this as a Zeldovich mechanisms. And, this thermal mechanism we will recognize only when you have temperature is above 1800 K. It means that during a reaction process when the temperature is above 1800 K, thermal or Zeldovich mechanisms dominates.

But, this thumb rule is also not true because we have seen in their previous slides that when we have propane air mixture combustion, NO is formed throughout all the equivalence ratio. Then, even NO is also seen in the lower equivalence ratio, but still the temperature is not too high. So, for that Zeldovich mechanism or thermal mechanism is answer less.

For that reason, another mechanism that comes in what we call as Fenimore or prompt mechanisms. And, this prompt mechanism arises and it is a short time scale event and it is answerable for rich mixtures for which equivalence ratio less than 1.2. But, still this is also not possible because most of the combustion process when you do the equivalence ratio is maintained between 0.8 to 1.2.

So, both Fenimore or prompt mechanism and Zeldovich mechanisms, they are sufficient to answer both the cases. But, there are some situation at low temperatures, if at all and during lean mixtures, less than 0.5, if there are NO formations; we call them as a N_2O intermediate mechanisms. So, this is the three ways that NO can form over wide range of equivalence ratio with respect to temperatures, a low temperature, medium temperature and high temperature during a reaction process.

So, as a rule of thumb, we consider the thermal or Zeldovich mechanism only when the temperature is very high. When the NO formation happens in a short duration time scale, answer will come from the Fenimore or prompt mechanisms and of course, it is for rich combustion. And, when you talk about lean mixture and low temperatures, N_2O mechanism is plays a crucial role.

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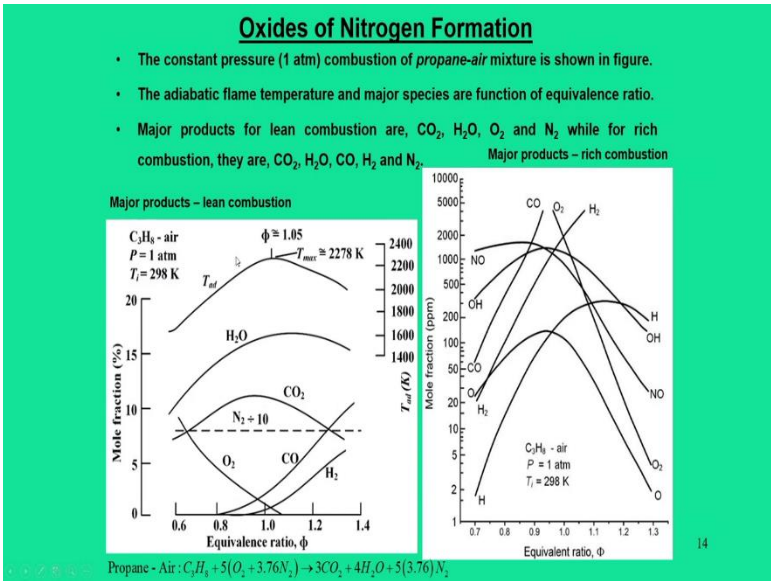

Oxides of Nitrogen Formation

- The constant pressure (1 atm) combustion of *propane-air* mixture is shown in figure.
- The adiabatic flame temperature and major species are function of equivalence ratio.
- Major products for lean combustion are, CO_2, H_2O, O_2 and N_2 while for rich combustion, they are, CO_2, H_2O, CO, H_2 and N_2.

Major products – lean combustion

Major products – rich combustion

Propane - Air : $C_3H_8 + 5(O_2 + 3.76N_2) \rightarrow 3CO_2 + 4H_2O + 5(3.76)N_2$

So, I revisit this slide again as you can see over wide range of equivalence ratio. We can see the formation of NO is throughout the all the equivalence ratio. Even your adiabatic temperature is almost more than close to 2278 K. At that point it is quite obvious, that we will have thermal or Zeldovich mechanism.

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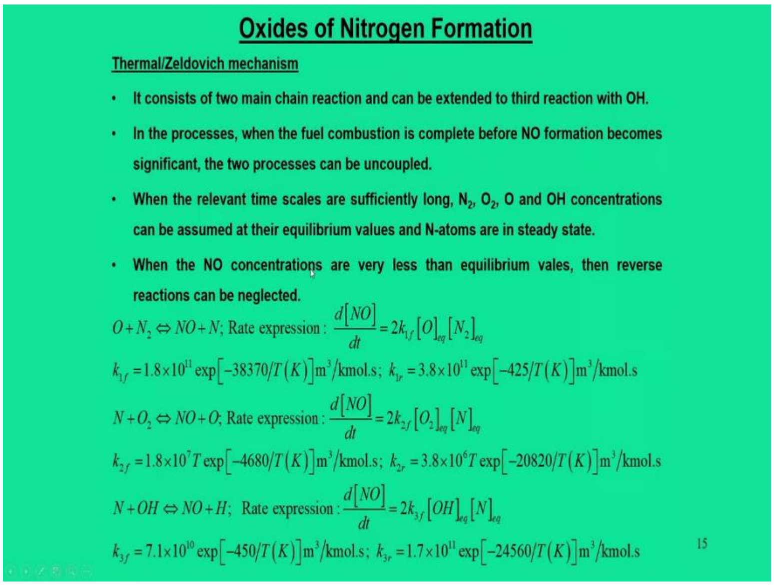

Oxides of Nitrogen Formation

Thermal/Zeldovich mechanism

- **It consists of two main chain reaction and can be extended to third reaction with OH.**
- **In the processes, when the fuel combustion is complete before NO formation becomes significant, the two processes can be uncoupled.**
- **When the relevant time scales are sufficiently long, N_2, O_2, O and OH concentrations can be assumed at their equilibrium values and N-atoms are in steady state.**
- **When the NO concentrations are very less than equilibrium vales, then reverse reactions can be neglected.**

$O+N_2 \Leftrightarrow NO+N$; Rate expression : $\frac{d[NO]}{dt}=2k_{1f}[O]_{eq}[N_2]_{eq}$

$k_{1f}=1.8\times10^{11}\exp[-38370/T(K)]\,\mathrm{m^3/kmol.s}$; $k_{1r}=3.8\times10^{11}\exp[-425/T(K)]\,\mathrm{m^3/kmol.s}$

$N+O_2 \Leftrightarrow NO+O$; Rate expression : $\frac{d[NO]}{dt}=2k_{2f}[O_2]_{eq}[N]_{eq}$

$k_{2f}=1.8\times10^{7}T\exp[-4680/T(K)]\,\mathrm{m^3/kmol.s}$; $k_{2r}=3.8\times10^{6}T\exp[-20820/T(K)]\,\mathrm{m^3/kmol.s}$

$N+OH \Leftrightarrow NO+H$; Rate expression : $\frac{d[NO]}{dt}=2k_{3f}[OH]_{eq}[N]_{eq}$

$k_{3f}=7.1\times10^{10}\exp[-450/T(K)]\,\mathrm{m^3/kmol.s}$; $k_{3r}=1.7\times10^{11}\exp[-24560/T(K)]\,\mathrm{m^3/kmol.s}$

Now, let us understand the first one that when this thermal or Zeldovich mechanism happens, what are the elementary reactions. First thing is that $O + N_2 \Leftrightarrow NO + N$. Again, $N + O_2 \Leftrightarrow NO + O$.

And, if we have radicals in the systems, $N + OH \Leftrightarrow NO + H$. So, NO formation can happen in three ways and the rate at which they form, it all depends with respect to the rate coefficients. So, these are some sample expressions, that talks about how NO formation is comes into picture through these three different routes.

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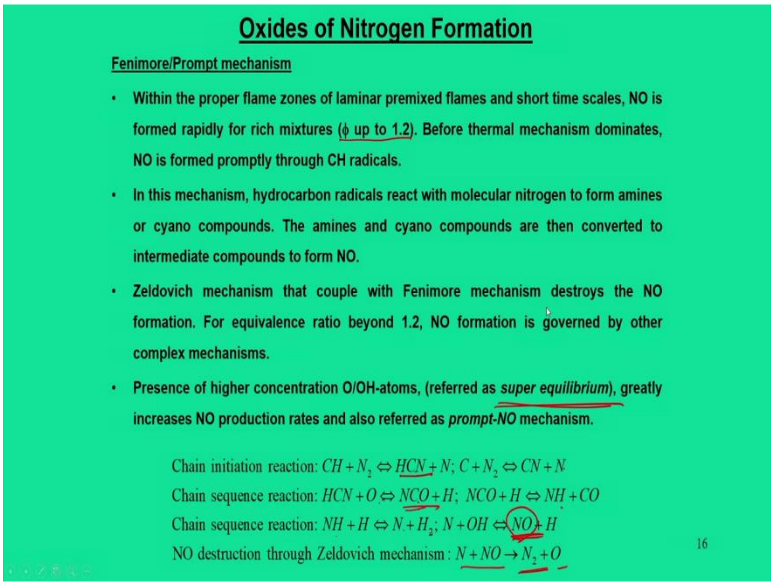

Oxides of Nitrogen Formation

Fenimore/Prompt mechanism

- **Within the proper flame zones of laminar premixed flames and short time scales, NO is formed rapidly for rich mixtures (ϕ up to 1.2). Before thermal mechanism dominates, NO is formed promptly through CH radicals.**
- **In this mechanism, hydrocarbon radicals react with molecular nitrogen to form amines or cyano compounds. The amines and cyano compounds are then converted to intermediate compounds to form NO.**
- **Zeldovich mechanism that couple with Fenimore mechanism destroys the NO formation. For equivalence ratio beyond 1.2, NO formation is governed by other complex mechanisms.**
- **Presence of higher concentration O/OH-atoms, (referred as *super equilibrium*), greatly increases NO production rates and also referred as *prompt-NO* mechanism.**

Chain initiation reaction: $CH+N_2 \Leftrightarrow \underline{HCN+}N$; $C+N_2 \Leftrightarrow CN+N$

Chain sequence reaction: $HCN+O \Leftrightarrow \underline{NCO+}H$; $NCO+H \Leftrightarrow NH+CO$

Chain sequence reaction: $NH+H \Leftrightarrow N+H_2$; $N+OH \Leftrightarrow \underline{NO+}H$

NO destruction through Zeldovich mechanism : $\underline{N+NO} \rightarrow \underline{N_2}+\underline{O}$

Then, next mechanism is Fenimore or prompt mechanism. So, here you have to see that this formation is mainly the equivalence ratio up to 1.2. And, when I say equivalence ratio 1.2 and if you try to map this for a combustion process, you can correlate that they are in the zone of laminar premixed flames. And, during this process, there is a formation of hydrogen cyanide, NCO. And, these two we call them as a chain initiation, chain sequence reactions and these reactions finally, gives rise to NO formations.

So, it starts with $CH + N_2 \Leftrightarrow HCN + N$, and $HCN + O \Leftrightarrow NCO + H$, $NCO + H \Leftrightarrow NH + CO$ and $NH + H \Leftrightarrow N + H_2$ and finally $N + OH \Leftrightarrow NO + H$. So, this NO formation is there and through a sequence process of chain initiation and chain sequence process.

And, because of these reasons, we say that all these things happens in a very short duration events may be in a milliseconds or less time scale. So, it is called as a prompt mechanisms. Another important consequence is that when we have higher equivalence ratio and side by side temperature is also high, then we can say Zeldovich mechanism can couple with Fenimore mechanism.

When both the mechanisms happen, this $N + NO \rightarrow N_2 + O$. Means in fact, on a Fenimore mechanism, if there is a Zeldovich mechanism which dominates, it tries to destroy the NO formations. I also mentioned that why it is called as a prompt NO mechanisms. Many a times, the presence of O and H_2 atom, we call this as a super equilibrium conditions. So, because of this reasons the formation of NO is accelerated.

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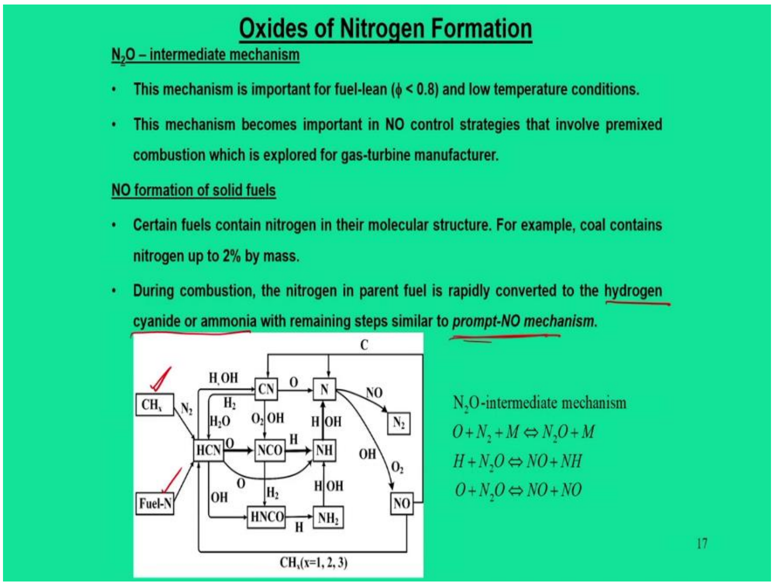

Oxides of Nitrogen Formation

N_2O – intermediate mechanism

- This mechanism is important for fuel-lean ($\phi < 0.8$) and low temperature conditions.
- This mechanism becomes important in NO control strategies that involve premixed combustion which is explored for gas-turbine manufacturer.

NO formation of solid fuels

- Certain fuels contain nitrogen in their molecular structure. For example, coal contains nitrogen up to 2% by mass.
- During combustion, the nitrogen in parent fuel is rapidly converted to the hydrogen cyanide or ammonia with remaining steps similar to *prompt-NO mechanism.*

N_2O-intermediate mechanism

$$O + N_2 + M \Leftrightarrow N_2O + M$$
$$H + N_2O \Leftrightarrow NO + NH$$
$$O + N_2O \Leftrightarrow NO + NO$$

Now, moving further in the third category, we have N_2O intermediate mechanisms. And, in this intermediate mechanisms where $O + N_2 + M \Leftrightarrow N_2O + M, H + N_2O \Leftrightarrow NO + NH, O + N_2O \Leftrightarrow NO + NO$. So, and this typical situation happens, we call this as a fuel lean condition at low temperature conditions.

And, there are some situations, when NO formation is initiated through a solid fuel. Because, if you look at a typical solid fuel like a coal, they have nitrogen in their molecular structures. And, when you have nitrogen in their molecular structures and typically, they are 2 percent by mass. And, if they get a very friendly environment, they form rapidly through this hydrogen cyanide or ammonia route to form NO and this will fall under the prompt NO mechanisms.

So, if you look at the complete NO formation analysis, if you have a hydrocarbon and fuel and from any route if you come, this is a complete process that talks about all the three mechanisms, either the NO formation can happen with H or OH radicals or through HCN or through HNCO, NCO. So, this picture gives the complete picture of NO formations at different temperature and pressure conditions.

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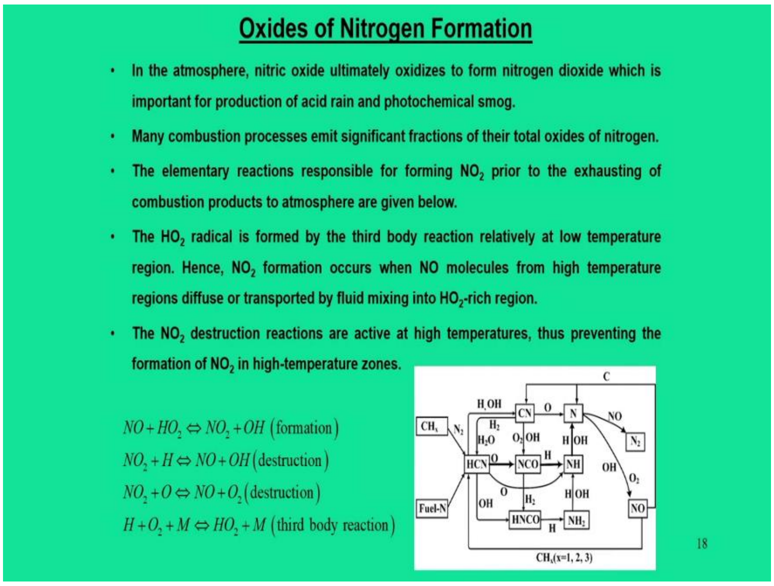

Oxides of Nitrogen Formation

- In the atmosphere, nitric oxide ultimately oxidizes to form nitrogen dioxide which is important for production of acid rain and photochemical smog.
- Many combustion processes emit significant fractions of their total oxides of nitrogen.
- The elementary reactions responsible for forming NO_2 prior to the exhausting of combustion products to atmosphere are given below.
- The HO_2 radical is formed by the third body reaction relatively at low temperature region. Hence, NO_2 formation occurs when NO molecules from high temperature regions diffuse or transported by fluid mixing into HO_2-rich region.
- The NO_2 destruction reactions are active at high temperatures, thus preventing the formation of NO_2 in high-temperature zones.

$NO + HO_2 \Leftrightarrow NO_2 + OH$ (formation)

$NO_2 + H \Leftrightarrow NO + OH$ (destruction)

$NO_2 + O \Leftrightarrow NO + O_2$ (destruction)

$H + O_2 + M \Leftrightarrow HO_2 + M$ (third body reaction)

And, to give another kind of emphasis that how this NO formations affects in an atmospheric situations, we can say that in the atmosphere, nitric oxide ultimately oxidizes to form nitrogen dioxide and which is more important to production of acid rain and petrochemical smoke. So, you can say $NO + HO_2 \Leftrightarrow NO_2 + OH$, this is the NO_2 formation process.

And, NO is also gets destroyed through reaction with hydrogen and then this NO_2 also gets destroyed through oxygen and this combination process happens in the atmosphere itself. Many a times when this formation of NO_2 becomes significant, it leads to acid rain or petrochemical smog which is not a desirable with respect to atmospheric view point.

And, we can say these formations are happens mainly due to the radicals like HO_2, NO_2. And of course, the atmosphere has different a temperature zones, low temperature to high temperatures that effect is also very significant, at what altitude where this NO_2 formations happens.

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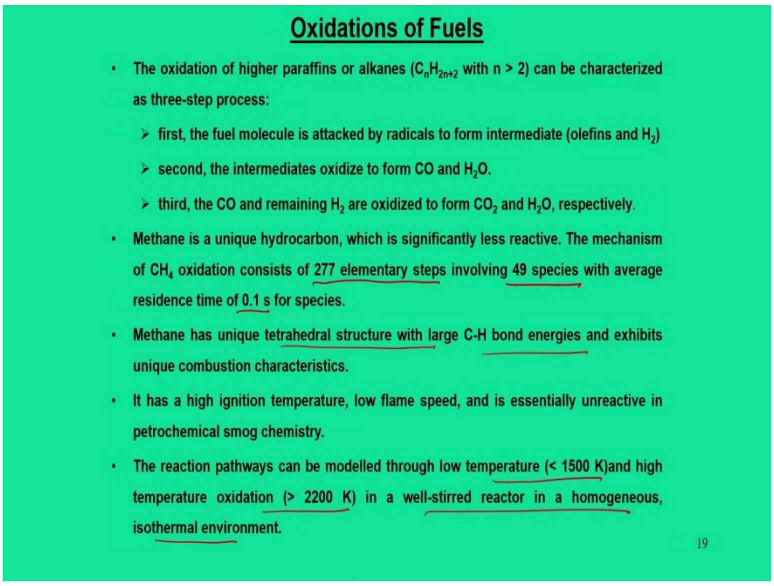

Oxidations of Fuels

- The oxidation of higher paraffins or alkanes (C_nH_{2n+2} with n > 2) can be characterized as three-step process:
  - first, the fuel molecule is attacked by radicals to form intermediate (olefins and H_2)
  - second, the intermediates oxidize to form CO and H_2O.
  - third, the CO and remaining H_2 are oxidized to form CO_2 and H_2O, respectively.
- Methane is a unique hydrocarbon, which is significantly less reactive. The mechanism of CH_4 oxidation consists of 277 elementary steps involving 49 species with average residence time of 0.1 s for species.
- Methane has unique tetrahedral structure with large C-H bond energies and exhibits unique combustion characteristics.
- It has a high ignition temperature, low flame speed, and is essentially unreactive in petrochemical smog chemistry.
- The reaction pathways can be modelled through low temperature (< 1500 K)and high temperature oxidation (> 2200 K) in a well-stirred reactor in a homogeneous, isothermal environment.

And, in the last I will just try to explain the concept of oxidation of fuel. In fact, we have also seen many combustion reaction mechanism processes. But, here the oxidation of fuels comes on a very complicated process, a complete understanding is required. But, I will just give some introduction that when you say oxidation of fuels, we are essentially looking at the hydrocarbons. And, may be for higher paraffins and alkanes for which you we can say chemical formula C_nH_{2n+2}, they are characterized in three step process.

In the first step, fuel molecule is attacked by radicals to form an intermediate which is in the olefins or hydrogen. Second one is the intermediate process that oxidizes to form CO and H_2O and third one, the CO and remaining H_2 they are oxidized to form CO_2 and H_2O. So, this is the three oxidation process and in fact, we are not going to details. But, a simple hydrocarbon is nothing, but a methane and it is a unique hydrocarbon and its a less reactive.

But, even though its less reactive, it consists of 277 elementary reactions with 49 species and 0.1 second residence time of each species; that means it forms and there gets destroyed. So, the residence time is of each species is close to you can say about 0.1 seconds. And, since methane has also tetrahedral CH bond energy which gives a very unique combustion characteristics.

It has a very high ignition temperature, low flame speed and it is not reactive in terms of petrochemical smoke chemistry; that means, methane if you are using its a good fuel with respect to atmospheric view point. The reaction pathways for this methane can be modelled in two temperature range, one is mainly less than 1500 K. Other is the high temperature oxidation which is higher than the more than 2200 K in a well stirred reactor with homogeneous, isothermal environment.

So, for more details we can refer the books. We are not going to details, more details on this reaction mechanisms. But, in summary what we can say that the mechanism of oxidation of fuels is a very complicated process involving many number of reactions. And, it has to be modelled in a accurate manner and reaction kinetics has to be included simultaneously and such reaction mechanisms, we call this as a chemical reactor which will come in the subsequent modules.

So, with this, this is the complete description about this model and module that is chemical kinetics. So, before we close, let us understand one of the basic problem which we have covered in our earlier lecture with a concept of EGR. So, EGR why we have introduced here? Because, it has a definite link with nitric oxide oxidations.

Normally, exhaust gas is recirculated in an IC engine to control the NOx formations. So, through this problem, we will try to see how much EGR is advisable to be circulated into the engine for an efficient combustion process.

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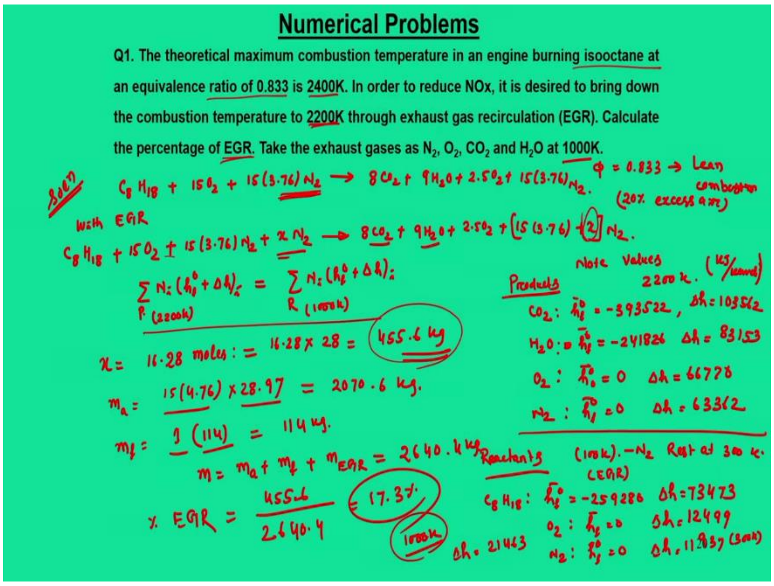

Numerical Problems

Q1. The theoretical maximum combustion temperature in an engine burning isooctane at an equivalence ratio of 0.833 is 2400K. In order to reduce NOx, it is desired to bring down the combustion temperature to 2200K through exhaust gas recirculation (EGR). Calculate the percentage of EGR. Take the exhaust gases as N_2, O_2, CO_2 and H_2O at 1000K.

Sol^n

$C_8H_{18} + 15O_2 + 15(3.76)N_2 \rightarrow 8CO_2 + 9H_2O + 2.5O_2 + 15(3.76)N_2$.

$\phi = 0.833 \rightarrow$ Lean combustion (20% excess air)

With EGR

$C_8H_{18} + 15O_2 + 15(3.76)N_2 + x N_2 \rightarrow 8CO_2 + 9H_2O + 2.5O_2 + [15(3.76) + \boxed{x}]N_2$.

$$\sum_{P\,(2200K)} N_i(h_f^0 + \Delta h)_i = \sum_{R\,(1000K)} N_i(h_f^0 + \Delta h)_i$$

$x = 16.28$ moles $:= 16.28 \times 28 = 455.6$ kg

$m_a = 15(4.76) \times 28.97 = 2070.6$ kg.

$m_f = 1\,(114) = 114$ kg.

$m = m_a + m_f + m_{EGR} = 2640.4$ kg

$\%\ EGR = \frac{455.6}{2640.4} = 17.3\%$

Note Values 2200 K. (kJ/kmol)

Products

CO_2: $\bar{h}_f^0 = -393522$, $\Delta h = 103562$

H_2O: $\bar{h}_f^0 = -241826$ $\Delta h = 83153$

O_2: $\bar{h}_f^0 = 0$ $\Delta h = 66778$

N_2: $\bar{h}_f^0 = 0$ $\Delta h = 63362$

Reactants (1000K). $-N_2$ (EGR) Rest at 300 K.

C_8H_{18}: $\bar{h}_f^0 = -259280$ $\Delta h = 73473$

O_2: $\bar{h}_f = 0$ $\Delta h = 12499$

N_2: $\bar{h}_f^0 = 0$ $\Delta h = 11937$ (300K)

1000K $\Delta h = 21463$

So, let us understand the problem first. Theoretical maximum combustion temperature in an engine while burning an isooctane with an equivalence ratio of 0.833 is 2400 K. At this temperature, this NOx problem formation is quite important. So, it is reduced to lower this temperature to 2200 K. What it we do is instead of sending the exhaust gas directly to the atmosphere, we recirculate into the engine. So, we call this as a exhaust gas recirculation into the engines.

Now, question is how you have to find out the percentage of EGR, how much percentage we should advise? And of course, there is some temperature you need to look at, all the data has to be referred at these temperatures. So, exhaust gases are expected temperature is 1000 K and we also need to find out the enthalpy of formation for the products at these temperatures. So, to solve this problem, first thing what we should attempt is that what happens for an isooctane condition for an equivalence ratio 0.833.

So, 0.833 means it is a lean combustion and if you can closely find the value, it is 20 percent excess air. Now, if you do that then reaction could be $C_8H_{18} + 15O_2 + 15(3.76)N_2 \rightarrow 8CO_2 + 9H_2O + 2.5O_2 + 15(3.76)N_2$. Now, we have to write another equation by incorporating EGR. So, we do not know how much exhaust gas is going to be recirculated. So, basically it has only effect with respect to NO.

So, we have to revise this equation with EGR. So, we can rewrite this equation as $C_8H_{18} + 15O_2 + 15(3.76)N_2 + xN_2 \rightarrow 8CO_2 + 9H_2O + 2.5O_2 + [15(3.76)+x]N_2$. So, this reaction needs to be handled properly.

So, we have to recall this equation, enthalpy of reactants and products that has to be matched. $\sum_{P\ (2200\ K)} n_i\left(\bar{h}_f^o + \Delta\bar{h}\right)_i = \sum_{R\ (1000\ K)} n_i\left(\bar{h}_f^o + \Delta\bar{h}\right)_i$

So, for each case we need to find out and we have to note the values one at 2200 kelvin. So, this enthalpy of formation of product side:

$$CO_2 : \ \bar{h}_f^o = -393522, \Delta\bar{h} = 103562$$

$$H_2O : \ \bar{h}_f^o = -241826, \Delta\bar{h} = 83153$$

$$O_2 : \ \bar{h}_f^o = 0, \Delta\bar{h} = 66770$$

$$N_2 : \ \bar{h}_f^o = 0, \Delta\bar{h} = 63362$$

So, this is for products and for reactants we have to note down this value at 1000 K for N_2 and rest at 300K.

$$C_8O_{18} : \bar{h}_f^o = -259280, \Delta\bar{h} = 73473$$

$$O_2 : \bar{h}_f^o = 0, \Delta\bar{h} = 12499$$

$$N_2 : \bar{h}_f^o = 0, \Delta\bar{h} = 112837\ (300K);\ \Delta\bar{h} = 21463\ (1000K)$$

So, this 1000 kelvin we will refer to component x. So, based on this formulation by inserting this value, we will have a big expressions. But, by inserting the value the we can solve this equations for x as unknown and that x is 16.28 moles. And, this when converted to mass so, 16.28 into molecular weight of N_2 28 gives 455.6 kg. So, means this much kg of EGR has to be circulated to bring down to this temperature.

So, correspondingly we can find out what is the mass of air which is $15 \times 4.76 \times 28.97$, this many moles and molecular weight will give 2070.6 kg and mass of fuel, not mass flow rate. So, it is a mass flow, we can say 1 molecular weight of fuel 1×114 (mole into molecular weight) so, it is 114 kg. So, ultimately we can find out what is the total mass; $m = m_a + m_f + m_{EGR} = 2640.4\ kg$.

And, we can say percentage EGR so, this number would be $\frac{455.6}{2640.4} = 17\%$. So, basically speaking normally when exhaust gas is recirculated in the engines, its typical number is limited within the 20 percentage of EGR. Then, only we can get the better or effective utilization of energy in the engines from the fuels. So, with this I conclude this lecture for today.

Thank you, for your attention and also we completed this module, that is chemical kinetics. Once again, thank you for your attention.