

Combustion in Air Breathing Aero Engines
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Lecture - 05
Chemical Kinetics – II

Hello friends, welcome back.

(Refer Slide Time: 00:17)

Multiple Reactions

Practical reactions involving
Reactants → Products
 e.g.: $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$
rarely (never!) occur in one step between reactants
 (e.g.: two H_2 and one O_2)

Reality:
 For $\text{H}_2\text{-O}_2$: (at least)
 \uparrow 19 reversible reactions and
 \downarrow 8 species ($\text{H}_2, \text{O}_2, \text{H}, \text{O}, \text{OH}, \text{H}_2\text{O}, \text{HO}_2, \text{H}_2\text{O}_2$)

No.	Reaction	k_f (m, mol, s)	α	E_a (cal/mol)
H₂-O₂ Chain Reactions				
(1)	$\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$	1.9×10^{14}	0	16.44
(2)	$\text{O} + \text{H}_2 \rightleftharpoons \text{H} + \text{OH}$	5.1×10^{16}	2.67	6.29
(3)	$\text{OH} + \text{H}_2 \rightleftharpoons \text{H} + \text{H}_2\text{O}$	2.1×10^{16}	1.51	3.43
(4)	$\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{OH} + \text{OH}$	3.0×10^{16}	2.02	13.40
H₂-O₂ Dissociation/Recombination				
(5)	$\text{H}_2 + \text{M} \rightleftharpoons \text{H} + \text{H} + \text{M}$	4.6×10^{17}	-1.40	104.38
(6)	$\text{O} + \text{O} + \text{M} \rightleftharpoons \text{O}_2 + \text{M}$	6.2×10^{17}	-6.50	0
(7)	$\text{O} + \text{H} + \text{M} \rightleftharpoons \text{OH} + \text{M}$	4.7×10^{16}	-1.0	0
(8)	$\text{H} + \text{OH} + \text{M} \rightleftharpoons \text{H}_2\text{O} + \text{M}$	2.2×10^{17}	-2.0	0
Formation and Consumption of HO₂				
(9)	$\text{H} + \text{O}_2 + \text{M} \rightleftharpoons \text{HO}_2 + \text{M}$	6.2×10^{16}	-1.42	0
(10)	$\text{HO}_2 + \text{H} \rightleftharpoons \text{H}_2 + \text{O}_2$	6.6×10^{17}	0	2.13
(11)	$\text{HO}_2 + \text{H} \rightleftharpoons \text{OH} + \text{OH}$	1.7×10^{16}	0	6.67
(12)	$\text{HO}_2 + \text{O} \rightleftharpoons \text{OH} + \text{O}_2$	1.7×10^{17}	0	-6.40
(13)	$\text{HO}_2 + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{O}_2$	1.9×10^{16}	-1.00	0
Formation and Consumption of H₂O₂				
(14)	$\text{HO}_2 + \text{HO}_2 \rightleftharpoons \text{H}_2\text{O}_2 + \text{O}_2$	4.2×10^{14}	0	11.98
(15)	$\text{H}_2\text{O}_2 + \text{M} \rightleftharpoons \text{OH} + \text{OH} + \text{M}$	1.3×10^{17}	0	-14.29
(16)	$\text{H}_2\text{O}_2 + \text{H} \rightleftharpoons \text{H}_2\text{O} + \text{OH}$	1.0×10^{17}	0	3.39
(17)	$\text{H}_2\text{O}_2 + \text{H} \rightleftharpoons \text{H}_2 + \text{HO}_2$	4.8×10^{17}	0	7.95
(18)	$\text{H}_2\text{O}_2 + \text{O} \rightleftharpoons \text{OH} + \text{HO}_2$	9.5×10^{16}	2.0	3.97
(19)	$\text{H}_2\text{O}_2 + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{HO}_2$	1.0×10^{17}	0	0
Oxidation of CO				
(1)	$\text{CO} + \text{O} + \text{M} \rightleftharpoons \text{CO}_2 + \text{M}$	2.5×10^{17}	0	-4.54
(2)	$\text{CO} + \text{O}_2 \rightleftharpoons \text{CO}_2 + \text{O}$	2.5×10^{17}	0	47.69
(3)	$\text{CO} + \text{OH} \rightleftharpoons \text{CO}_2 + \text{H}$	1.5×10^{16}	1.3	-6.765
(4)	$\text{CO} + \text{HO}_2 \rightleftharpoons \text{CO}_2 + \text{OH}$	6.0×10^{17}	0	22.95

Now, why did we do all these, why do we need a very generalized formulation for a given chemical reaction, why cannot we just write one reaction? The reason is that practical reaction, practical combustion, the mechanism by which a fuel reacts with oxygen, and it goes to products it does not happen in one-step. If you consider these things that are the combustion of hydrogen and oxygen, we all know what the product is we know that the product is water, but this does not happen in one step. This is the reason is that really this the collision of two molecules like this H 2 and O 2 cannot make a product, there has to be is like very energetic intermediates which needs to be involved in this reaction mechanism which can lead to this which can basically carry the reaction forward. H 2 and O 2 are like two molecules and as such they do not react among themselves to form the water.

So, as you see for hydrogen-oxygen combustion, it involves 19 reversible reactions and 8 species and of those 8 species of course, two are the two reactants and the product the

three are the reactants and the products H₂O₂ and water. But rest you see there lot of like intermediates being formed H atom, O atom, OH radical, H O₂ radical, H₂O₂ radical. And these are the whole reactions scheme that is involved, not this part sorry. This is the typically this is also normal, but this part 19 reactions and 8 species, so that is why now this is for hydrogen oxygen which you see hydrogen is simplest molecule possible and oxygen is another reasonably simple molecule.

So, when they react and I mean when the combustion of these two things happen, the number of reactions and species are not very large as such, it is still controllable or still manageable 8 and 19. But as I said before in say combustion of something like jet fuel which is the fuel of choice in aviation propulsion or like things like j p 7, j p 8 which are the fuels of choice in a in military engines, the combustion of those are very very complex. Those can involve like even 5,000 reactions 5,000 species and 25,000 reactions 10,000 species 50,000 reactions, so that is why now when you involved when your n goes to like 50,000 you cannot write simple relations for this and there for that you need this generalized description. Now, you are in a position to handle as many reactions and as many species as possible, but of course, you still need some more information.

(Refer Slide Time: 03:33)

Multiple Reactions

Generalized expression for reaction rate:

$$\sum_{i=1}^N \nu_{i,k}^r M_i \xrightleftharpoons[k_{-k}]{k_{+k}} \sum_{j=1}^N \nu_{j,k}^p M_j, \quad k=1,2,\dots,K,$$

↓ Number of reactions

i, j → i th or j th species

k → k th reaction.

10

And this is the those extra information that is now since you have seen that only the number of species is not large, yes number of species can be large 8, but the number of reactions also can be large 19 as such the number of reactions are always greater than the

number of species. So, we can now have we will use the variable k to represent the number of reactions. So, i and j if it is there, these involve means i-th or j-th species; and if k is involved it means k-th reaction. So, please remember this nomenclature. So, in this case, you see nu i dash k means it is the stoichiometry coefficient of the i-th species in the k-th reaction m i is the species number. k k f means the rate constant of the k-th reaction in the forward mode and K k v means the reaction rate constant of the k-th reaction in the backward mode. And nu i k double dash double prime once again means that it is the stoichiometric coefficient of the i-th species in the k-th reaction on the product side.

(Refer Slide Time: 05:22)

Multiple Reactions

Generalized expression for reaction rate:

$$\sum_{i=1}^N \nu_{i,k}^r M_i \xrightleftharpoons[k_{k,b}]{k_{k,f}} \sum_{i=1}^N \nu_{i,k}^p M_i, \quad k=1,2,\dots,K,$$

↓ Number of reactions

$$\omega_k = k_{k,f} \prod_{i=1}^N c_i^{\nu_{i,k}^r} - k_{k,b} \prod_{i=1}^N c_i^{\nu_{i,k}^p}, \quad k=1,2,\dots,K,$$

↓ 19

Generalized expression of kth reaction rate.

i = 1...8
k = 1...19
for H₂, O₂

10

So, please keep this convention in mind which will simplify many things. So, we need this as I said that then because in the previous example our k essentially the number of reaction goes from 1 to up to capital K is essentially 19, whereas i goes equal to 1 to 8. So, this is the generalized expression of k-th reaction rate. Now, please once again note the difference between reaction rate and reaction rate constant. This is the reaction rate constant K k f, actually it is not a constant it a function of temperature, but we represent we name it as reaction rate constant as such. And omega k is the reaction rate for the k-th reaction and i is the number of species.

(Refer Slide Time: 06:50)

Multiple Reactions

Generalized expression for reaction rate:

$$\sum_{i=1}^N v'_{i,k} M_i \xrightleftharpoons[k_{k,b}]{k_{k,f}} \sum_{i=1}^N v''_{i,k} M_i, \quad k=1,2,\dots,K, \quad \downarrow \text{Number of reactions}$$

$$\omega_k = k_{k,f} \prod_{i=1}^N c_i^{v'_{i,k}} - k_{k,b} \prod_{i=1}^N c_i^{v''_{i,k}}, \quad k=1,2,\dots,K,$$

$$\dot{\omega}_i = \sum_{k=1}^K (v''_{i,k} - v'_{i,k}) \omega_k.$$

10

Now, using that is in this information and the previous relations, now we can find the rate of change of the i -th species which is given by this thing ω_i cap and that should be now summed over all reactions that is the contribution of the production or consumption of the species i should this taken from all reactions because species i can appear in many reactions it need not just appear in one reaction. So, we need to sum over all of them. If they do not appear then of course, you see that there these stoichiometry coefficient will be 0. So, there will be no contribution as such, but if it nonzero then it means that there is a contribution and you to take in to account of that. So, this is the power of the generalized expressions.

(Refer Slide Time: 07:44)

Rational Approximations

Approximations based on comparison of rates of certain reaction entities

1. Quasi-steady-state (QSS) species approximation
(For a species)
2. Partial equilibrium (PE) reaction approximation
(For a reaction)

11

Now you see here we were discussing 19, we were discussing about hydrogen-oxygen combustion which involves 8 species and 19 reversible reactions. Now, if you know combustion or you know that or if you have worked on mixing problems or anything similar for with multi component systems, you know that we solve a given configuration using the governing equations and where we solve for the momentum conservation where we solve mass conservation, momentum conservation, energy conservation, and also for species conservation.

Now, when you apply species conservation what it means is that you write a conservation equation, you write a partial differential equation or a integral or in an differential form or an in integral form for each of this species i . So, if you are dealing with hydrogen-oxygen combustion, we will be writing 8 where 8 such governing equations only for to account for the species conservation or you can write seven because or some of the mass fractions or mole fractions will be one, but any ways 7 or 8 as your choice may be you have to write.

Now, this till ok, you can incorporate these in a CFD computation and do a CFD involving hydrogen oxygen combustion, but imagine you are doing it for kerosene, which involves 1000 of species and 1000 of reactions. I mean even with modern powerful computers it is like prohibitively expensive, you cannot manage, we cannot manage to do that. So, what we do is that we will introduce certain approximations based

on comparison of the rates of certain reaction entities here reaction entities are very generalize term. Based on the consumption based on it can be like a species involving a rate of change of a species of their rate of a reaction itself. Using that using certain approximation based on the comparisons of the rates of a certain reaction entities which can be species or reactions, you introduce some approximation such that the number of this species and reactions involved can be reduced or they can be lumped together.

How do you do that? You do that basically by using two approximations which are generalized generally known as QSS approximation that is a quasi-steady-state species approximation for a species. You apply please understand this thing here apply the quasi-steady-state species approximations for a species. And you apply the partial equilibrium as some approximation - PE for a reaction. You will see that applying one or both of these in a judicious manner, you can reduce the number of reactions or the number of equations that need to be solved; and when you reduce that your computational load actually decreases.

(Refer Slide Time: 11:11)

QSS Species Approximation

- Some chain carriers are generated and consumed at rapid rates such that their concentrations remain at low values and their net change rates are very small.

→ For $\hat{\omega}_i = \frac{dc_i}{dt} = \hat{\omega}_i^+ - \hat{\omega}_i^-$

→ If $\left| \frac{dc_i}{dt} \right| \ll (\hat{\omega}_i^+, \hat{\omega}_i^-)$

→ Then $\hat{\omega}_i^+ = \hat{\omega}_i^-$

- **Consequence:** (implicit) algebraic instead of differential solution

Note: dc_i/dt may not be negligible compared to other rates

12

So, what is QSS species approximation? Now, you will see later that we will talking about chain carriers chain carriers, let us consider these to be now this intermediates like H, O, OH these intermediates are chain carriers these are very energetic in nature. And these a generated and consumed at very rapid rates. Please note this term that is their generated and consumed at a very rapid rate such that their concentrations remain at low

values the concentration of this intermediate H, OH, O these are always very small in a combustion reaction in comparison to other like bulk species like H₂, O₂, water etcetera. And also the net rate changes the net change rates or the net rate of change of these species is also very small, but that does not mean that they are not important you cannot eliminate them.

Please understand this difference. You cannot say that I will not consider H, O, OH in my combustion calculation then you will get wrong answers. But you can introduce this kind of approximations on them in which you will consider that yes by noting that their concentration remains small. You can consider that the rate of change of this species, the rate of change of concentration of this species is small. What is the rate of change of concentration that is you know it is given by ω_i here i stands for chain carrier like H, O, OH etcetera this is equal to dc_i/dt and that is as you know this is comes from the production and this comes from consumption, let say it like that.

This is the rate of production of that species which adds to the concentration or adds to the rate of change of concentration and this is the rate of consumption of the species i which needs to reduce reduction of the rate of change of the concentration of the species i . Now, if the individual rates of this ω_i plus ω_i^{cap} plus ω_i^{cap} minus are much larger that is the rate of production and rate of consumption. If these are much larger than the absolute rate of change of the species of the concentration of species i then we can approximate that these two things are equal. So, this is called then it means that the concentration of the species i does not change too much.

So, what it means is that this is an ordinal differential equation, whereas this is an algebraic equation. So, even though it is implicit we have reduced the complexity of our problem by going from a differential equation to a algebraic equation. But it is very, very important to note that this is true in this equation only, it does not mean that dc_i/dt is equal to 0 universally; dc_i/dt may not be zero or may not be is not even is not zero at all. And it may not be negligible also when you compare it with other reaction rates, other rates which can be reaction rate or which can be the species production rate.

So, you have to be very careful about this. It does not mean dc_i/dt equal to 0; it only means that it is small when we compare with two other rates which are the rate of production rate of consumption. So, this is this goes to the QSS approximation. And as

you see here the most importance of hallmark of this, it is applied on a given species. It is not applied on a reaction rate it is applied on a species rate of change of species concentration that is not changing too much in comparison to the rate of change of in comparison to its state of production and rate of consumption.

(Refer Slide Time: 15:31)

Partial Equilibrium Approximation

- If both the forward and backward rates of a reaction k are much larger than the net reaction rate, then we can set:

$$\omega_k = k_{k,f} \prod_{i=1}^N c_i^{\nu_{i,k}} - k_{k,b} \prod_{i=1}^N c_i^{\nu'_{i,k}} \approx 0$$
- such that $k_{k,f} \prod_{i=1}^N c_i^{\nu_{i,k}} \approx k_{k,b} \prod_{i=1}^N c_i^{\nu'_{i,k}}$ (2.1.17)
- which yields an algebraic relation between the c_i 's.

Note: ω_k not necessarily small compared to $\hat{\omega}_i$ 13

What is partial equilibrium approximation? Now, as you know in contrary to the previous one previous approximation which is applied on a species partial equilibrium approximation is applied on a reaction, so that was applied on i, j etcetera this is applied on k which is denotes the reaction. So, what does it state it states that, so this is the net this is the total reaction rate. So, it states that if the forward and the backwards reaction rates of a reaction k are much larger than the net reaction rate we can set this thing to be 0. So, ω_k is given by $K_{k,f}$ times product of i equal to 1 to n $c_i^{\nu_{i,k}}$ to raise to the power of $\nu_{i,k}$. And $K_{k,b}$ this is the backward reaction rate this is the forward reaction rate forward rate of reaction this is the backward rate of reaction.

So, some of these two when you have equilibrium of course, this will be zero here we assume that that this guy is much greater than ω_k , and this guy is also much greater than ω_k . And as a result we say that in comparison to this, this is almost equal to 0. So, it means that this reaction is in partial equilibrium; so this is what is the consequence of this. And once again you see that we go here from algebraic, we can get an algebraic relation between the species concentrations in this form. Once again, this means that it

does not mean that ω_k is necessarily small compared to any given rate of change of species concentration or any other reaction rate; it is only applied in this particular context.

(Refer Slide Time: 17:36)

Example

- Assume 1st reaction ($k=1$) is in PE, then solve for concentration of species-1 (c_1) in terms of $c_i, i \neq 1$.
- Since $\omega_{k=1}$ is not necessarily small when compared to $\hat{\omega}_i$, it needs to be kept in $\hat{\omega}_i = \sum_{k=1}^K (v_{i,k}'' - v_{i,k}') \omega_k$.

$$\hat{\omega}_i = \frac{dc_i}{dt} = (v_{i,1}'' - v_{i,1}') \omega_1 + \sum_{k=2}^K \hat{\omega}_{1,k}, \quad i = 1, 2, \dots, N,$$

- for $i=1$: $\hat{\omega}_1 = \frac{dc_1}{dt} = (v_{1,1}'' - v_{1,1}') \omega_1 + \sum_{k=2}^K \hat{\omega}_{1,k}$
- Eliminating ω_1 yields:

$$\frac{dc_i}{dt} = \sum_{k=2}^K \hat{\omega}_{i,k} + \left(\frac{v_{i,1}'' - v_{i,1}'}{v_{1,1}'' - v_{1,1}'} \right) \left[\frac{dc_1}{dt} - \sum_{k=2}^K \hat{\omega}_{1,k} \right] \quad i=2, \dots, N$$

Number of equations reduce from N to N-1

14

Example, this is a generic example. We will actually come to actual examples when we use this QSS approximation and the partial equilibrium approximation very soon. Now, let us say that the first reaction for k equal to 1 is in partial equilibrium, and then we solve for the concentration of the species one c_1 in terms of c_i . Now, since $\omega_{k=1}$ is not necessarily small when compared to ω_i , it needs to be kept in this equation, in the equation of ω_i which is the rate of change of the concentration of species i . And that is given by, so we can split up the contribution from the first reaction and all other reaction.

So, ω_i is essentially it has contributions from the first reactions and it has contribution from all other reactions. And then what we can do is that for i equal to we can write we can put i equal to 1 here and we can again get the contribution for ω_1 and the contribution for all other reactions. But this is only for species i and then we can basically substitute this here this actually we can subtract these two things. And when we subtract we see that we have a dc_i/dt is given by this form. And now we need to only consider for i is equal to 2 to N . So, the we can have been we have been able to eliminate ω_1 , that is we have been able to eliminate the reaction rate of ω_1 of

the first reaction and we can only consider now from species from 2 to N. So, the number of equations have reduced from N to N minus 1. So, clearly we see that this application of this thing has reduced to N to N minus 1.

(Refer Slide Time: 19:44)

Approximation by Global and Semi-global Reactions

- Successive application of **QSS species** and **PE reactions** will eventually lead to a **one-step global reaction** (at least theoretically!). The process is tedious, with the results depend on the individual reaction rate parameters most of which are not known.
- May as well just start with a one-step reaction

$$\text{Fuel} + \text{Oxidizer} \xrightarrow{k} \text{Products}$$

described by: $\omega = k \prod_{i=1}^N c_i^{n_i}$,

where n_i is called the **reaction order**, and is empirical in nature.

Now, what actually it is done is that in reality what is done is we have we successively apply QSS approximation and partial approximation. And if you continue to apply this thing, we can arrive at a one step global reaction at least theoretically, but then the process is tedious and the results depend on the individual reaction parameters most of which are not known.

So, we then it becomes something like this fuel and oxidizer goes to products and this is given by this. And we can arrive at a global approximate semi global reaction, but this is of course, comes at a penalty that you lose the fidelity or the lose the detail nature of your reactions, but sometimes that is also required when you want to do un approximate calculation or when the reaction rate kinetics is. You know that it is not very important because of certain external parameters.

(Refer Slide Time: 20:38)

Reaction Order and Molecularity

1. **Molecularity, v_i** : number of colliding molecules in an elementary reaction; a fundamental parameter; v_i is the reaction molecularity w.r.t. i . $\sum_{i=1}^N v_i$ is reaction molecularity. $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$
2. **Reaction order, n_i** : influence of concentration of i on the reaction rate; an empirical parameter; $n_i < 2$; n_i can also be negative. For elementary reactions, reaction order is the respective molecularity of the reaction. *Reaction Molecularity = 2*
3. For global/semi-global reactions, reaction orders represent the net effects of the molecularities of the individual elementary reactions.

16

So, now we will go with certain definitions which are essentially the reaction order and molecularity. What is molecularity? Molecularity is the number of colliding molecules in an elementary reaction; it is the number of colliding molecules in an elementary reaction. As you see that if you consider the reaction like H plus O₂ going to H plus O, so the number of molecules involves H and O₂ essentially. So, the molecularity is essentially 2. So, whereas, here we define that the n_i is the reaction molecularity with respect to species i , whereas $\sum_{i=1}^n n_i$ is the reaction molecule it is. So, once again if H plus O₂, so this is one, this is one. So, the summation of over one plus one is equal to molecularity, reaction molecularity is equal to 2.

Reaction order, what is reaction order, reaction order is the influence of concentration of i on the reaction rate. Now, for elementary reactions like this, reaction order is essentially the respective molecularity of the reaction, but that is not that is also a sometimes important. The most important contribution of reaction order comes first global and semi global reactions where the reaction orders represent the net effects of the molecularities of the individual elementary reactions. So, this is where the reaction order is important.

(Refer Slide Time: 22:32)

The Arrhenius Law

- The Arrhenius Law states the dependence of the reaction rate constant on temperature:
$$\frac{d \ln k(T)}{dT} = \frac{E_a}{R^0 T^2}$$

Activation Energy
 E_a : cal/mole
- For constant E_a : $k(T) = A e^{-E_a/R^0 T}$

$B, \propto (E_a)$
- Modified form: $A = A(T) = B T^{\alpha}$

17

Now, next we go to Arrhenius law. So, far you have seen that using the law of mass action we have written how are reaction rate, how we can obtain a reaction rate which is essentially proportional to the product of the concentrations of the reactants raised to their stoichiometric coefficients or the stoichiometry constants in front of them. Now, this proportionality constant of the reaction rate and this product of the species concentration raise to their stoichiometry coefficients, these proportionality constant is called the weight constant reaction rate constant or reaction rate coefficient, we will call it reaction rate constant.

Now, what does the reaction rate constant depend on that is given by Arrhenius law? The reaction rate constant is given by this form in a differential form, which says that $d \log k / dT$ is equal to $E_a / R^0 T^2$. E_a is called activation energy. It is very, very important significance in combustion; and R^0 is of course, the universal gas constant. So, if we integrate on both sides after taking dT to RHS, what we see is that we can write $k(T)$ which is the more general form as a frequency factor A that is the constant of integration actually of this integration which comes times E to the power of minus E_a by $R^0 T$. This is very, very important. And you will be quite surprised to believe that in today's modern combustion research at least 50 percent of the activity not 50 percent at least 30 percent of the recent activity of many people of combustion kineticists goes into determining A and E_a .

Because you see that combustion involves hundreds and thousands of reactions; and each of these reactions each of these thousands and thousands of reactions that you see elaborate constant. And those rate constant and each of these thousands and thousands of reactions will have $1/A$ and $1/E_a$. So, to utilize to know comprehensively about how the system is behaving in a if you want to solve this numerically, you need to know here A and E_a . So, the reaction rate constant is of is of paramount importance in combustion. So, we need to develop a thorough understanding of this.

And the modified form actually A also depends on temperature in some cases. And when then you can write it as we can decompose A into a constant B and T to the power of α where α is a constant. So, now then we have three constants to have a comprehensive reaction mechanism of combustion, we need to first know what are the species being formed, we need to know what are the reactions being formed or reactions being involved and then we need to know A or B α and E_a . And you will see that this reaction mechanisms that is being developed which is very important activity essentially list this three parameters B , α and E_a .

So, as you see that we have now appreciated that the combustion of the kerosene that happens in a gas turbine engine that does not happen in one step. The vapor of course, kerosene combustion happens in a gas phase that is it kerosene vapor is mixed with oxygen and with which has got nitrogen and then you begin a you provide a spark. And then series of reactions hundreds and thousands of reactions are formed are happened and thousands and thousands of species are formed.

And each of this is governed by the law of mass action; and law of mass action involves this rate constant k_T . And the rate constant k_T as a give you form given by the Arrhenius law and where which involves this constants B , α , E_a . Of course one would like to experimentally determine this constants, but it is not possible because you see they are involves thousands and thousands of reactions how many will you determine experimentally. So, you need to determine this by using theory what kind of theory.

(Refer Slide Time: 28:18)

The Activation Energy

Activation energy represents the minimum energy the colliding molecules must possess for reaction to be possible.

$$E_{a,f} + Q_c = E_{a,b}$$

For $Q_c > 0$ (exothermic reaction), $E_{a,f} < E_{a,b}$ and forward reaction is preferred.

18

We will come to that, but before that we need to have a little bit some more discussion about activation energy. But this theory of determining this k is very important. But as you see that this is E_a which is one of the most important constants for a given reaction involved in combustion, this E_a has a very strange behavior, this E_a exponential raise to the power of minus E_a by $R T$ or $0 T$. So, whenever something is got exponential, you have to be very careful.

So, we will come to this. What is the consequence of this exponential nature, but what is this E_a , this activation energy physically represent. Physically it means it represents the minimum energy of the colliding molecules that they must possess for reaction to be possible that is why it is called activation energy. And the activation energy of a forward reaction plus the heat release is equal to the activation energy of the backward reaction. So, if this is essentially potential energy of the molecules, so in this potential energy y -axis and in the reaction coordinate where this is your reactants which can be like H plus O_2 , and this is your product for the reaction OH plus O . Actually I am not give this example because this is it is a different reaction actually.

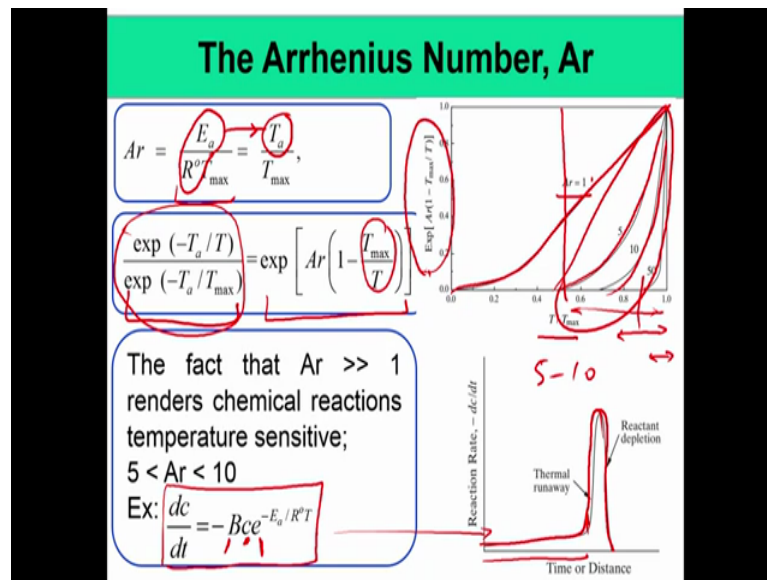
So, let us consider any reactants, which has got which is an exothermic in nature, so which starts with this reactants and which goes into this products. So, you see the reactants itself they have a potential energy which is a heat release during combustion. So, they have are already energized, whereas the products do not have the heat of

combustion as such because it has been already release, so the products at a lower energy state. But you see the reactant does not go to the products directly because if it would have gone then you could not have utilized combustion for power generation. You keep hydrogen and oxygen in a mixture they will spontaneously burn. Does that happen? It does not happen like that if you keep methane and oxygen in a in a bottle it does not spontaneously react. So, it has to cross if it would have spontaneously reacted then everything in this universe in this world would have been just carbon dioxide and water.

So, you see the beauty of nature here. So, all these fuels have a large activation energy which must be crossed for these reactants to become products. So, you need to supply this activation energy in some form or the other. For Q_c equal to 0, your activation energy the forward reaction is greater than the activation of the backward reaction that means, the forward reaction is preferred because while going back you have to cross a higher hill. For going from here to here you have to cross a hill a potential energy barrier which is of this magnitude. For going from products to reactants, you have to cross a potential energy barrier which is of this magnitude. So, of course, that is why this reaction is preferred this path is preferred.

But that is the yes, of course, when you have activation energy, you will see the other beauties of activation energy also that is there are other things. But if the activation energy was not large everything would have spontaneously reacted which does not happen you need to provide a spark for the reactions to begin or you need to compress. You need to compress your compresses your gases that is your fuel air mixture that is present in your diesel engine to a very high pressure, but it is spontaneously ignites because of the higher temperature and the higher pressure; that means, your crossing the activation energy. This has got other significance.

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Now, you can write you see the unit of E a is calorie per mole or joule per mole. Now, so is the if it is e to the power of minus E a by R T of course, the exponent of an exponential cannot have a unit. So, of course, you can see this be sure that R 0 times T is also unit is also as a unit of calorie per mole or joule per mole. So, then you can define an non dimensional number called Arrhenius number which is essentially E a by R 0 times T max.

What is T max? T max can be considered to be the maximum temperature that is involved in a combustion reaction which can be as you know like something like adiabatic flame temperature. It is very hard to cross adiabatic flame temperature right which can be like say 2500 Kelvin, 3000 Kelvin depending on how much oxygen you have or or how much nitrogen you have. So, Arrhenius number is essentially the ratio of the activation temperature which is nothing but this thing E a by R 0 is equal to activation temperature divided by T max.

Now, you can look into this function that is e to the power of minus T a by T divided by e to the power of minus T a by T max. Now, we see this is the constant in a given reaction and we can write this as e to the power of Arrhenius number times 1 minus T max by T. And if you plot this as a function of T max by T, if you plot this quantity this can be considered like part of the reaction rate normalized by a constant. What you will find is that the nature of this reaction rate constant as a function of T by T max for different

Arrhenius number. You see that when Arrhenius number is small one, it is a smoothly behavior, but as Arrhenius number increases it becomes this gradients becomes steeper and steeper. And this nonzero essentially this non-negligible, this function this guy which is essentially a normalized reaction rate constant is only becomes concentrated at higher T by T_{max} values.

So, it means that reaction now happens only at very, very high temperature or the reaction rate constant is active at very, very high temperature. Whereas for small Arrhenius number it was active at almost all temperature; whereas, for Arrhenius number of fifty its only active when it is beyond 0.9. For combustion reactions, Arrhenius number is typically in this range 5 to 10. So, it means that in combustion reactions are characterized by varies temperature sensitive reactions.

Now, if you take the example that if you consider this is the example of a homogeneous combustion reaction there is no transport that is a no conduction or a diffusion combustion happen in homogeneous reactor which is given by $d c_i / d t$ is equal to then minus $B c$ you see where this comes from this comes from law of mass action. And the formula for k_f when you substitute every things this comes from the law of mass action this and this comes from the definition of k_f . And when you write when you plot this as a function of a time or distance we will find that for large Arrhenius number the reaction rate becomes a very sharp peaked function like this.

So, for a long time that is no activity. And then when it crosses certain temperature activity picks up, and it becomes completed in a very short amount of time because of reaction dilution. It does not monotonically go off because you are then c also decreases as a reaction is consumed. So, this is hallmark of combustion reactions that is they happen within a very short time or within a very short distance. Short time if you are considering a homogeneous reactor that is why we almost call it like a explosion. It is called thermal renovates; it is not explosion in this course does not mean a blast or something. It means a very quick reactions with very large release of energy.

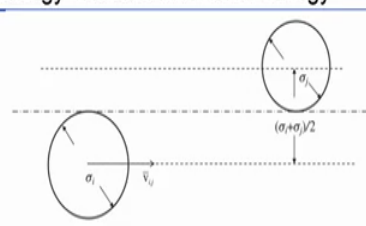
And combustion reactions in a homogeneous reactor are characterized by this explosive nature where they happen within a very short amount of time and there confined within small distances which are characterized by flames. So, flames are very thin in nature and that is because of the fact that Arrhenius number is large in this reactions.

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Collision Theory of Reaction Rate (1/3)

Assumptions:

1. Equilibrium Maxwell velocity distribution
2. Two-body hard-sphere collision
3. Reaction occurs if collision (translational) energy exceeds activation energy



20

So, the next we will go into collision theory of reaction rate, but that is this much for this class.

Thank you.