Combustion in Air Breathing Aero Engines

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Lecture - 07
Chemical Kinetics IV

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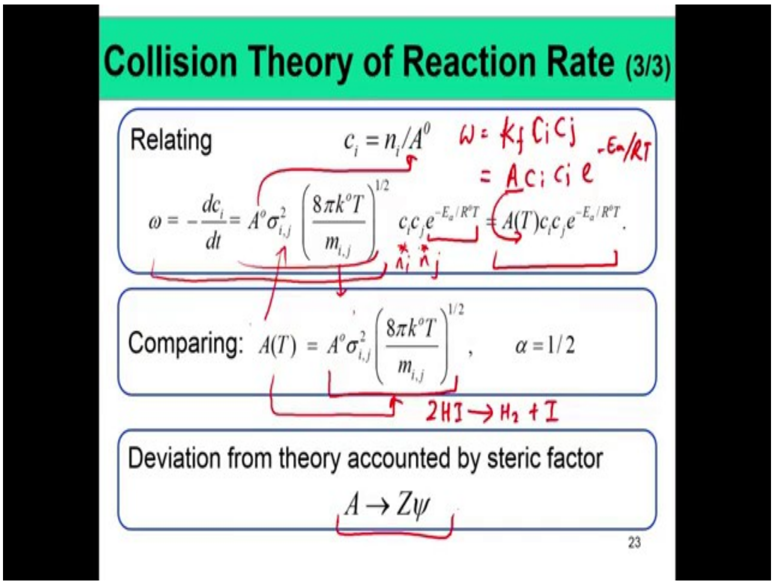

Collision Theory of Reaction Rate (3/3)

Relating $c_i = n_i/A^0$ $\omega = k_f C_i C_j = A c_i c_j e^{-E_a/RT}$

$$\omega = -\frac{dc_i}{dt} = A^o\sigma_{i,j}^2\left(\frac{8\pi k^o T}{m_{i,j}}\right)^{1/2} c_i c_j e^{-E_a/R^oT} = A(T)c_i c_j e^{-E_a/R^oT}.$$

$n_i^* \; n_j^*$

Comparing: $A(T) = A^o\sigma_{i,j}^2\left(\frac{8\pi k^o T}{m_{i,j}}\right)^{1/2}$, $\alpha = 1/2$

$2HI \rightarrow H_2 + I$

Deviation from theory accounted by steric factor

$$A \rightarrow Z\psi$$

This we can increase the level of complexity in this analysis by using this transition state theory.

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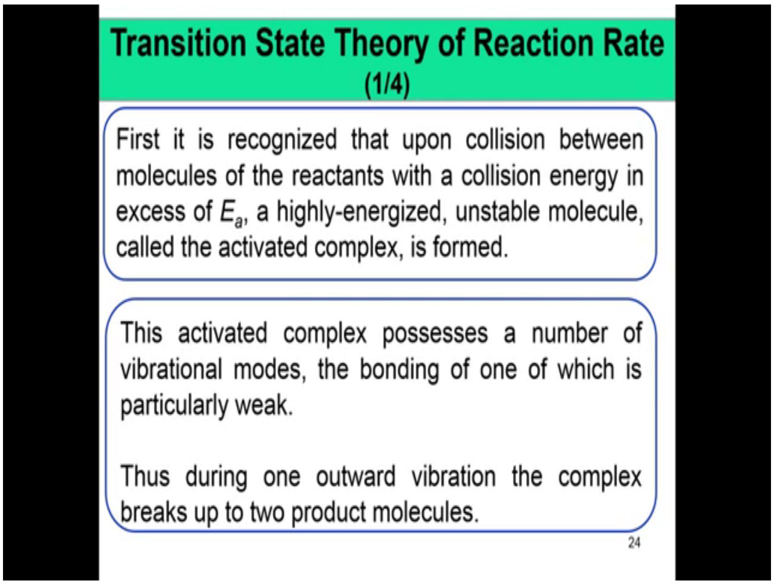

Transition State Theory of Reaction Rate (1/4)

First it is recognized that upon collision between molecules of the reactants with a collision energy in excess of E_a, a highly-energized, unstable molecule, called the activated complex, is formed.

This activated complex possesses a number of vibrational modes, the bonding of one of which is particularly weak.

Thus during one outward vibration the complex breaks up to two product molecules.

Which we will go into a little bit details, the reason for going into these details is not only about learning about this itself. But it will also clear our understanding of how to apply different techniques or how do you expand how do you write this reaction rates as such for generalised reactions, how do you apply the QSS assumption, how do you apply the partial equilibrium assumption. So, in this that is why I have chosen this transition state theory state theory derivation, because it only gives you a an very interesting idea of what is happening what are the steps involved it is not only just collision.

There are more steps involved and it will become very apparent that there must be a step involved in chemical reaction which actually comes from the concept of activation energy, but it will also this this analysis will also tell you will also give you the confidence to basically apply reactions, right. Reactions in the generalised form and then apply the QSS assumption and the partial equilibrium assumption as a case may be.

Now, yes we taught about activation energy in the collision theory in the coalitional theory of chemical reactions, but here we see that it is recognised that upon collision of between molecules of the reactants with the collision energy in excess of E a that is what we assumed also, but here we add one more thing which was not there, we considered the formation of a highly energised unstable molecule called the activated complex. So, this we did not consider before.

Now this is important because this basically accounts for all the different changes of the structure that is taking place in the molecule all right. So, this theory is actually a very sophisticated theory and present day calculations of this rate constants k e a t and alpha b all these things actually use transition state theory of course, in higher level of complexity that what we will be doing here, but the foundations are will be learned here and those calculations those very modern calculations, involve transition state theory to calculate the right constants ok.

But the basic [FL] is this that is a highly energised unstable molecule called the activated complex is formed. Now these activated complex once formed possesses a number of vibrational modes and the bonding of one of these modes is particularly weak; and during one the first or one or the first such outward vibration the complex breaks up to produce two product molecules. So yes, reactant goes into products as it happens, but it does not go into a product directly, it goes into the products through an intermediate step which is the formation of this activated complex. Now, let us consider the how this activated complex is formed.

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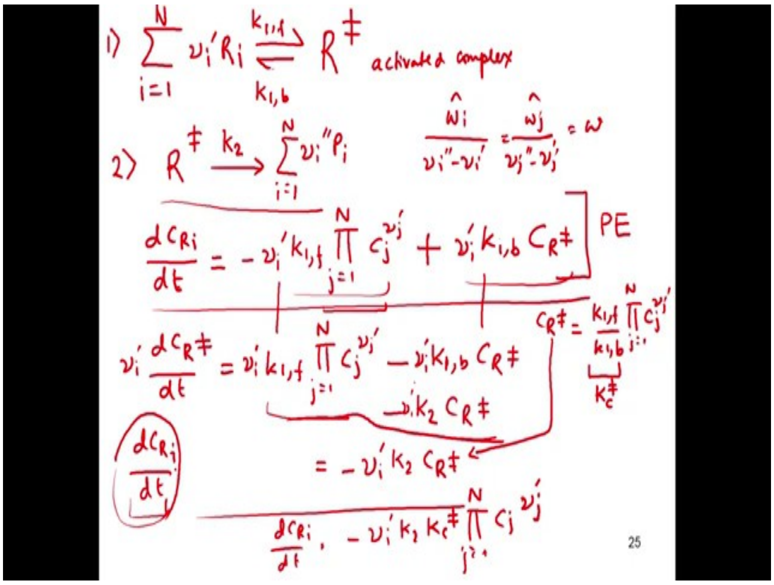

1) $\sum_{i=1}^{N} \nu_i' R_i \underset{k_{1,b}}{\overset{k_{1,f}}{\rightleftharpoons}} R^{\ddagger}$ activated complex

2) $R^{\ddagger} \xrightarrow{k_2} \sum_{i=1}^{N} \nu_i'' P_i$ $\qquad \frac{\hat{\omega}_i}{\nu_i''-\nu_i'} = \frac{\hat{\omega}_j}{\nu_j''-\nu_j'} = \omega$

$$\frac{dC_{R_i}}{dt} = -\nu_i' k_{1,f} \prod_{j=1}^{N} C_j^{\nu_j'} + \nu_i' k_{1,b} C_{R^{\ddagger}}$$ PE

$$C_{R^{\ddagger}} = \underbrace{\frac{k_{1,f}}{k_{1,b}}}_{K_c^{\ddagger}} \prod_{j=1}^{N} C_j^{\nu_j'}$$

$$\nu_i' \frac{dC_{R^{\ddagger}}}{dt} = \nu_i' k_{1,f} \prod_{j=1}^{N} C_j^{\nu_j'} - \nu_i' k_{1,b} C_{R^{\ddagger}} - \nu_i' k_2 C_{R^{\ddagger}}$$

$$\frac{dC_{R_i}}{dt} = -\nu_i' k_2 C_{R^{\ddagger}}$$

$$\frac{dC_{R_i}}{dt} = -\nu_i' k_2 K_c^{\ddagger} \prod_{j=1}^{N} C_j^{\nu_j'}$$

25

So, the reaction scheme of this is actually we will see is very interesting it is given by like a generalised reaction scheme it is given like R i is the reactants, K 1 f is a forward reactant reaction rate constant K 1, b is the backward react constant reactant rate constant reaction rate constant and this R cross is formed R cross is the activated complex ok.

So, this is the first step, step 1; step 2 is this activated complex being a highly unstable molecule decomposes throughout reaction rate constant K 2 to form products. So, in this case we say that the backward reaction is slow. So, we do not consider that now. So, you say that this is a very generalised reaction scheme that we have written, and this will also allow us to understand the whole things that we discussed previously.

Now, we are interested in the rate of change of concentration of the reactant. So, we will write d C R i d t; that is given by now you remember the thing that is omega i cap, divided by nu i double dash minus nu i dash is equal to omega j cap by nu j double dash minus nu j dashed is equal to omega reaction rate right remember this, and this is nothing but d c i d t this is nothing but d c j d t ok.

So, now we can write as this for d C R i you see this is 0, this is 1 this is essentially nu i dash not one sorry. So, we can write. So, the rate of change of concentration of R i changes because it is consumed in the forward reaction, but it is also being produced in the backward reaction when R cross recombines back reforms back to R i.

So, that will contribute, what will be the next, what we will write; what is this this form take for R i R plus plus. You see that there is only one species involved that is R sorry not R plus plus R cross. So, and that is exponent the stoichiometric exponent of that is one. So, we will only write similarly for the next reaction we can write. Not only for the next reaction for the formation of the activated complex the rate of formation of the activated complex we can write right because the rate of the activated complex this leads to the production and this leads to the depletion of the activated complex.

Now, we assume that this reaction partial equilibrium exists in this reaction; that means partial equilibrium exists between the reactants and the activated complex, and then we will assume that the activated complex itself is a steady state species. So, these are the two assumptions we will make, but what is the consequence of this? The consequence of this is that if this is 0 we basically this goes on this side and this goes on this side we can write C R plus plus is nothing but and these two cancels and this we write as K 1 f by K 1 b times product of j is equal to 1 to n C j nu j dashed write and this is we know it is K c. So, we will represent this by this equilibrium constant for the reaction in which the activated complex is formed all right.

Now, if you multiply this reaction with nu i dashed, nu i dashed, nu i dashed nu i dashed and add these two reactions what will you find? You will find that d C R i d t plus nu i dashed d C R d t is equal to what? This goes to 0. I think I have missed not I think this is a one reaction is missed actually here there is also. So, in this reaction we considered this is we are considering the product we are considering the rate of change of R i right. So, R i formed by basically this by decomposition of we are considering the rate of change of concentration of R cross. So, R cross if formed by basically what are the processes it is formed y the decomposition of R i which is accounted for this, it is formed it is formed it is reduced by the by when R r cross goes back to R i, but it also involves a second reaction we have not considered that. So, it is essentially minus K 2 C R plus plus. So, that we have not considered.

So, now when we add these things we see that this one cancels this this cancels this and this is this and we are left with only this reaction only left with this contribution K 2, C R plus plus alright. Now you see we applied partial equilibrium of this thing of the first reaction, but which, but that does not mean that this can be 0 when you compare with the production of the rate of the change of the consideration of R cross alright. In fact, we would argue that this is a steady state species and this rate of change of this species is equal to 0.

In fact, partial equilibrium assumption does not have anything to do with a rate of change of R I, here it is equal to 0 because this is also the total reaction rate this is a forward reaction and this is the backward reaction rate. So, the sum of these two is essentially omega that is why this is equal to 0, but here we say that his quantity because it is essentially a because it is essentially a chain carrier it is this quantity which goes to 0 and which is rather much small than this quantity.

So, then what we are left with is this part this and we can substitute the relationship from here to here and we can find that d C R i d t is equal to minus nu i dashed K 2 K c cross j dashed. Now if we erase everything here if we erase everything and sum these two reactions.

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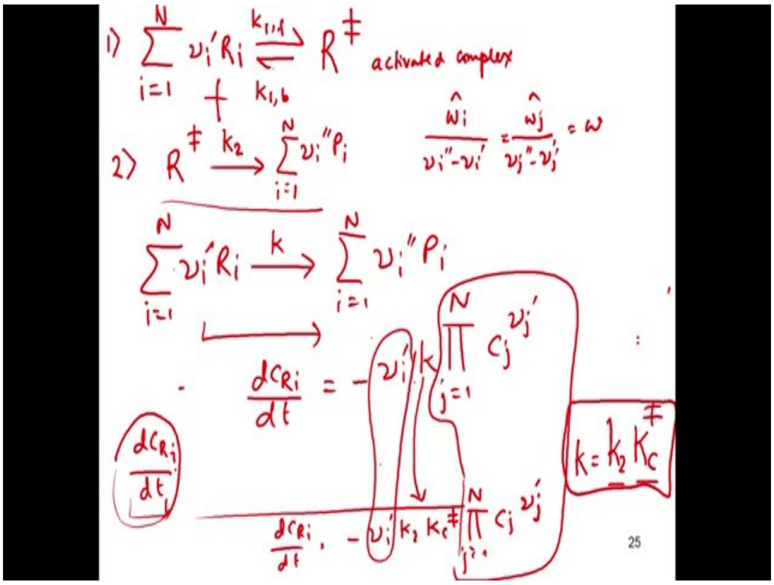

$$1)\ \sum_{i=1}^{N} \nu_i' R_i \underset{k_{1,b}}{\overset{k_{1,f}}{\rightleftharpoons}} R^{\ddagger} \text{ activated complex}$$

$$+$$

$$2)\ R^{\ddagger} \xrightarrow{k_2} \sum_{i=1}^{N} \nu_i'' P_i \qquad \frac{\hat{\omega}_i}{\nu_i''-\nu_i'} = \frac{\hat{\omega}_j}{\nu_j''-\nu_j'} = \omega$$

$$\sum_{i=1}^{N} \nu_i' R_i \xrightarrow{k} \sum_{i=1}^{N} \nu_i'' P_i$$

$$\frac{dC_{R_i}}{dt} = -\nu_i' k \prod_{j=1}^{N} C_j^{\nu_j'}$$

$$\frac{dC_{R_i}}{dt}$$

$$\frac{dC_{R_i}}{dt} = -\nu_i' k_2 K_c^{\ddagger} \prod_{j=1}^{N} C_j^{\nu_j'}$$

$$\boxed{k = k_2 K_c^{\ddagger}}$$

What we will get the overall reaction is this thing with the overall rate constant reactant goes to products right. Now if you compare now and how they would have written this thing? They would have written this thing in this manner that is d C R i for this overall reaction you could have written d C R i d t is equal to minus nu i dashed reaction rate constant k, right. And see what we have got here. Is exactly similar this part and this parts are exactly similar this part is also similar. So, then it means that K is essentially this remaining part it means K is equal to K 2 and K c plus cross you must not confuse between K 2 and K c this is a equilibrium constant and this is a rate constant of the second reaction ok.

So, then using this we can obtain the net rate constant of this reactants going into products, but for an elementary reaction. This is definitely not for global reactions where methane plus oxygen goes to water and carbon dioxide this is true for a reaction which interacts with a molecular level H plus O2 going is to H plus O. We are decomposing that reaction h plus o two going to H plus O into 2 steps, where H plus O 2 reactants to form an activated complex. But the overall rate constant of this elementary reaction h plus O2 going to H plus 0 that is given by this kind of a thing K is equal to 2 plus K c cross, alright.

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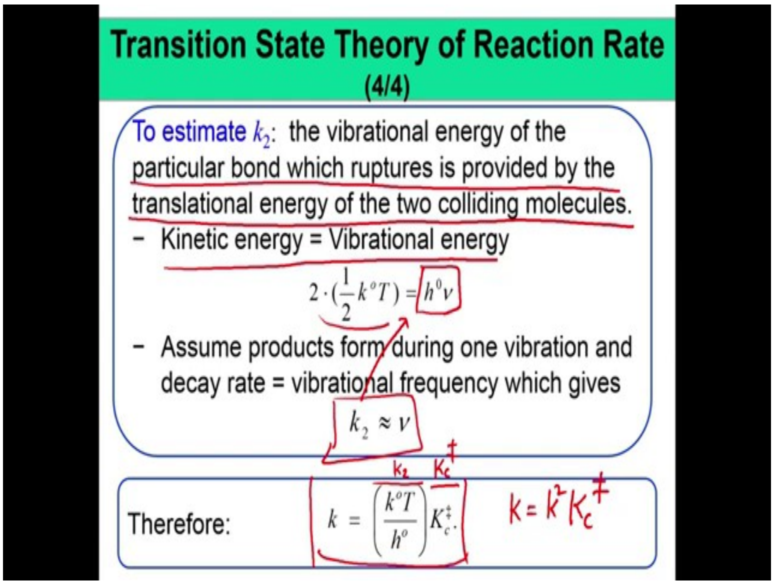

Transition State Theory of Reaction Rate (4/4)

To estimate k_2: the vibrational energy of the particular bond which ruptures is provided by the translational energy of the two colliding molecules.

- Kinetic energy = Vibrational energy

$$2\cdot\left(\frac{1}{2}k^oT\right) = \boxed{h^0\nu}$$

- Assume products form during one vibration and decay rate = vibrational frequency which gives

$$\boxed{k_2 \approx \nu}$$

Therefore: $$k = \underbrace{\left(\frac{k^oT}{h^o}\right)}_{}\overset{k_2\quad K_c^{\ddagger}}{}K_c^{\ddagger}.$$

$K = k^2 K_c^{\ddagger}$

Now, how do you obtain K c cross? We obtain that one we can obtain K c cross by the equilibrium it can which can be tabulated, K c obtaining K c is not difficult obtaining K 2 is a difficult part. We can obtain K 2 by considering that the vibrational energy of the particular bond which ruptures is provided by the translational kinetic energy of the two colliding molecules, this is where the collision comes in.

So, we assume that the coalitional kinetic energy is equal to the vibrational energy, coalitional kinetic energy is given by 1 K T is equal to h naught which is the Planck's constant times the nu which is the frequency; and we assume that the products formed during one vibration and the decay rate is given by K 2, and the vibrational frequency are given by nu, and we said the decay rate is equal to the vibrational frequency, because both you see both are (Refer Time: 17:38) of one per second decay rate and then we can set it like this is equal to nu, and then we can if we substitute this here what you will get is this is your K 2 essentially and this is your K c cross . So, the overall rate constant for the reaction is was if you remember K 2 times K c cross and then that is given by this.

So, now using the law of mass action, using the this postulates this this assumption from this actually comes from quantum mechanics that the vibrational energy is equal to h 0 times nu the first mode of vibration, we can essentially find the this thing the reaction rate constant.

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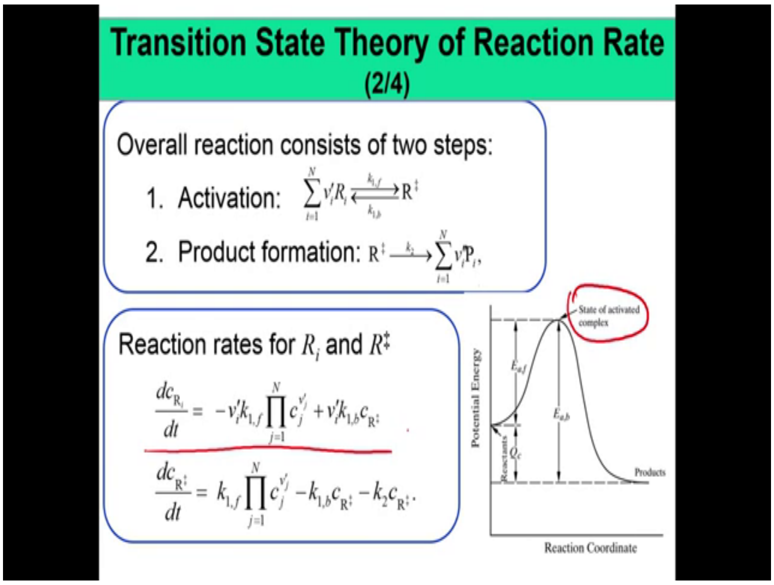

Transition State Theory of Reaction Rate

(2/4)

Overall reaction consists of two steps:

1. Activation: $\sum_{i=1}^{N} \nu_i' R_i \underset{k_{1,b}}{\overset{k_{1,f}}{\rightleftarrows}} \mathrm{R}^{\ddagger}$
2. Product formation: $\mathrm{R}^{\ddagger} \xrightarrow{k_2} \sum_{i=1}^{N} \nu_i'' \mathrm{P}_i$,

Reaction rates for R_i and $R^{\ddagger}$

$$\frac{dc_{\mathrm{R}_i}}{dt} = -\nu_i' k_{1,f} \prod_{j=1}^{N} c_j^{\nu_j'} + \nu_i' k_{1,b} c_{\mathrm{R}^{\ddagger}}$$

$$\frac{dc_{\mathrm{R}^{\ddagger}}}{dt} = k_{1,f} \prod_{j=1}^{N} c_j^{\nu_j'} - k_{1,b} c_{\mathrm{R}^{\ddagger}} - k_2 c_{\mathrm{R}^{\ddagger}}.$$

So, if just recapitulate what we have done, we have done that we have what we have done is that we have considered the activation formation of this activated complex where this reactants goes to form this activated complex and this activated complex goes to form the products in two steps, first one involves K 1 f k b and the second one rate constant K 2. And this is actually the state of the activated complex that we can consider and this involves the two reaction rates the rate of change of the concentration of R i and the rate of change of the concentration of R cross.

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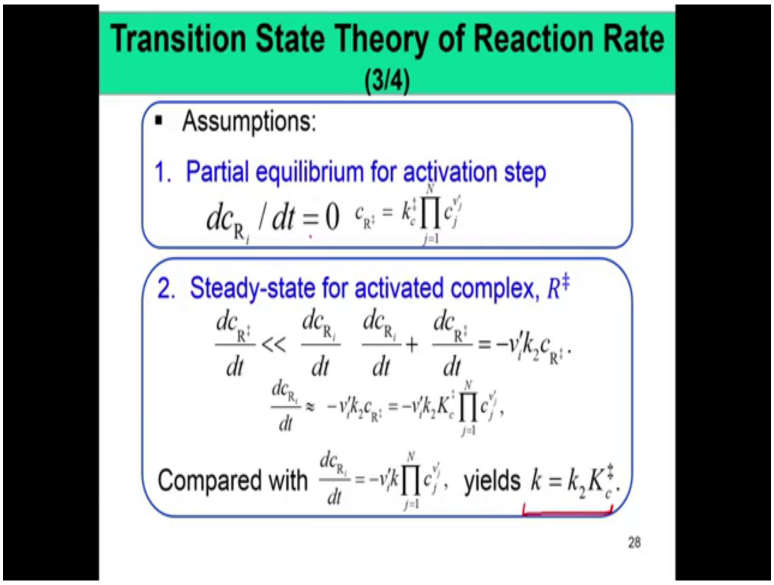

Transition State Theory of Reaction Rate
(3/4)

- Assumptions:

1. Partial equilibrium for activation step

$$dc_{\mathrm{R}_i} / dt = 0 \quad c_{\mathrm{R}^\ddagger} = k_c^\ddagger \prod_{j=1}^{N} c_j^{\nu'_j}$$

2. Steady-state for activated complex, $R^\ddagger$

$$\frac{dc_{\mathrm{R}^\ddagger}}{dt} << \frac{dc_{\mathrm{R}_i}}{dt} \quad \frac{dc_{\mathrm{R}_i}}{dt} + \frac{dc_{\mathrm{R}^\ddagger}}{dt} = -\nu'_i k_2 c_{\mathrm{R}^\ddagger}.$$

$$\frac{dc_{\mathrm{R}_i}}{dt} \approx -\nu'_i k_2 c_{\mathrm{R}^\ddagger} = -\nu'_i k_2 K_c^\ddagger \prod_{j=1}^{N} c_j^{\nu'_j},$$

Compared with $\frac{dc_{\mathrm{R}_i}}{dt} = -\nu'_i k \prod_{j=1}^{N} c_j^{\nu'_j}$, yields $\underline{k = k_2 K_c^\ddagger}$.

And these are given by these two sets of equations and we can apply partial equilibrium for the activation step which gives this thing, and we can apply the partial steady quasi steady state assumption for R cross which gives this, and then when we compare with the overall reaction we get K is equal to K 2 times K c cross, and assuming that the kinetic energy is equal to the vibration energy, we can arrive at this formula that is equal to sorry this is K 2, K is equal to K c and K c cross and we can arrive at this formula that K is equal to K 0 t divided by the Planck's constant times K c plus ok.

So, this is a very very important derivation, this tells you how actually the this not only tells you how to derive the rate constant, but also tells you how the reaction is happening between two molecules.

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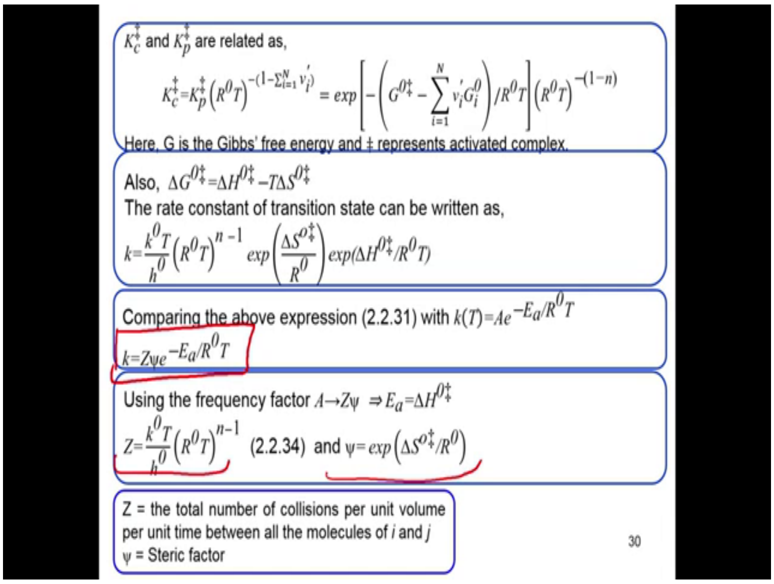

$K_c^{\ddagger}$ and $K_p^{\ddagger}$ are related as,

$$K_c^{\ddagger}=K_p^{\ddagger}\left(R^0T\right)^{-(1-\Sigma_{i=1}^{N} v_i')} = exp\left[-\left(G^{0\ddagger}-\sum_{i=1}^{N} v_i' G_i^0\right)/R^0T\right]\left(R^0T\right)^{-(1-n)}$$

Here, G is the Gibbs' free energy and ‡ represents activated complex.

Also, $\Delta G^{0\ddagger}=\Delta H^{0\ddagger}-T\Delta S^{0\ddagger}$

The rate constant of transition state can be written as,

$$k=\frac{k^0T}{h^0}\left(R^0T\right)^{n-1} exp\left(\frac{\Delta S^{o\ddagger}}{R^0}\right) exp(\Delta H^{0\ddagger}/R^0T)$$

Comparing the above expression (2.2.31) with $k(T)=Ae^{-E_a/R^0T}$

$$\boxed{k=Z\psi e^{-E_a/R^0T}}$$

Using the frequency factor $A\rightarrow Z\psi \Rightarrow E_a=\Delta H^{0\ddagger}$

$\underline{Z=\frac{k^0T}{h^0}\left(R^0T\right)^{n-1}}$ (2.2.34) and $\underline{\psi=exp\left(\Delta S^{o\ddagger}/R^0\right)}$

Z = the total number of collisions per unit volume per unit time between all the molecules of *i* and *j*
ψ = Steric factor

Now, of course, then you can relate this we can go from K c to k p I mean just I will just you the steps and by using this and then you can use the use in terms of write in terms of Gibbs free energy, and the you can use the rate constant in terms of the Gibbs rate as you know that delta g 0 cross for this change of the Gibbs energy for this process is given by the enthalpy change in enthalpy times the temperature times change in entropy and then you can write it like this.

And you can basically if you can find it in this kind of a form if you are interested you can look into laws book or any other book on this transition state theory. But I will not go into the details, but this is how you can finally, represent k in this kind of a manner which is similar to our Arrhenius form ok.

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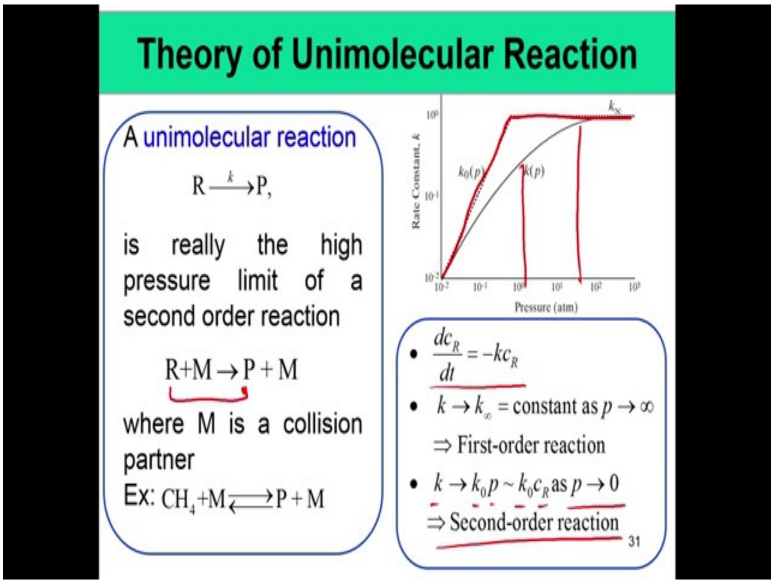

Theory of Unimolecular Reaction

A unimolecular reaction

$R \xrightarrow{k} P,$

is really the high pressure limit of a second order reaction

$\underbrace{R+M}_{} \rightarrow P + M$

where M is a collision partner

Ex: $CH_4 + M \rightleftarrows P + M$

- $\underline{\frac{dc_R}{dt} = -kc_R}$
- $k \rightarrow k_\infty =$ constant as $p \rightarrow \infty$

  $\Rightarrow$ First-order reaction
- $k \rightarrow k_0 p \sim k_0 c_R$ as $p \rightarrow 0$

  $\Rightarrow$ Second-order reaction

So, now then the last thing of this reaction rate theory that remains as the theory of essentially unimolecular reaction. The unimolecular reaction is a kind of an isomerisation reaction or an decomposition reaction when a when a molecule itself spontaneously you can go into form a product is a really high pressure limit of a second order reaction actually the this does not happens spontaneously or itself, it needs to be collided with another molecule M, but m as such does not participate in the reaction, because it does not change in it is own structure. So, M can be a inert gas or any other molecule as such which does not participate in the reaction, but it changes the R to p. As you see here now these unimolecular reactions are very interesting character the rate constant of this reactions have they have become basically pressure dependent.

Now, when the rate constant become pressure dependent if you are a if you are an engineer if you are an if you are designing an engine, which works at for a gas turbine engine or an ice engine, you must be concerned. Because all these engine separate at high pressure and you need to basically have a reaction rates at high pressure, gas turbine engine operates at 30 40 bar or 30 40 atmosphere which is roughly about say here. So, as you can see that the rate constant for this unimolecular reactions are 30 40 bar is very different from the rate constant what is at here, right.

And basically it comes from the fact that that is basically the change of the order of the reaction. So, for the spontaneous reaction we can write that d C R d t is equal to minus k times C R, where at the when pressure tends to infinity this is essentially a first order reaction, but when pressure tends to 0 this becomes the second order reaction we can we can write the pressure k is a basically you see that it has a it behaves in a linear manner and when it behaves in a linear manner we can write k is equal to 0 times P, and pressure as you know is proportional to the number of moles p is equal to n R t p is equal to p v is equal to n R t v is equal to 1 if you said v is equal to 1 then you can write p is equal to n i and you can as you know you can convert n i to concentration.

So, we can p is equal to k 0 times C R and as p tends to 0 you can it becomes the second order reaction.

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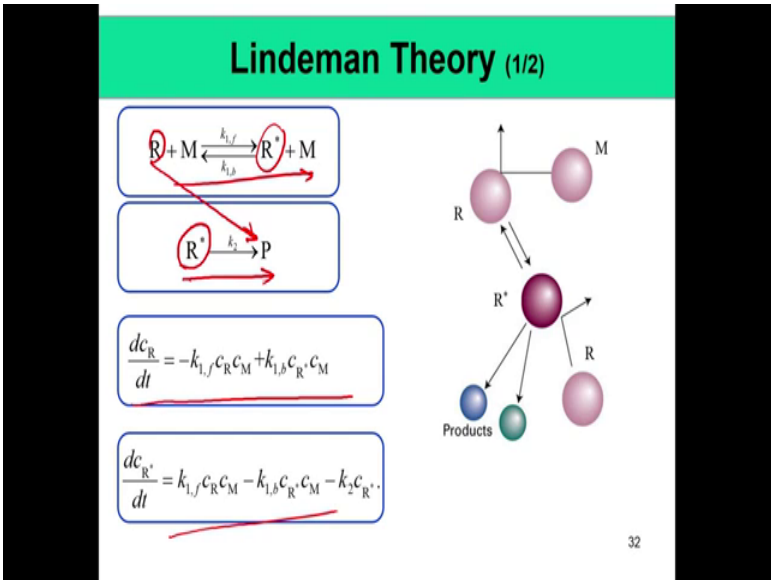

Lindeman Theory (1/2)

$$R + M \underset{k_{1,b}}{\overset{k_{1,f}}{\rightleftarrows}} R^* + M$$

$$R^* \xrightarrow{k_2} P$$

$$\frac{dc_R}{dt} = -k_{1,f} c_R c_M + k_{1,b} c_{R^*} c_M$$

$$\frac{dc_{R^*}}{dt} = k_{1,f} c_R c_M - k_{1,b} c_{R^*} c_M - k_2 c_{R^*}.$$

So, you see that up to an high pressure limit this k infinity is equal to constant in the low pressure limit it k is equal to k 0 times p is a linear as a linear behaviour. Now how why does this happen this can be explained by Lindeman’s theory, we can which also considers this form of a state of an energized state, where R plus R is the is a molecule or reactant it is collided with another third body M, which can be the R itself which can be a inert nitrogen or some other things and it becomes an energized it achieves an energies energy state R star and there is m and then there is another step it is very similar to the previous transition state theory though their important steps points have deviation.

So, here also we see that it gives the formation from R to p essentially involves in two steps this one and this one, it first goes into an energised state and then the energized state decays to form this p and then once again similar to that we can write this equation like this I will go into the details and then further we can first write.

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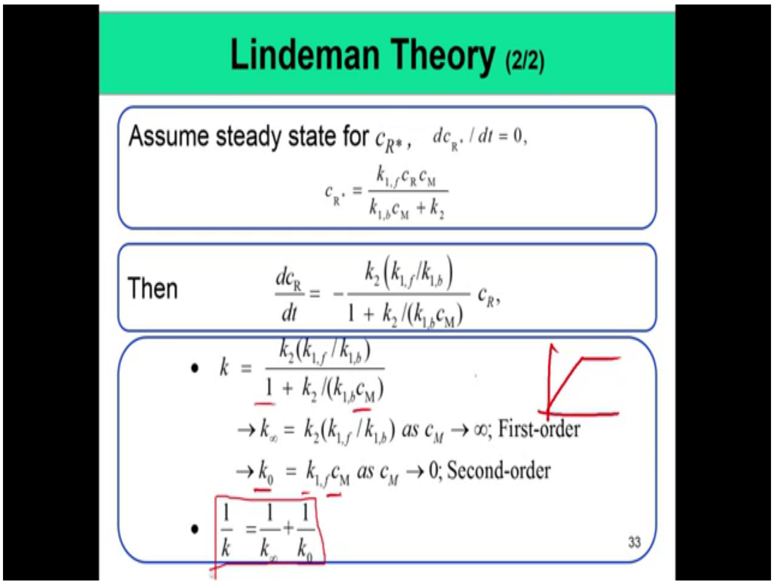

Lindeman Theory (2/2)

Assume steady state for c_{R*}, $dc_{R^*}/dt = 0$,

$$c_{R^*} = \frac{k_{1,f} c_R c_M}{k_{1,b} c_M + k_2}$$

Then $$\frac{dc_R}{dt} = -\frac{k_2 \left(k_{1,f}/k_{1,b}\right)}{1 + k_2/(k_{1,b} c_M)} c_R,$$

- $k = \dfrac{k_2(k_{1,f}/k_{1,b})}{\underline{1} + k_2/(k_{1,b}\underline{c_M})}$

  $\rightarrow k_\infty = k_2(k_{1,f}/k_{1,b})$ as $c_M \rightarrow \infty$; First-order

  $\rightarrow \underline{k_0} = \underline{k_{1,f}}\underline{c_M}$ as $c_M \rightarrow 0$; Second-order

- $\boxed{\dfrac{1}{k} = \dfrac{1}{k_\infty} + \dfrac{1}{k_0}}$

33

And similar to the transition state theory we can write an equation for d C R d t we can write an equation from d C R star d t like this please proceed with this steps this will give you the confidence of how to write reactions; as such and then we can assume steady state for the species R of star, but we will not assume this partial equilibrium for the for the first reaction, this is because this will give you the second order nature of the reaction and then you set basically what we find is that this is this final result is interesting this final result that you find is that k can be expressed as K 2 times K 1 f divided by K 1 b divided one plus K 2 by K 1 b times C M.

So, you see that C M appears in the down stairs of the noun stairs. So, it appears as a denominator of the full denominator. So, you see that if you set C M to infinity that is at very high pressure and very high pressure this concentration of C M can be very high. So, you see what happens is that k infinity tends to this constant value whereas, if C M tends to 0 it becomes k 0 becomes this is because if C M tends to infinity, what happens is that this whole term tends to 0, right.

So, you are only left with this which is a constant that is what you get here right whereas, on the second case if C M tends to 0 f C M tends to 0 what you will see is that you can basically neglect this one and this appears in the full upstairs and k 0 is nothing but K 1 times C M, and as C M tends to 0. We can write this as essentially proportional to pressure and this becomes a second order and this gives you the this and this kind of a behaviour.

So, we can combine the two and write 1 by k is essentially 1by k is nothing but this thing 1 by k infinity plus 1 by K 0. So, this is the thing of the Lindeman reaction, Lindeman mechanism.

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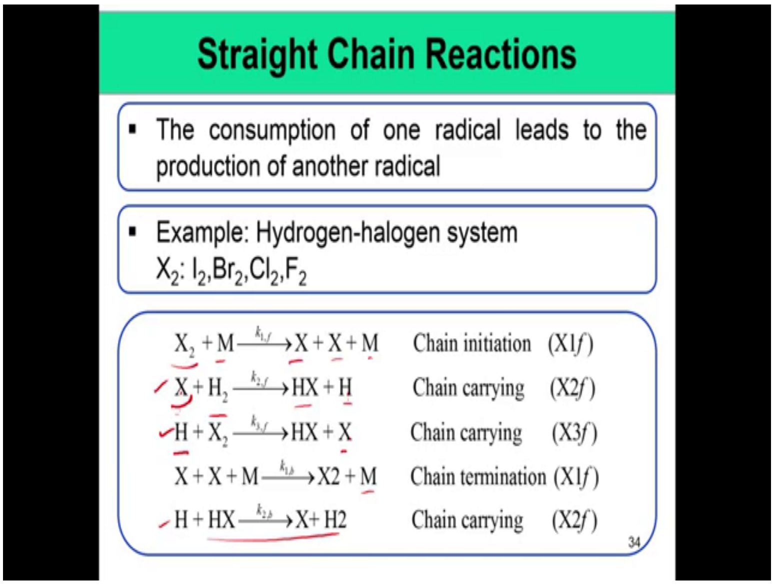

Straight Chain Reactions

- The consumption of one radical leads to the production of another radical

- Example: Hydrogen-halogen system
  X_2: I_2,Br_2,Cl_2,F_2

$X_2 + M \xrightarrow{k_{1,f}} X + X + M$ Chain initiation (X1*f*)
$X + H_2 \xrightarrow{k_{2,f}} HX + H$ Chain carrying (X2*f*)
$H + X_2 \xrightarrow{k_{3,f}} HX + X$ Chain carrying (X3*f*)
$X + X + M \xrightarrow{k_{1,b}} X2 + M$ Chain termination (X1*f*)
$H + HX \xrightarrow{k_{2,b}} X + H2$ Chain carrying (X2*f*)

Straight chain reactions straight chain what do you mean by straight chain carriers or those things are those basically the intermediaries that is formed as a result of the reaction between the reactants breaking down into forming several things. So, as I said if you are comparing if you are considering hydrogen oxygen combustion, it is nothing but your if you are considering the 2 n o 2 reaction mechanism it is nothing but this chain carriers are nothing h o o h all these things right.

Now, what is straight chain reactions? Straight chain reaction is when consumption of one radical leads to production of another radical, but one more only one radical goes to radical not more radicals. So, these are examples of hydrogen halogen systems. So, for example, you see that he chain initiation this is how the X 2 that is halogen when it attacked to the third body M (Refer Time: 27:21) into X and X and forms M this is the chain initiation and then it this x reacts with H 2 X is essentially the chain carrier which reacts with H 2 to form H X plus HX, but 1X give rise to 1H. So, another H that is formed gives rise to another X.

So, X plus X this is the termination chain termination reaction and this is once again a chain carrier reaction, but everywhere you see that these and these one X gives rise to 1H, one chain carrier gives rise to another chain carrier one chain carrier gives to another chain carrier one chain carrier gives rise to another chain carrier and they are associated with termination reaction.

So, in these reactions there is no like form a multiplication of these chain carriers; but that is very important as we will see later.

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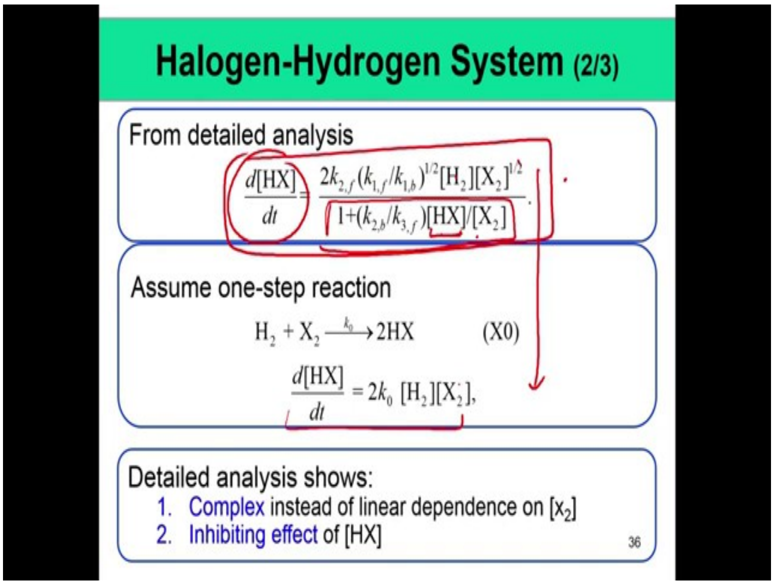

Halogen-Hydrogen System (2/3)

From detailed analysis

$$\frac{d[\mathrm{HX}]}{dt} = \frac{2k_{2,f}(k_{1,f}/k_{1,b})^{1/2}[\mathrm{H}_2][\mathrm{X}_2]^{1/2}}{1+(k_{2,b}/k_{3,f})[\mathrm{HX}]/[\mathrm{X}_2]}.$$

Assume one-step reaction

$$\mathrm{H}_2 + \mathrm{X}_2 \xrightarrow{k_0} 2\mathrm{HX} \qquad (\mathrm{X0})$$

$$\frac{d[\mathrm{HX}]}{dt} = 2k_0\,[\mathrm{H}_2][\mathrm{X}_2],$$

Detailed analysis shows:

1. Complex instead of linear dependence on $[x_2]$
2. Inhibiting effect of [HX]

So, I will not go into the details of this we can find out all these analysis and we can show that different things of the complex that that we can obtain for example, the final rate of formation of this d H X d t and compare that with the global one strip reaction, and the only that I would like to make here is that this slide shows you the importance of the consideration of the detail reactions. So, from the detailed analysis which you can if you want you can go through.

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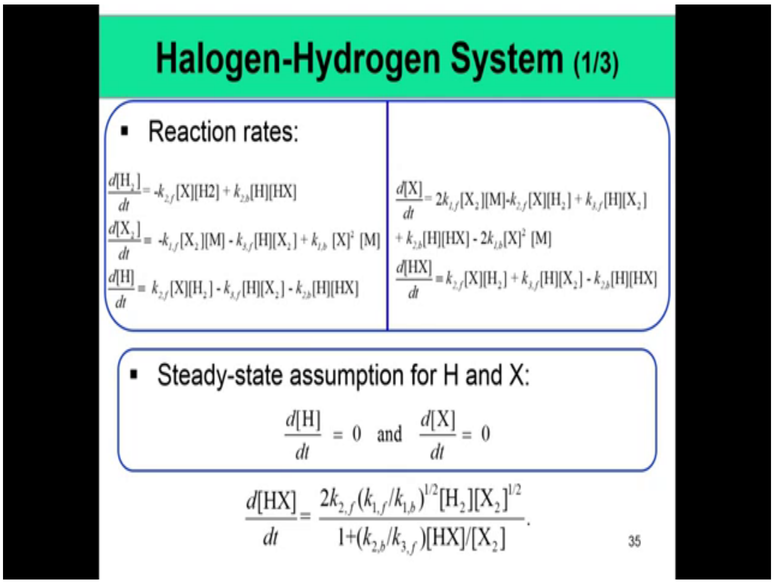

Halogen-Hydrogen System (1/3)

- Reaction rates:

$$\frac{d[\mathrm{H_2}]}{dt} = -k_{2,f}[\mathrm{X}][\mathrm{H2}] + k_{2,b}[\mathrm{H}][\mathrm{HX}]$$

$$\frac{d[\mathrm{X_2}]}{dt} = -k_{1,f}[\mathrm{X_2}][\mathrm{M}] - k_{3,f}[\mathrm{H}][\mathrm{X_2}] + k_{1,b}\,[\mathrm{X}]^2\,[\mathrm{M}]$$

$$\frac{d[\mathrm{H}]}{dt} = k_{2,f}[\mathrm{X}][\mathrm{H_2}] - k_{3,f}[\mathrm{H}][\mathrm{X_2}] - k_{2,b}[\mathrm{H}][\mathrm{HX}]$$

$$\frac{d[\mathrm{X}]}{dt} = 2k_{1,f}[\mathrm{X_2}][\mathrm{M}] - k_{2,f}[\mathrm{X}][\mathrm{H_2}] + k_{3,f}[\mathrm{H}][\mathrm{X_2}]$$
$$+ k_{2,b}[\mathrm{H}][\mathrm{HX}] - 2k_{1,b}[\mathrm{X}]^2\,[\mathrm{M}]$$

$$\frac{d[\mathrm{HX}]}{dt} = k_{2,f}[\mathrm{X}][\mathrm{H_2}] + k_{3,f}[\mathrm{H}][\mathrm{X_2}] - k_{2,b}[\mathrm{H}][\mathrm{HX}]$$

- Steady-state assumption for H and X:

$$\frac{d[\mathrm{H}]}{dt} = 0 \quad \text{and} \quad \frac{d[\mathrm{X}]}{dt} = 0$$

$$\frac{d[\mathrm{HX}]}{dt} = \frac{2k_{2,f}(k_{1,f}/k_{1,b})^{1/2}[\mathrm{H_2}][\mathrm{X_2}]^{1/2}}{1+(k_{2,b}/k_{3,f})[\mathrm{HX}]/[\mathrm{X_2}]}.$$

Once again this at the different reaction rates considering all these different 1, 2, 3, 4, 5 steps can write down the reaction rates for each of these 5 steps and then you can apply this steady state assumption and then you can find out the net (Refer Time: 29:01) of formation of the product which is for our interest that is the d H X which is the H X.

So, we see that d H X d t is given by this complex form which is this ok.

Now, the thing is that if you had considered one step reaction you would have got d H X d t is nothing but twice times k 0 which is the overall rate constant times H 2 and X 2. Now you see the big difference between these things you see exponents of H 2 and H 2 is same fine, but this is one this is half there is no H X in the there is h in the denominator here, there is no H X in the denominator here, there is X 2 in the denominator here there is no X 2 in the denominator here right. So, all these differences and this this is a little bit complicated step. So, the overall rate of formation of d H X d t which is our final product is drastically different; when you consider the detailed mechanisms or else when you consider the one step mechanism ok.

So, you see that instead of the linear dependence, here this is a half to the power of half dependence and formation of h f H X itself inhibits the reaction inhibit is a formation of H X which is not at all captured here. So, vital information is missing and this is one of the reasons why you need to undergo despite the effort and despite the computational power required to include detailed reactions in your code, we must always look forward to at least some level of details of reaction mechanisms when you do combustion calculations unless there is some specific need that it is not at all required. Now this shows you why it is required, right. Now we will talk about branched chain reaction in hydrogen oxygen system and branch chain reactions are very very important and the hallmark of combustion.

Now, why because you see here there is a very big difference between the halogen systems versus the hydrogen oxygen system, which is the combustion reactions you see three important.

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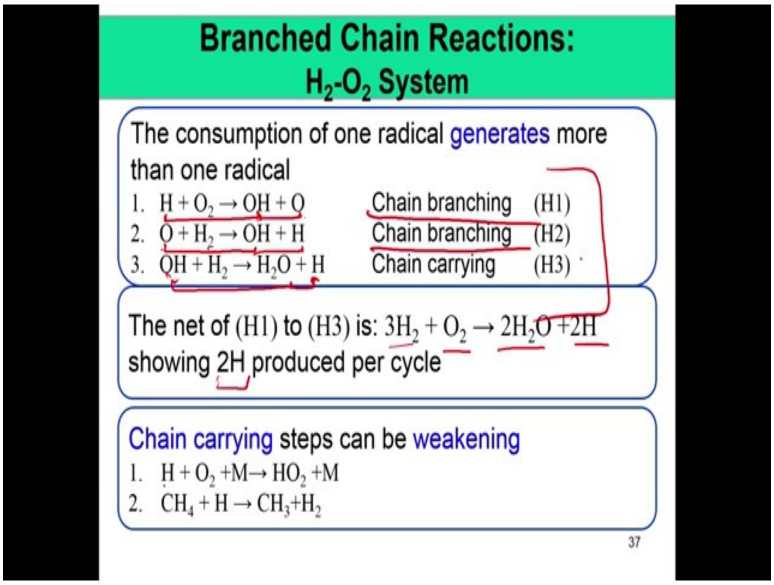

Branched Chain Reactions:
H_2-O_2 System

The consumption of one radical generates more than one radical

1. $H + O_2 \rightarrow OH + O$ Chain branching (H1)
2. $O + H_2 \rightarrow OH + H$ Chain branching (H2)
3. $OH + H_2 \rightarrow H_2O + H$ Chain carrying (H3)

The net of (H1) to (H3) is: $3H_2 + O_2 \rightarrow 2H_2O + 2H$ showing 2H produced per cycle

Chain carrying steps can be weakening

1. $H + O_2 + M \rightarrow HO_2 + M$
2. $CH_4 + H \rightarrow CH_3 + H_2$

Chain reactions involving chain carrier the most important hallmark of combustion reaction is the introduction of these chain branching reactions. Now you must remember that these chain carriers H O O H these are very high energetic molecules very highly energetic radicals. So, you see when H atoms attacks an oxygen molecule it forms OH and O. So, one radical gives rise to two radicals this is the chain branching step and that is very important one O atom when it attacks an hydrogen molecule gives rise to 2 radicals. So, here it is chain carrying one radical gives rise to another radical that is H, but here one radical gives rise to OH and another radical gives to O your one radical gives rise OH another and it gives rise to another radical H.

So, there is a multiplication of these chain carriers that is happening in these steps and of course, this does not happen in one mole it happens with series of molecules right. So, in each if there is a factor of two of involved in each reaction that is happening with many many molecules of oxygen many many molecules of hydrogen that is there. So, it each of these involved like multiplication of OH and multiplication of this chain carriers and these result in the explosive of this very rapid reactions that are involved in combustion is the chain branching reaction and also of course, the thermal nature of the reaction that which involves large Arrhenius number which confines reactions in a very short amount of time.

So, this exponential nature of this reaction rates large Arrhenius number and these things are actually contribute to the large things large very fast nature of the combustion reactions. So, you see that in this H 1 to H 3 if you can see that the next overall step three H 2 plus 2 O plus O 2 give rise to H 2 O plus 2 H which shows 2 H radicals are produced per cycle right. So, that is very very important. So, these radicals are multiplied now chain carrying steps can be weakening because you see here H plus O 2 plus M goes to form HO2 plus M and HO2 is rather (Refer Time: 33:22) rather in reactive radical which does not is not very which is not very energetic. So, it can be weakening also.

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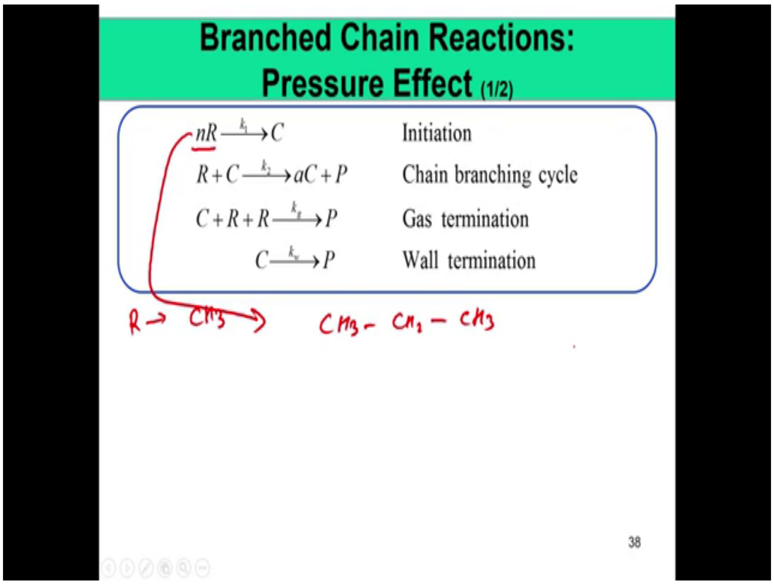

Branched Chain Reactions: Pressure Effect (1/2)

$nR \xrightarrow{k_1} C$	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

$R \rightarrow CH_3 \rightarrow CH_3 - CH_2 - CH_3$

Now, here we will consider a very generalised description of combustion reactions this is very important. Now if they we understand this we will basically understand the basic structure by which a fuel becomes a product we will consider n R what is R? R can be considered a radical like say methyl radical. So, n R means nothing but this sort of things, many number of c s t c s t c s t c s t involved or it can be like this itself where n is equal to 2 all right. So, let us consider this reaction. Let us consider how basically the combustion happens now the most important thing is that when you have this n R which is a fairly large molecule it must be broken down into small molecules. So, there must be it must broken down and it through a series of steps, it will go and form the products what are those steps.

So, you see the n R first forms a C what is C? C is nothing but a chain carrier it can be h it can be o h it can be o anything. Now this chain carrier that is formed goes and attacks R in this step. So, R plus C leads to production of more chain carriers now you would ask that this is not balanced, but here.

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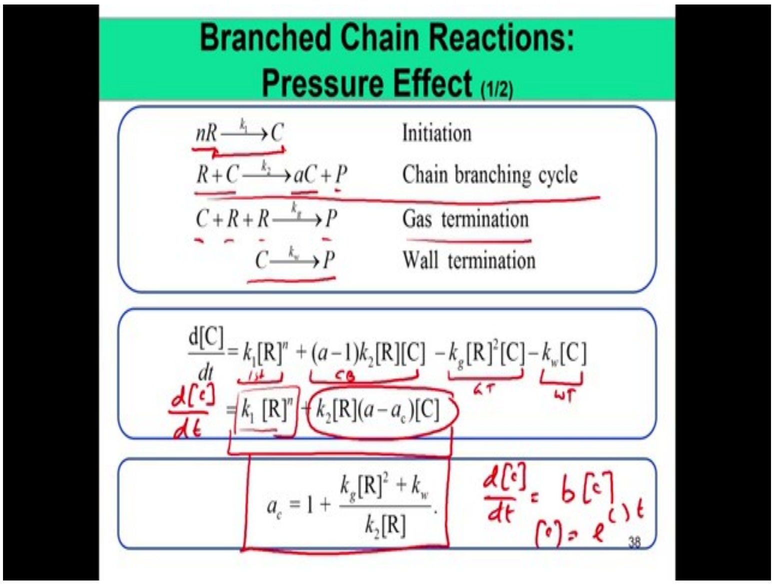

Branched Chain Reactions: Pressure Effect (1/2)

$nR \xrightarrow{k_1} C$	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

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

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

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

$$\frac{d[c]}{dt} = b[c]$$

$$[c] = e^{( )t}$$

We are talking about generalised chain carriers. So, this R can be c s t c s c s t etcetera this c can be h and this a c means there are multiple chain carriers been formed it can be h it can be it can be h plus o plus o h something like that a is a multiplication factor of the chain carrier not the species itself and (Refer Time: 35:28) is formed.

So, C then this chain carrier then attacks R plus R plus R and t basically forms products. So, you see that C is basically now absorbed to form the product that is why it is a gas termination and the previous is basically the chain branching cycle, and then this c can also go and hit a wall and it can get deactivated and that is basically the grow in form of product that is basically the wall termination.

But we can write down the full thing we can we are interested basically in the rate of change of C, and we can write down the full thing you should write it down yourself we can write down the full thing as considering all the reactions this comes from the first reaction chain carrying initiation step these carriers comes from the second reaction chain branching step a minus 1 is becomes a s-th of corresponds the production of c and minus because c is ne C is consumed. So, it is essentially a minus 1, this considers comes from the gas termination step and this comes from the wall termination step.

So, summing up all these 4 contributions we can arrive at this thing one up to the power of n plus K 2 times R times a minus a c times c. Now you see I will ask what a c is? A c is a result I mean this is resulted written in a very compact form where a c is nothing but this one this is nothing but algebra, but it is correct. So, we can be with this. So, when you write it in this form you see the benefit. So, each has got K 1 up to the power of n times 2 R and this c. So, we can write d c d t is called to this. Now you see if we just forget about this part now and just focus only on this part you will see that this is of the form d c d t id equal to some constant b times c. Now what is this form? If you solve it you will find that it is essentially becomes d lawn c d t times b d t d lawn c is equal to b d t and if you integrate that you will have c ids equal to e to the power of some things times t.

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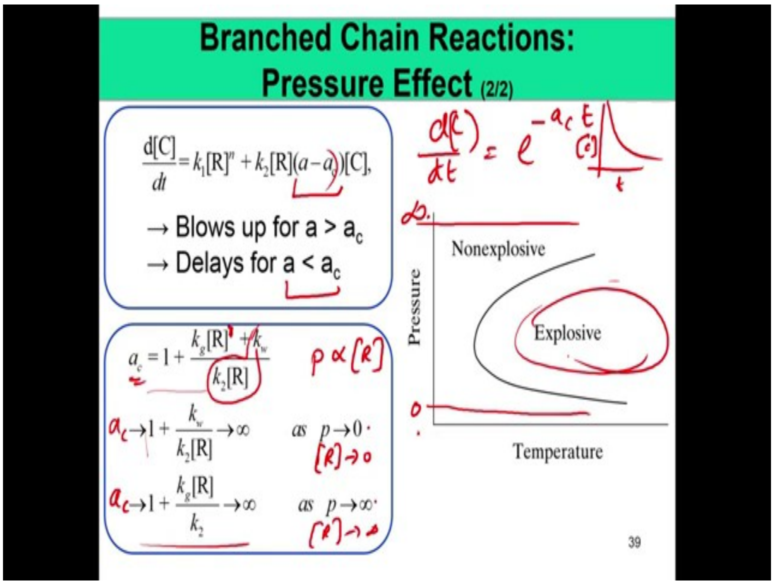

Branched Chain Reactions: Pressure Effect (2/2)

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

→ Blows up for a > a_c

→ Delays for a < a_c

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

$p \propto [R]$

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

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

$$\frac{d[C]}{dt} = e^{-a_c t}$$

So, it has got an exponential behaviour, it can have an exponential behaviour now when can a exponential blow up an exponential blow up when it is exponent is positive right. So, you see that this is essentially our exponent. So, when it when a greater than a c this this essentially blows up then c essentially the c concentration rapidly increases, and you know that when c concentration rapidly increases the reaction will proceed very very fast because c are very energetic, why as if delays or decays if a is less than a c. Now what is happening how can we find out where it will blow up and where it will not blow up we have to look into basically a c, now a c is a form 1 plus k g times R square plus k w divided by R. Now as you know we can think that as pressure increases the concentration of R increases as pressure decreases the concentration of R decreases. So, we can think that pressure is essentially proportional to R.

So, in the low pressure limit as pressure goes to 0 we can say that R also goes to 0. So, when R goes to 0 this term becomes immaterial. So, we can write a c as 1plus k w by K 2 times R this is what we get. And now if R goes to 0 a c goes to infinity of course, if a c is very large then this whole term is negative and there is no explosion that is there is no rapid increase of c and then there is no rapid increase in the overall reaction rate, whereas if p tends to infinity R also tends to infinity and a c becomes.

Now, in this case what we can write is that we can get a this in the absorbed into this and this can be neglected this part can be neglected and this becomes essentially this. So, a c basically becomes 1 plus k g times R k g times R divided by K 2. As p tends to infinity R tends to infinity this whole term tends to infinity. So, we see that both when pressure is very low when pressure is very small a c tends to infinity, since a c has a negative sign in front when a c tends to infinity the d c d t term invariably is basically becomes the form of e to the power of minus a c times t and that decays ok.

So, reaction rate of c will decay with time. So, there is no rapid explosion. So, a c can only be small in the intermediate range when p is neither too close to 0 neither too close to infinity. And that is what you see here that is when pressure is small it is no explosive non explosive means once again explosive does not have nothing to do with a blast or anything it only means that there is a rapid increase of the reactions with rapid release of energy. So, large pressure small pressure reactions are non-explosive reactions are not favoured combustion reactions are not favoured and only in this intermediate peninsula that combustion reactions are figured.

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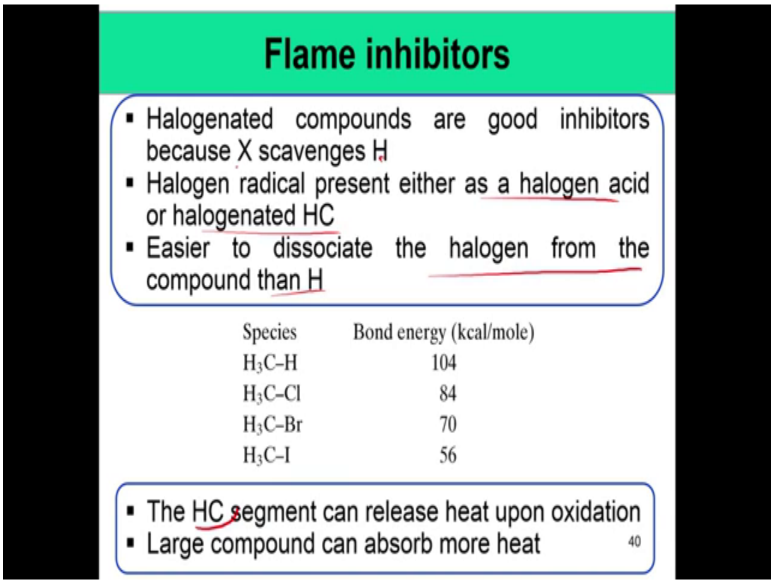

Flame inhibitors

- Halogenated compounds are good inhibitors because X scavenges H
- Halogen radical present either as a halogen acid or halogenated HC
- Easier to dissociate the halogen from the compound than H

Species	Bond energy (kcal/mole)
$H_3C–H$	104
$H_3C–Cl$	84
$H_3C–Br$	70
$H_3C–I$	56

- The HC segment can release heat upon oxidation
- Large compound can absorb more heat

We will just briefly describe the flame inhibitors that these are the halogenated compounds are good inhibitors because this halogen X scavengers hydrogen atom which is a very highly energetic basically chain carrier, when the halogen radical present either as halogen acid or halogenated hydro carbon and it is easier to dissociate the halogen from the compound than hydrogen these are the different bond energies, but you know sometimes remember that there is a hydro carbon segment which can release heat upon oxidisation.

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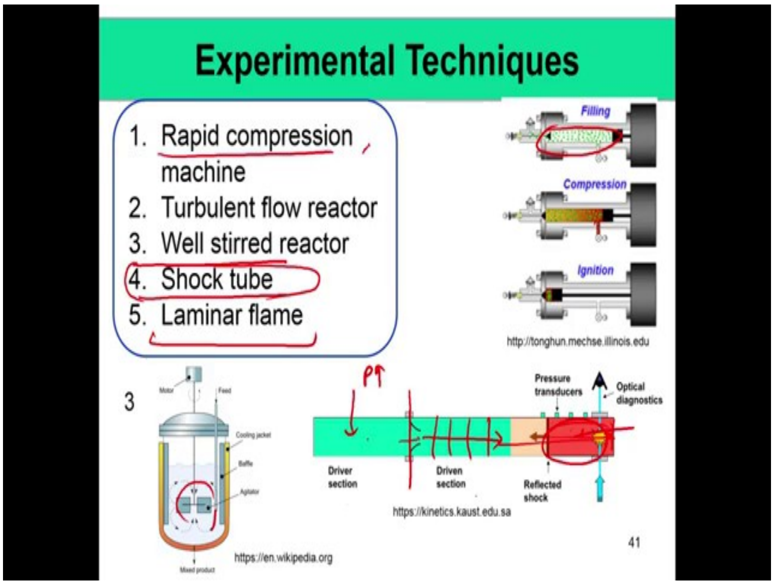

Experimental Techniques

1. Rapid compression machine
2. Turbulent flow reactor
3. Well stirred reactor
4. Shock tube
5. Laminar flame

http://tonghun.mechse.illinois.edu

https://kinetics.kaust.edu.sa

https://en.wikipedia.org

And the large compounds can also absorb more heat and finally, we have discussed lot about the theoretical derivation about of k which is very important, but these theory as you know in any branch of science the theory that you deliver that you develop or the computations that you do that has to be validated by experiments. So, those reaction rates constant must be validated by experiments either for individual reactions or for global parameters how do you do that.

So, these are few of the techniques we are few of the experimental setups actually see to which uses through which this reaction rate constants are evaluated is rapid compression machine. Rapid compression is very much like a combination spark and s i engine or a diesel engine that it fills up you, fill up this, this part of the of this rapid compression machine with this your charge with the reactant and then you compress it as the as you increase and temperature ignition happens ok.

But still there are some problems with flow effect and etcetera turbulent flow reactor is when you mix it this this reactants and you increase a feed of a hot gas switch initiate the reactions. And the most important experimental setup that has evolved for evaluating things like ignition delay which will come later or even reaction rate constants for single reactions is a chock tube. And what it has is basically it has a driver section on a reverse section driven section. So, this part has got very you fill it up and you increase the pressure at a very very high level.

So, when the pressure increases this driver section and the driven section is initially before you start the experiment separated by diaphragm. Now when the pressure increases in this driver section the diaphragm raptures, and the shock wave propagates and the shock wave propagates it hits back here it goes into the end wall this part you fill it up with a with a reactants the rate constants of which you want to measure or the ignition delay of which you want to measure.

So, in this part you fill up you fill it up with the fuel air mixture. So, the shock goes and hits this end wall and it reflects back and as you know the downstream of a shock you have got increase pressure and temperature. So, there is almost an instantaneous increase in pressure and temperature and you can by controlling the shock motion you can control the pressure and temperature that is been rise raised to and you can basically estimate you rate constant at that given temperature and pressure.

Laminar flame is also useful, but then you know the difference between the flame and this kind of reactor is that that flame involves transport it involves conduction it involves diffusion it, whereas these things that we have discussed in the shock tube even though there are some problems with recent problems that has involved with fuel and non-homogeneities, but still it is the it is as close to homogenous as possible it is one of the best methods to obtain the reaction rate constants. And because there is no only reaction is happening in a given amount of time there is no transport effects involved, but still the laminar flame is used to basically validate things like as you will see later when you can combine reaction rate and transport and obtain quantities like laminar flame speed.

But, so with this class we have covered lot of ground in the sense that we have discussed laws of mass action we have discussed basically, how to write a reaction rate in terms of the reactants raised to their stoichiometric coefficients. We have covered how basically what is the Arrhenius law, what is actually activation energy, and then we have gone onto describe the reaction rate constants which is very very important parameter in combustion research and combustion study as such, because as you will see later these will these basically determines how fast the reaction proceeds and the rate at which the if the reaction proceeds fast, you can have a liberty to design your combustor in some manner if the reaction proceeds too slow you have to redesign it in a different manner.

So, this somewhat goes into combustion engineering and design in a big manner and of course, as you will see later this rate constants have a very big revolve in how pollutants are being formed, that some pollutants performed quickly some pollutant perform slowly. So, these rate constants also determine the formation of the time scale for the formation of the pollutants and this determine whether ultimately this determine how a flame will could be stabilised inside a combustor or it cannot be stabilised inside a combustor.

So, then we have developed further mechanistic understanding of the reaction rate constants and how reactions actually take place we have gone onto describe two kinds of theories; which is a collision rate theory which is a collision theory, and the transition state theory. And also we have discussed unimolecular reactions how pressure can affect reactions and the two high pressure limit the low pressure limit. And then we have gone onto describe this generalised behaviour of combustion reactions, where which highlights that in combustion the very important part is this chain branching cycle alongside this large activation energy.

So, these large activation energy on this chain branching these are the two most important hallmarks of combustion science, and we need to determine the experimental also and that we have seen that where this rapid compression machine and shock tubes and these are the most important techniques by experimental setup where which these parameters can be determined.

So, thank you we will meet again and there we will discuss the oxidation mechanism of fuels, where we will use these kinetic principles to discuss actual reactions that happen in combustion reaction.

Thank you very much.