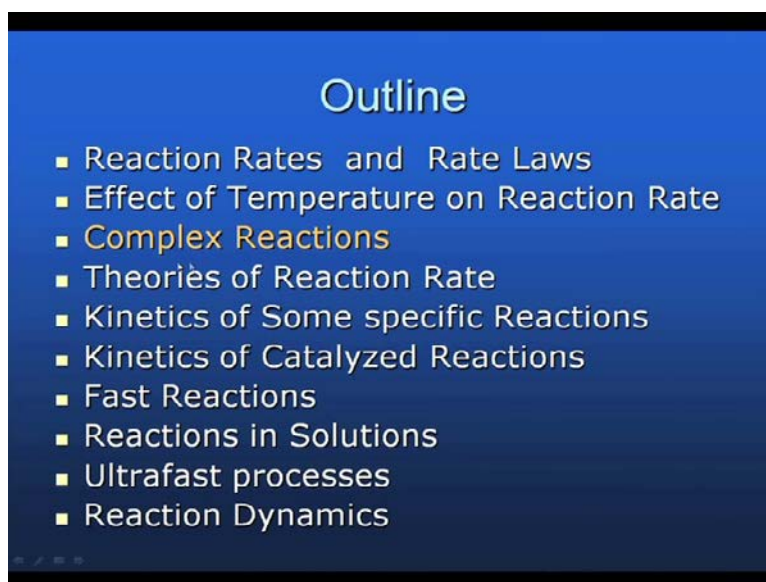


Rate Processes
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Module No. # 01
Lecture No. # 06
Complex Reaction (Contd.)

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Hi, good morning everybody, so today we will continue with complex reactions last lecture was also on complex reactions. So, we will, we will you know talk about some more aspects of complex reactions.

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Complex Reactions

An elementary reaction is a chemical reaction in which one or more of the chemical species react directly to form products in a single reaction step

$$\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr}(\text{g})$$
$$\begin{aligned} \text{Br}_2 &\rightarrow \text{Br} + \text{Br} \\ \text{Br} + \text{H}_2 &\rightarrow \text{H} + \text{HBr} \\ \text{H} + \text{Br}_2 &\rightarrow \text{Br} + \text{HBr} \\ \text{Br} + \text{Br} &\rightarrow \text{Br}_2 \end{aligned}$$

In kinetics, a 'complex reaction' simply means a reaction for which mechanism comprises of more than one elementary steps. Here we will focus on a range of different complex reactions.

The types of complex mechanisms are: consecutive (or sequential) reactions; competing reactions; pre-equilibria; unimolecular reactions; enzyme reactions; chain reactions; explosions.

Now, like we talked about consecutive reaction and competing reactions. Now, today we will talk about you know this pre equilibria then may be unimolecular reactions and how to treat these complex reactions. So, there are various you know ways to treat these reactions I mean theoretically.

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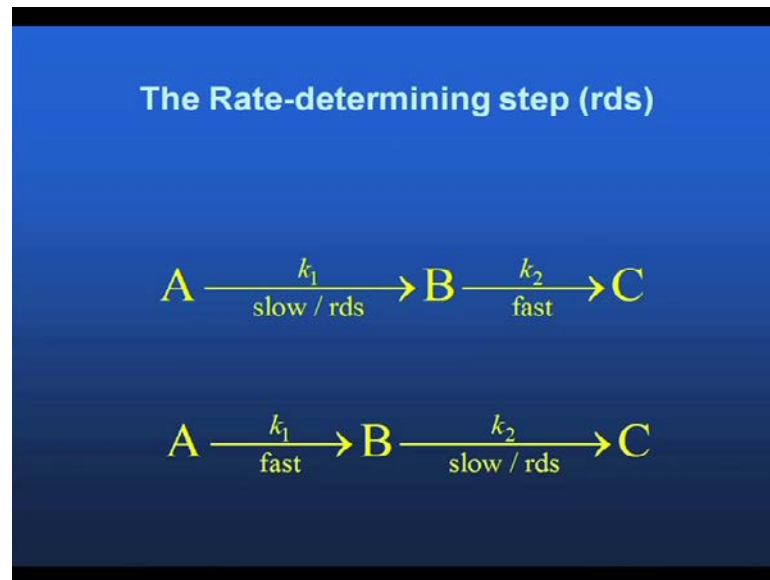
Complex reactions

- **Treatment.....**
 - Rate-determining step
 - Pre-equilibrium state
 - Steady-state

So, basically you know in treating with complex reactions there are things that are to be taken into consideration.

One is called the concept of rate determining step; that is the step that is an elementary step, which determines the overall rate of the reaction, so that is called the rate determining step. Another is the pre equilibrium state and also another thing which is called the steady state approximation, so we will take up these issues one after another.

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So, what is a rate determining step now in short it is called r d s. So, a complex reaction suppose we have a complex reaction of the form A to B to C. Now, of which this first step is you know rate constant is k 1 and the last step is having the rate constant k 2 and among these two steps the A 2 step is slower one and B 2 state is the fast one that is it occurs very fast means it does not take time.

So, this slow step is the bottle neck for the process you know if the bottle neck is you know narrow then if you think of flux going out of the bottle, so if the bottle neck is reduced, I mean bottle neck diameter is reduced then out going flow will be less. So, it does not really matter at what rate it is being, there is inside is being filled up suppose there is an inlet and there is an outlet, so inlet is having A say A constant diameter and there is an outlet whose diameter can be varied, so if you change the diameter of the outlet keeping the inlet diameter fixed for a bottle may be having to you know openings. So, in that case this outgoing diameter is the determining factor for the overall output of the process.

So, A to B to C this is you know it is the fast step is the slower one, so it is called the rate determining step situation can be different that is A to B is the fast and B to C is A slow or rds.

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Example

$2A + B \rightarrow \text{Products}$

- Mechanism
 - $A + B \xrightarrow{k_1} C$
 - $C + A \xrightarrow{k_2} D$ (slow)
 - $D \xrightarrow{k_3} F$ (fast)
 - $F \xrightarrow{k_4} P$ (fast)
- second step -- rate-determining

$$\frac{dc_P}{dt} = k_2 c_C c_A$$

So, let us have an example that 2A plus B producing or giving rise to products and if the mechanism of such A process is like A plus B giving rise to C.

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$$\begin{array}{l}
 A + B \xrightarrow{k_1} C \\
 C + A \xrightarrow{k_2} D \text{ (slow)} \checkmark \\
 D \xrightarrow{k_3} F \text{ (fast)} \\
 F \xrightarrow{k_4} \text{Prod (fast)}
 \end{array}$$

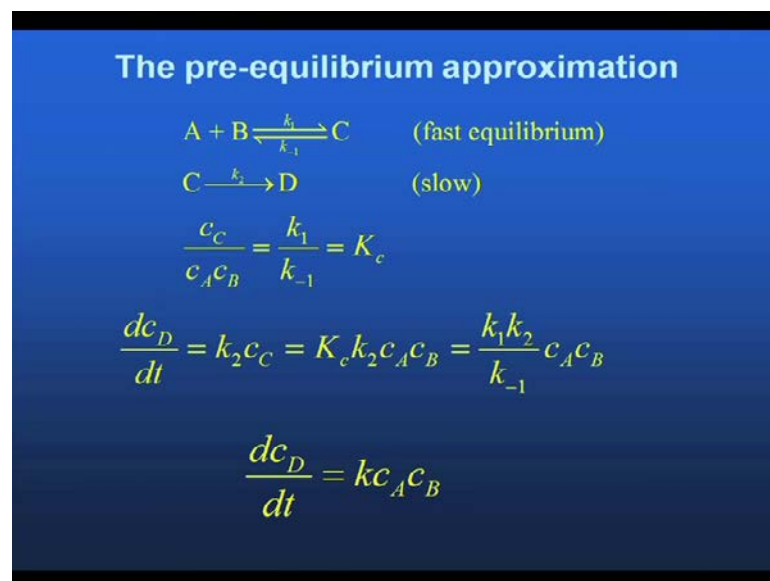
$$\frac{d}{dt} C_P = k_2 C_C C_A$$

So, A plus B giving rise to C with A rate constant k 1 is C plus A with k 2 giving rise to D then D with k 3 giving some F then F with k 4 giving rise to product

both are fast, so this step is the rate determining step so overall rate of reaction will depend on this particular step.

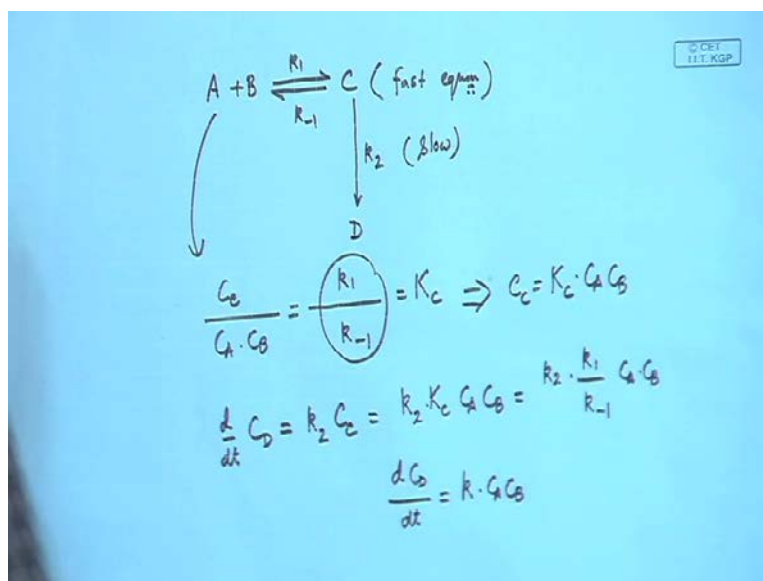
So, this is an elementary step so there are 4 steps 1, 2, 3, 4 of which each and every one corresponds to one elementary step. So, this is one elementary step for which the rate it is the slowest process, so therefore, rate of formation of the product $\frac{dC}{dt}$ of product for concentration of p is equal to $k_2 C$ concentration of C into concentration of A into concentration of A therefore, elementary steps in elementary steps number of species which are involved in this elementary step should come into the rate equation. So, this elementary step is A is A second order process already we regarded as A by A molecular process or by species process, so $\frac{dC}{dt}$ is your $k_2 C C$ into C A d this being be you know the rate determining step.

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Now, what is the pre equilibrium concept? Pre equilibrium concept is that like.

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Let us have the have A have A some example that A plus B giving rise to C, but this is an equilibrium process, so k_1 k_{-1} is the reverse rate constant and k_1 is the forward rate constant, so this the fast equilibrium so this equilibrium is established very fast then the C undergoes for the reaction with k_2 producing d and this is the slow slowest step. So, equilibrium constant for this particular state where the fast equilibrium has been established is your C C divided by C A into C B of course, under dilute solution approximation because, if it is A concentrated solution then you have to invoke the concept of activity. So, C C divided by C A into C B is k_1 divided by k_{-1} is equal to K_c it is A concentration equilibrium constant, so rate of formation of your product d d t of C d will be k_2 times C C why k_2 times C C because, in this particular elementary step this product is formed with A slow slowest you know rate; that means, this is the rate determining step so rate kinetics of rate determining step is the deciding factor.

So, rate equations should include this particular step because other steps are basically you know all on A sudden it happens very fast, so the whole process that is the speed of the whole process will depend typically on this particular step therefore, d d t of C C d is equal to k_2 into C C C k_2 times C C is equal to k_2 then C C is equal to this gives you C C is equal to k_2 into C C concentration equilibrium constant into C A C B, so that is you just plug in this. So, k_2 into k_2 into C A into C B that is equal to k_2 into k_1 by k_{-1} this is in A equilibrium constant is this, so you just plug in this over here equal to C into C A into C B.

So, this is A overall you know these 3 are constants rate constants at a given temperature as long as temperature is fixed you know, so these three you know rate constants are constant that is they do not change therefore, dC/dt is equal to A overall constant k into $C^A C^B$. So, although you know it is the fast equilibrium, but the overall rate will depend on the concentration of A and the concentration of B.

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■ Derive the rate law for the following reaction in which steps 1 and 2 are in equilibrium, step 3 is a rate-determining step

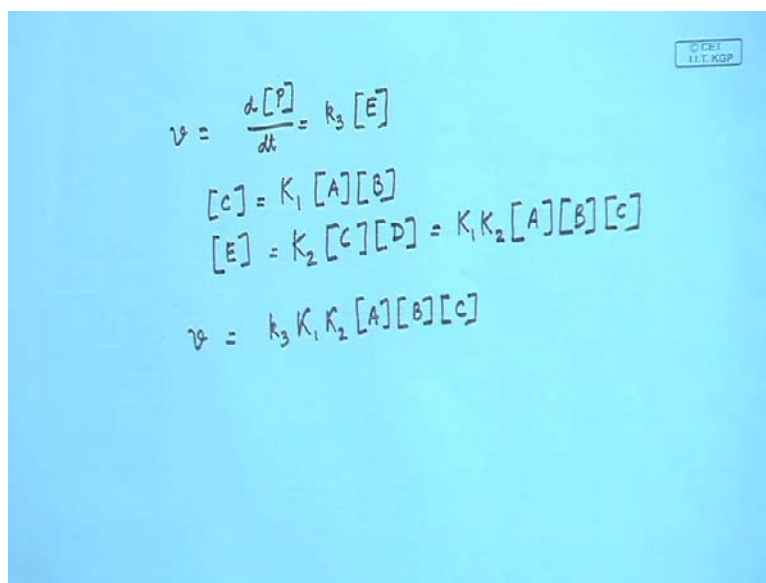
(a) $A + B \rightleftharpoons C \quad K_1$
 (b) $C + D \rightleftharpoons E \quad K_2$
 (c) $E \xrightarrow{k_3} F \quad (\text{slow})$
 (d) $F \xrightarrow{k_4} P$

■ **Solution**

$$v = \frac{d[P]}{dt} = k_3[E]$$

Now, let us have some concrete example another example that is derive the rate law for the following reaction of which there are you know four elementary steps of which steps 1 and 2 are in equilibrium that is these are equilibrium steps these two steps A and B with equilibrium constant K_1 and K_2 then third step with rate constant K_3 is the slowest one. So therefore, this is your rate determining step and d is the product formation also this is fast it is not mentioned means, it is fast compared to this one.

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So, that means, product formation rate that is velocity is equal to d product $d t$ is equal to K_3 into E because, you know because, here, this is the slowest step, so this is your product, so its since this happens fast therefore, your product formation will depend on this step therefore, $d d t$ of product formation is nothing, but the nothing, but K_3 into concentration of E and concentration of C will be equal to K_1 into $A B$ that is from the equilibrium constant and also E concentration of E is equal to K_2 times C times d is equal to $K_1, K_2 A, B, C$ therefore, velocity is equal to your $K_3, K_1, K_2, A B$ and C . So, basically you see that it is A overall third order reaction that is three concentration terms involved for this particular you know mechanism.

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The steady-state approximation

- The **steady-state approximation**

$$A \xrightarrow[\text{slow}]{k_1} B \xrightarrow[\text{fast}]{k_2} C$$
$$\frac{dc_B}{dt} = 0$$

Next we will move on to steady state approximation what is meant by steady state approximation.

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$A \xrightarrow[\text{slow}]{k_1} B \xrightarrow[\text{fast}]{k_2} C$

$$\frac{dC_B}{dt} = 0$$

$2N_2O_5 \rightleftharpoons 2NO_2 + O_2$

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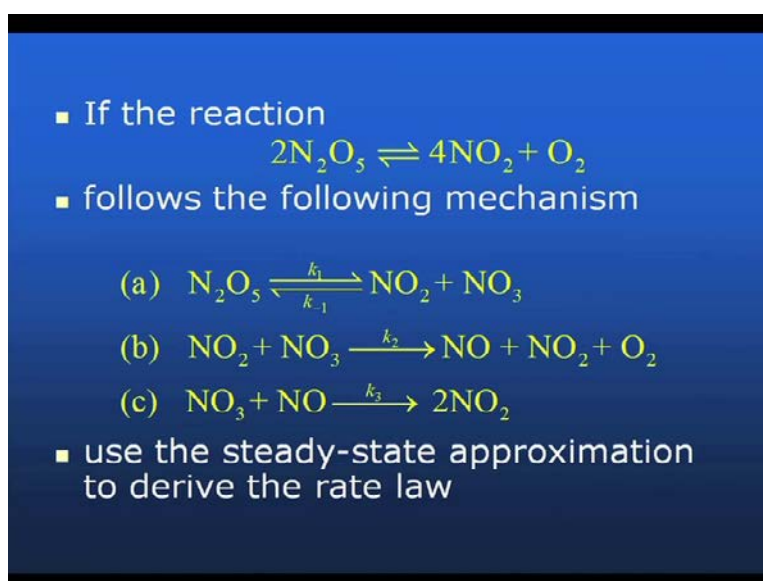
Now, again consider A 2 step process A to B to C of which this is k_1 , this is k_2 , this is slow rds and this is fast, so that means it is produced that is B is produced from this that is slower rate and then it is depleted to give rise to C. So, steady state approximation means that as if for at least for certain period of time the concentration of B does not

change recall the you know consecutive reaction discussion that it is like you know it is going like this and then it is decaying.

So, this is you know the time when this is maximum, so you this concentration of B, C, B is maximum. Now, you see that in this vicinity of time the concentration of B is not changing A lot that means, for this period of time you may think that the concentration of B is not changing although if you think of the whole time course then you will be seeing that at the end the product is primarily, I mean the reaction product is primarily composed of C, but for certain period of time the concentration of B is remaining constant.

So, that means it remains steady with time does not change, so that is called the steady state approximation, so $\frac{dC_B}{dt}$ under steady state condition is equal to zero that means, concentration of the B is not changing with time, so that is called your steady state approximation.

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- If the reaction
$$2\text{N}_2\text{O}_5 \rightleftharpoons 4\text{NO}_2 + \text{O}_2$$
- follows the following mechanism
 - $\text{N}_2\text{O}_5 \xrightleftharpoons[k_{-1}]{k_1} \text{NO}_2 + \text{NO}_3$
 - $\text{NO}_2 + \text{NO}_3 \xrightarrow{k_2} \text{NO} + \text{NO}_2 + \text{O}_2$
 - $\text{NO}_3 + \text{NO} \xrightarrow{k_3} 2\text{NO}_2$
- use the steady-state approximation to derive the rate law

So, consider a concrete reaction say dinitrogen pentoxide into O 5, giving rise to 2 into O 5 giving rise to 2 NO 2 plus O 2, so it follows the following mechanism the first step is that N 2 O 5, you know this is an equilibrium NO 2 plus NO 3 then NO 2 plus NO 3 with k 2 giving rise to N O, plus NO 2, plus O 2 then N O 3 plus N O to give you NO 2. So, we have to use or we have to employ the concept of steady state approximation for two species, so two species to find out the overall rate law.

See you see that this is one species and may be this is another species for which we can apply the steady state approximation, so NO and NO₃ so NO₃ and NO. So, we have to apply a steady state approximation for NO and NO₃ to find out or to derive out the rate law. So, steady state approximation this is basically this approximation is applied to a species which are generally reactive, so this is one reactive species and this is another reactive species, because actually this is an intermediate they do not really have any existence in you know existence means at the end of reaction you do not find any anything of this sort like NO₃ and NO, but you will be getting you will be getting NO₂ and O₂.

So, that is why we have to apply actually we are applying steady state approximation to these two species.

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■ NO and NO₃ are intermediates...
Applying steady state approximation on these two----

$$\frac{d[\text{NO}]}{dt} = k_2[\text{NO}_2][\text{NO}_3] - k_3[\text{NO}_3][\text{NO}] = 0$$

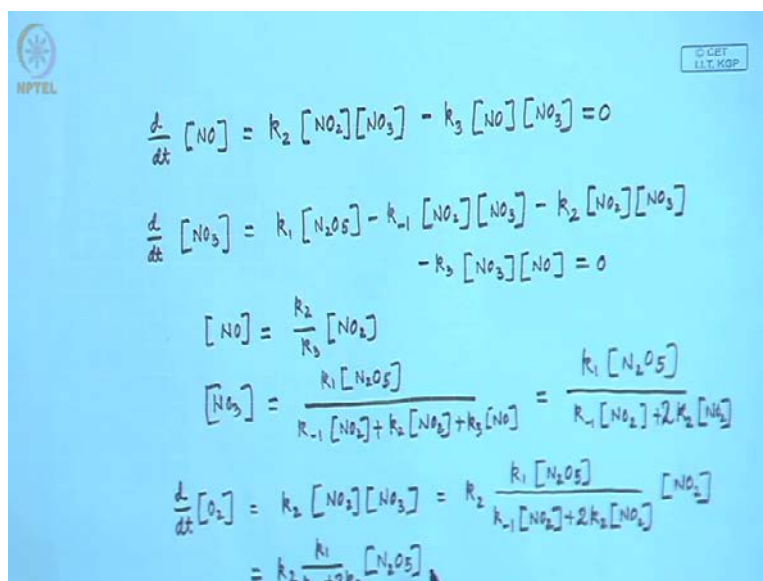
$$\frac{d[\text{NO}_3]}{dt} = k_1[\text{N}_2\text{O}_5] - k_{-1}[\text{NO}_2][\text{NO}_3] - k_2[\text{NO}_2][\text{NO}_3] - k_3[\text{NO}_3][\text{NO}] = 0$$

$$[\text{NO}] = \frac{k_2}{k_3} [\text{NO}_2]$$

$$[\text{NO}_3] = \frac{k_1[\text{N}_2\text{O}_5]}{k_{-1}[\text{NO}_2] + k_2[\text{NO}_2] + k_3[\text{NO}]} = \frac{k_1[\text{N}_2\text{O}_5]}{k_{-1}[\text{NO}_2] + 2k_2[\text{NO}_2]}$$

So, when we apply steady state approximation to this two species.

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Then, we get you know the following expressions. $\frac{d}{dt}$ of of NO nitric oxide is equal to, so where to get it you just try to find out where NO is produced and NO's may be used up.

So, here NO is produced and here NO is used up, so NO is produced means so later formation of NO₂, so that means, k_2 into it is an elementary step. So, you know you can directly write these concentration terms into your rate equation, so that means two concentration terms will be involved in this rate equation of production of NO, so that means NO₂ then NO₃ and here this is used up that is it you know used up to produce some other product, so that means, that means here it should come with A negative sign, because it is depleted so that means minus k_3 into NO, NO₃. So, you put this equal to zero that means, you are you are invoking steady state approximation on to this that is with time the concentration of NO does not change the same way $\frac{d}{dt}$ of NO₃.

So, let us go back again NO₃, so this NO₃ is produced with A forward rate of k_1 and it is used up **it is used up** to get N₂O₅ back with k_{-1} that means, from this equation you should be having **you should be having** 2 terms k_1 into 5 minus k_{-1} NO₂ NO₃, k_1 into 5 minus k_{-1} NO₂ NO₃, so k_1 into O₅ minus k_{-1} NO₂ NO₃ still other terms are there so NO₃ so NO₃ here it is again used up so therefore, it should come in a negative sign, so minus it is an elementary reaction so you can use directly the

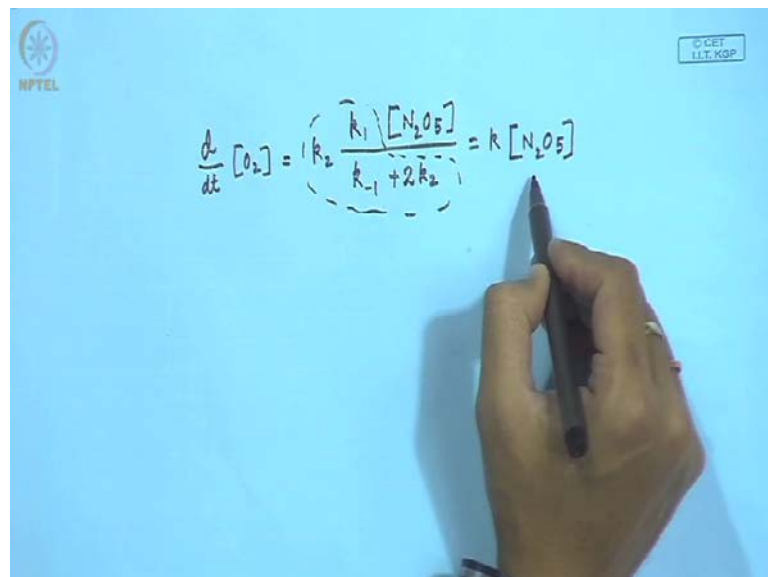
concentration terms NO_2 NO_3 because it is depleted and here again NO_3 is depleted with k_3 , so minus $k_3 \text{NO}_3$ NO so there are 4 terms, so you again put this to zero.

So, this gives you concentration of NO to be equal to after simplification k_2 by $k_3 \text{NO}_2$ and concentration of NO_3 it is a reactive intermediate, so that is equal to $k_1 \text{N}_2\text{O}_5$, that means from these 2 simultaneous equations from these 2 that is these 2 simultaneous equations you should find out the concentration of NO and NO_3 , so N_2O_5 divided by $k_{-1} \text{NO}_2$ plus $k_2 \text{NO}_2$ plus $k_3 \text{NO}$ and that gives you $k_1 \text{N}_2\text{O}_5$ divided by $k_{-1} \text{NO}_2$ plus $2k_2 \text{NO}_2$.

So, the all these we have got as A result of application of steady state approximation therefore, rate of formation of O_2 , so $\frac{d}{dt}$ of O_2 go back to, so rate formation of O_2 , so rate of formation of O_2 is here you see rate of formation of O_2 is here is equal to k_2 into concentration of NO_2 and concentration of NO_3 , so therefore, $k_2 \text{NO}_2$ concentration of NO_3 , concentration of NO_3 is from here concentration of NO_3 is from here means $k_1 \text{O}_5$ divided by $k_{-1} \text{NO}_2$ plus $2k_2 \text{NO}_2$ times NO_2

So, this gives you this gives you $k_2 k_1 k_{-1}^{-1} + 2k_2$ plus $2k_2$ into O_5 .

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So, we can write $\frac{d}{dt}$ of O_2 equal to $k_2 k_{-1}^{-1} + 2k_2$ $k_1 \text{O}_5$, so these together we can write as A constant k into N_2O_5 , so therefore, you see that rate of formation of O_2 is proportional to the concentration of nitrogen pentoxide. So basically you know

this from this although you see that its stoichiometry is 2 into O 5 plus giving rise to 4 N O 2 plus O 2, but it is you know rate of production of O 2 is only first power of the concentration of N 2 O 5.

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Unimolecular reactions

- Lindemann showed in 1921 how a bimolecular collision mechanism could lead to first-order overall rate law

$$A + A \xrightleftharpoons[k_{-1}]{k_1} A^* + A$$

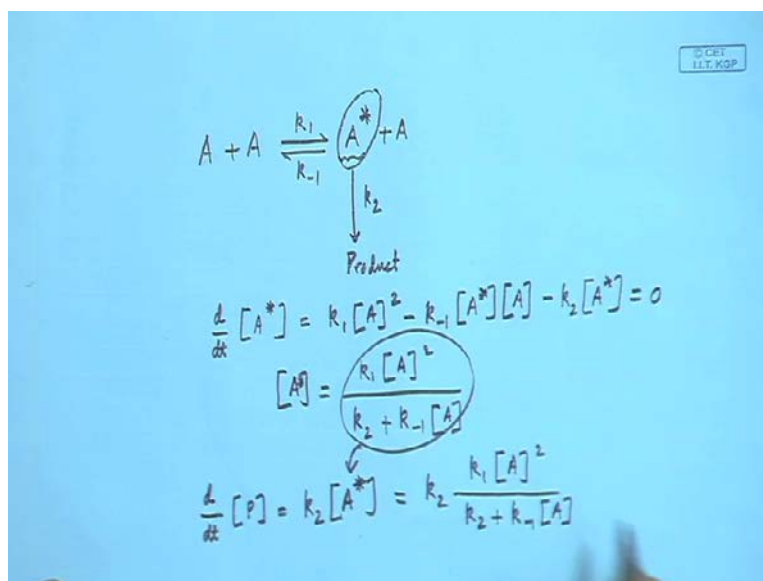
$$A^* \xrightarrow{k_2} \text{Product}$$

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*] = 0$$

$$[A^*] = \frac{k_1[A]^2}{k_2 + k_{-1}[A]}$$

Next we will move on to unimolecular reactions, so this is called the unimolecular mechanism which is which was proposed by Lindemann in 1921. So, how A bimolecular collision mechanism could lead to A first order overall rate law that was first showed by Lindemann in 1921, so the mechanism goes as like A plus A, so it is a collision process it is A bimolecular collision paramolecular is again a phenomenon of list probability, but bimolecular collision is possible that is one molecule is reacting with another molecule of same kind or one atom is reacting with another atom of same kind it is called a you know bimolecular collision.

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So, A plus A so there is an equilibrium like a pre equilibrium k minus 1 A star plus a, so it is energetically A star means it is energetically in a different state, energetically in an advantageous position to undergo reaction further to give you the product, so energetically it is A its A favourable situation.

So, basically you know collision means as a result of translation motion and temperature is a measure of mean random translational kinetic energy, so at a given temperature these molecules will have in gas phase these molecules will have you know some translational energy and they will move here and means to and fro inside the container sometime they will you know hit the wall or maybe they will make collision, so in that particular collision means, the collision. Which I am talking about that is the collision between two molecules these two molecules. So, this will lead to generation of an energetically excited it may be you know vibrationally excited or may be something else, so excited molecule of course, with one molecule of the same kind as the starting one and then this A star will undergo reaction to give you product to give you product with rate constant k_2 .

So, basically this is a quick equilibrium between you know unexcited and excited and unexcited case, so these two are unstarred and one star and here one unstarred and then this starred species is thought to be responsible for giving rise to the product. So, this is the concept of Lindemann which was you know put forward in 1921, that in a

bimolecular collision process you know a overall first order reaction may result it is a bimolecular you know gas phase I mean, it is a gas phase reaction, so $\frac{d}{dt}$ of A star. So, rate of you know depletion of A or may be how time rate of you know change of a, so it is basically you know formation rate of formation is k_1 , so since this is one elementary step this is another elementary step so k_1 into A square, because A is coming two times that is why A square minus k_{-1} A star into A, k_{-1} A star A minus why minus because, it is depleted this side also it is depleted and here also it is depleted.

So, k_2 A star, so this your you know this is your step for giving rise to the product, so therefore, if you apply steady state approximation on to this reactive specie again we want to apply steady state approximation to this reactive species then we have to put this to zero. So therefore, that means this one this species is steady that is the concentration of this species is steady with time therefore, concentration of A star A star is equal to k_1 A square divided by k_2 plus k_{-1} into a, so reactive species concentration has got you know A square term in the numerator and also there is a denominator term with which is a first power of A, so the numerator has got a square dependence and denominator has got it to the power 1 dependence, so it will give rise to some peculiar feature that I will talk about in the next slide.

So, your product formation $\frac{d}{dt}$ of product formation is equal to k_2 into concentration of A star, so you just plug in this over here this gives rise to k_2 times k_2 times k_1 into A square divided by k_2 plus k_{-1} into A.

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Lindemann....contd..

$$A + A \xrightleftharpoons[k_{-1}]{k_1} A^* + A$$
$$A^* \xrightarrow{k_2} \text{Product}$$
$$\frac{d[P]}{dt} = k_2[A^*] = k_2 \frac{k_1[A]^2}{k_2 + k_{-1}[A]}$$

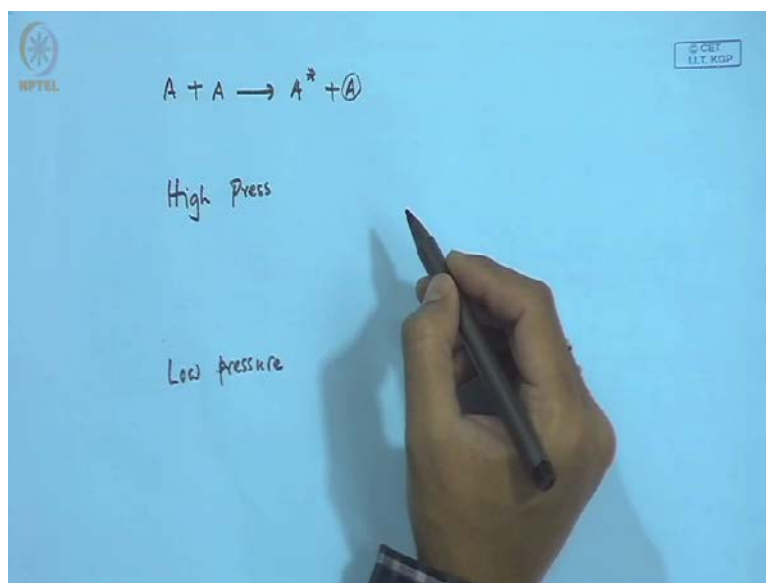
There is a time lag between the activation and the decomposition step. In that time the activated molecules arrange themselves to configuration favourable for product formation. But most of the activated molecules lose their energy through collisions. Only a very little fraction have energy with suitable configuration to undergo reaction

High pressures: Collisional deactivation of A* is more likely than unimolecular reaction, k' reduces to $k_1 k_2 / k_{-1}$ and the reaction is truly first order in A

Low pressures: Bimolecular excitation is the rate determining step; once formed A* is more likely to react than get collisionally deactivated. The rate constant reduces to $k' = k_1[A]$ and the reaction is second order

So, recall this one that your A plus A fast equilibrium giving rise to A star plus A then A star is undergoing A further reaction to give you product with rate constant k 2. Now, we have to consider one aspect that there is a time lack between the activation, so this process is activation and decomposition step, so as soon as it is produced it does not undergo further reaction, but there is a time lag that means, there is a time difference between these two steps. So, in that time these activated molecules arrange themselves to a configuration. Configuration means in a definitive you know arrangement of atomic atoms or molecule or you know parts of the molecule. In such a way which is favourable for product formation that means, they are rearranging them self in A proper way I mean within the molecule in this time lag means time lag between your activation and product formation, what is happening that these excited molecules this A star molecule they are reorganising themselves within the molecule such that you know it gives rise to products, but one point must be considered that most of the activated molecules these activated molecules most of the activated molecules means most of the A star molecules.

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So, produced due to collision between A and a, so these activated molecules most of the activated molecules they lose their energy through further collision may be collision with A second molecule but only a very little fraction of this overall A star have energy with suitable configuration to undergo reaction giving rise to product. So that means, say hundred A star molecules are produced as a result of collision of which major fraction is getting deactivated that may be a little fraction may be 10 to 15 percent of the total population remains and giving rise to products.

So, let us divide the whole course of the process into two regions one is high pressure region high pressure and the other one is low pressure region, so high pressure region means collisional deactivation is more likely why collisional deactivation is more likely because pressure high means these molecules are these gaseous molecules pressed from outside. So, that they come close to each other closer to each other this means that this they are coming close to each other means they have the larger probability they have the larger probability of being of being or having collision with another molecule another you know excited molecule, so that means collisional deactivation of A star is more likely than unimolecular reaction, so this unimolecular this is an unimolecular reaction.

So, collisional deactivation to give you A and A is more likely because you know they are coming close to each other they are coming close to each other as a result of high pressure, so as a result of high pressure means they are close and therefore, they'll

collide you often therefore, one A star molecule suppose this is an A star molecule, so moment it collides with another you know common molecule then its excitation is lost, so it becomes like this becomes a normal molecule.

So, high pressure collision in high pressure region collisional deactivation of A star is more likely than unimolecular reaction that is A star to product therefore, your k prime is reduced to k prime is reduced to $k_1 k_2$ divided by k minus 1 and the reaction is truly A first order I mean this reaction becomes A fast order process that is this one this one becomes important than this one as I told you that state is less likely A compared to this step when pressure is high that means, you can neglect this term and this gives rise to A constant of this form $k_1 k_2$ divided by k minus 1.

What happens to low pressure now for low pressure, so what is happening low pressure means this gas is rarefied gas is rarefied means they are you know put apart these molecules are put apart from one another that means, collisional probability becomes less. So, what is happening that if there is a collision, that collision could be termed as the effective collision for further reaction to take place because once this collision is happening in under low pressure then may be this molecule is getting time to move around here and there because it is not having any further collision to get deactivated. So, it is moving here and there and during that time this molecule is rearranging internally to a proper configuration that is suitable for giving rise to product that is why you know this bimolecular excitation process this one this bimolecular excitation process under low pressure condition is the rate determining step.

So, once it is formed it has got a high probability of undergoing this reaction rather than collisional deactivation giving rise to A plus A and under that condition your rate constant or the process becomes a second order.

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$A + A \xrightleftharpoons[k_{-1}]{k_1} A^* + A$
with: $A^* \xrightarrow{k_2} \text{Product}$

At high pressure: $A + A^*$ collisions likely-- so deactivation is fast:
unimolecular step is the slow step, should be first order

- At high pressure-- $[A]$ is large $k_2 \ll k_{-1}[A]$

$$\frac{d[P]}{dt} = \frac{k_1 k_2}{k_{-1}} [A] = k[A]$$

At low pressure: $A + A^*$ collisions unlikely--so will get slow deactivation:
should be second order reaction

- At low pressures-- $k_{-1}[A] \ll k_2$

$$\frac{d[P]}{dt} = k_1 [A]^2$$

So, let's again try to understand it $A + A$ giving rise to $A^* + A$ with k_1 k_{-1} then A^* giving rise to product at high pressures $A + A$ collisions likely, so deactivation is fast unimolecular step is the slow step. So, this is the slowest step because, this is the first one the $A + A$ under high pressure condition is the fast step it occurs very fast therefore, at high pressure your effective concentration of A is large and therefore, you can neglect you can neglect k_2 compared to $k_{-1} k_{-1} A$ and therefore, the expression for the overall product formation rate is reduced to $k_1 k_2$ divided by k_{-1} which is nothing but equal to some constant times the concentration of A that means, it is first order with respect to A , so under high pressure condition only one molecule is involved in the overall rate equation.

At low pressure $A + A^*$ collision is unlikely, so this collision is unlikely, so it'll get slow deactivation the molecule or the starred molecule gets more time, so that means it gets more time means you know this step this step is less compared to I mean this expression this has got less value compared to k_2 therefore, I mean this is less than k_2 means you can neglect this, so neglecting this the rate of formation of the product is equal to becomes equal to $k_1 A^2$. So, this is basically A second order, so under low pressure condition it is A second order or its A its A its A^2 molecule process I mean you know 2 molecules are involved 2 concentration terms are involved in the rate equation. So, you see peculiar feature of such A kinetics scheme is that I mean kinetic expression rate equation that if you, if you modulate these 2 terms I modulate means if

you can make this term predominate over here over this k_2 or may be if you can make this term predominate I mean more than this term then your kinetics or the overall rate equation becomes different under high pressure condition it is to the power one in A and under low pressure condition it is square.

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The slide contains the following mathematical expressions:

$$\frac{d[P]}{dt} = k_2[A^*] = k_2 \frac{k_1[A]^2}{k_2 + k_{-1}[A]}$$

Rewriting as

$$\frac{d[P]}{dt} = k' [A]$$

$$k' = \frac{k_2 k_1 [A]}{k_2 + k_{-1} [A]}$$

$$1/k' = 1/k_1 [A] + k_{-1} / k_1 k_2$$

The graph shows a linear relationship between $1/k'$ and $1/[A]$. The x-axis is labeled $1/[A]$ and the y-axis is labeled $1/k'$. An arrow labeled "high pressure" points to the right along the x-axis.

Therefore so, what is the evidence that this is happening, so again recall this expression recall this expression that $d p d t$ is equal to k_2 into $A d p d t$ is equal to k_2 into a . So, that is k_2 times $k_1 A$ square divided by k_2 plus $k_{-1} A$ it is very simple that I already told many times, so you can write you can write, you know this overall rate expression like this. Means in terms of the first power of A why I am writing in terms of first power because, you see A to the power one it is a. So, at least it will be A A to the power one this overall expression will be at least A to the power one that is why the minimum A to the power one term is written and the rest may be may be may be coming into action depending on the pressure condition.

So, therefore, remaining these terms like you know this $k_1 A$ divided by divided I mean $k_2 k_1 A$ divided by k_2 plus $k_{-1} A$ like this $k_2 k_1 A$ divided by k_2 plus $k_{-1} A$, so this way k_2 plus k_{-1} , so it is like $k_2 k_1 A$ divided whole divided by k_2 plus k_{-1} . So, there should be A bracket over here there should be A bracketed quantity, so these 2 it is non there is A type way you should put A bracket over here like k_2 plus $k_{-1} A$ these 2 terms should be within A bracket.

So, if you inverse it that is make take 1 by k product then this will be your 1 by k 1 A because, k 2 k 2 gets cancelled, so 1 by k 1 A and k minus 1 by k 1 k 2. So, you see that the, so this A constant quantity and this is you know A just 1 by A dependency. So, if it plot for certain you know if you plot like A with there are several examples, so like if we plot 1 by k versus 1 by A then it is informed that those reactions which follow this unimolecular mechanism. So, for which it is it is informed that 1 by k versus 1 by A it is like this it follows like this it is it is not truly A you know linear plot it maintains linearity up to certain one by A value and then it starts to deviate from linearity ,so this side is the high pressure side. So, pressure is increasing means 1 by A is decreasing.

So, that means this side is low pressure side this side is low pressure side this way and high pressure this way. So, you see in low pressure region this is linear this is linear, but in high pressure region it starts to deviate so that means, that means we can say that truly this Lindemann mechanism is operative otherwise it should not have deviated and it should not show a pressure dependence that is the rate constant should not have shown the pressure dependence, so it is a test of Lindemann's unimolecular mechanism whether it is operative or not.

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Activation energy for a complex reactions

- Lindemann Mechanism - High-Pressure Limit

$$\frac{d[P]}{dt} = \frac{k_1 k_2}{k_{-1}} [A] = k[A]$$

$$k = \frac{k_1 k_2}{k_{-1}} = \frac{A_1 e^{-E_{a,1}/RT} A_2 e^{-E_{a,2}/RT}}{A_{-1} e^{-E_{a,-1}/RT}} = \frac{A_1 A_2}{A_{-1}} e^{-(E_{a,1} + E_{a,2} - E_{a,-1})/RT}$$

$$E_a = E_{a,1} + E_{a,2} - E_{a,-1} \quad k = A e^{-E_a/RT}$$
- $E_a \rightarrow$ overall **Activation Energy**

Now, how to find next is how to find the activation energy for a complex reaction again, look into in Lindemann's mechanism Lindemann mechanism and also concentrate on to

high pressure region that in high pressure region your expression becomes $\frac{dP}{dt}$ is equal to some constant A which is nothing, but $k_1 k_2$ divided by $k_{-1} A$.

So that means, your rate constant overall rate constant is k is equal to $k_1 k_2$ divided by $k_{-1} A$ if you recall Arrhenius equation if you plug in the corresponding Arrhenius expression over here then you can write for k_1 you can write A_1 exponentially to the power minus E_A 1 by RT into A_2 into the power minus E_A 2 by RT divided by $A_{-1} A_{-1}$ means for the. So, the exponential term for the back reaction E to the power minus E_A minus 1 by RT , so that means, it gives you $A_1 A_2$ divided by A_{-1} times E to the power minus E_A 1 plus E_A 2 minus E_A minus 1 divided by RT .

So, if you can write this as overall E_A then your expression reduces to and also if you write this as overall A then your k is equal to A into E to the power minus E_A by $r t$. So, you can you can directly you know plug in this Arrhenius numbers into the into the overall rate expression, so what we have learnt today.

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Complex reactions

- Treatment.....
- Rate-determining step
- Pre-equilibrium state
- Steady-state

So, let us try to sum up let us try to sum up that we are still in complex reaction and treatment for the complex reaction is like you have to invoke the concept of rate determining step that is the slowest of all the elementary steps involved in the mechanism, so mechanism means your overall reaction can be divided into A number of elementary steps or your overall reaction can be regarded as a combination of such and such elementary steps, so each elementary step is a part of your mechanism, so of which

of these elementary steps the step with lowest rate that is A slowest rate or the or the step which is the slowest one is called the rate determining step.

You can invoke the concept of pre equilibrium and also you have to invoke steady state approximation to find out the concentration of the of the reactive species reactive intermediate involved in the particular reaction in particular reaction.

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Example

$2A + B \rightarrow \text{Products}$

- Mechanism
 - $A + B \xrightarrow{k_1} C$
 - $C + A \xrightarrow{k_2} D$ (slow)
 - $D \xrightarrow{k_3} F$ (fast)
 - $F \xrightarrow{k_4} P$ (fast)
- second step -- rate-determining

$$\frac{dc_P}{dt} = k_2 c_C c_A$$

So, we have given a example, and we have given one example, where you know that your this is your slowest step, so overall rate of the reaction will depend on this one that is this overall rate will depend on concentration terms involved in this particular elementary step it does not really matter whether you know whether this is still faster or you know it is little fast or like that, but this is the slowest one, so therefore, this will take care of the overall rate of the process.

Pre equilibrium means before the reaction takes can take place that is this is your final step to give you the product, so they are may be a very fast equilibrium to give you some intermediate and then this intermediate is slowly used up to give you product. So, therefore, your overall rate will depend on overall rate will depend on you know the concentration of this term and ultimately this will give you the concentration and overall rate is equal to $k C A$ into $C B$.

Next is we have also employed the concept of steady state approximation that that if A to B to C is A is A sequential process then B we will have A steady concentration at for certain period of time and you if you employ this steady state approximation. Then you can you can say that $\frac{dC_B}{dt}$ is equal to zero and therefore, using that you can find out the overall rate of process of a chemical process in terms of the concentration of your reactant then we talked about unimolecular mechanism unimolecular mechanism that is that was shown by Lindemann in 1922. That A plus A giving rise to A star plus A. so, therefore, this A star is A is an excited species and this excited means may be a different in energy state may be a little higher in energy compared to the starting material and this excited molecule may undergo several processes like it may just get deactivated, but by collision with A or may be by collision with wall or may be it under it will undergo A further reaction to give you product.

So, further reaction means further reaction might require some rearrangement of the molecular geometry, so you know and from this we arrive that the rate expression that product formation that is this and under 2 pressure conditions 2 pressure region one is high pressure and another is the low region, so in high pressure region this expression becomes a first order with respect to concentration of A and low pressure region it becomes a second order with respect to concentration of A and there is a test that if you plot $\frac{1}{k}$ versus $\frac{1}{A}$ then you know you will be getting a linear dependence up to certain concentration or up to certain pressure region, but beyond; that means, if you go to the high pressure region, it deviates substantially from linearity.

So, importance of this is that we have learnt you know although it is a it is a reaction between the you know same species, but it gives rise to you know product, but this product formation has got peculiar dependence and this has first put forward by Lindemann and also we can we can plug in the you know expression arising out of you know this Arrhenius equation, so this Arrhenius expression you can plug in to find out the overall activation energy of this process.

So, this is a very interesting example of a complex I mean how to deal with this complex reactions how to invoke the steady state approximation pre equilibrium and may be rate determining step in you know handling this complex reactions, so we will continue to this complex reactions in the next lecture also may be next to next lecture because, it has got many variations and many examples are there, so we should discuss then one after

another and then we will move on to theory of reaction rates, so next day we will talk more about complex reactions, so till then good bye.