

Rate Processes
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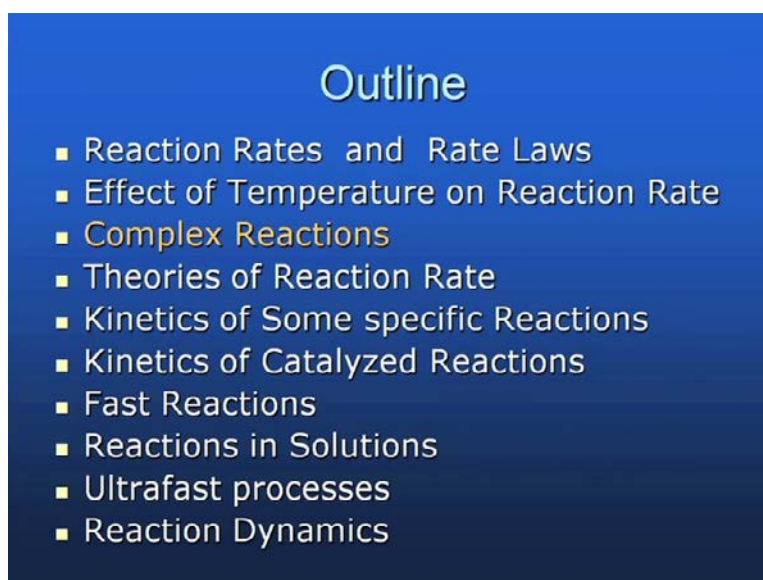
Module No. # 01

Lecture No. # 07

Complex Reaction (contd...).

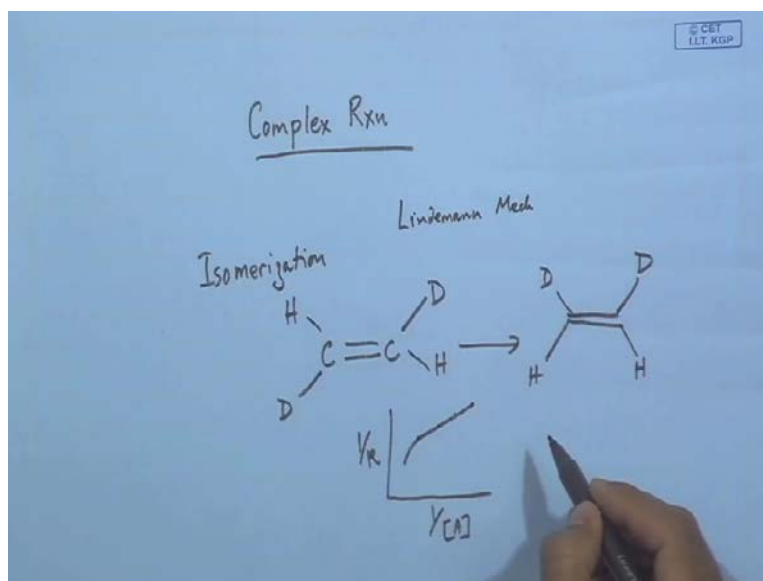
Hi, good morning everybody. So, today we will continue with complex reaction.

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So, last in in our last discussion, we you know finished with this Lindeman mechanism. So, I did not give any concrete example, really example of of a reaction where Lindeman mechanism is operative.

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So, let us take one example, that is isomerization, isomerization of trans **trans (())** like CD, so it isomerizes to **you know** C's form like this. So, this is found to follow Lindeman mechanism and it shows the **you know** pressure dependence. Like if this is 1 by k and if this is 1 by a, that is concentration of a, then it is found to follow like this, **deviates** it deviates from linearity when pressure is increased. So, under low pressure condition, low pressure condition means you introduce from outside some inert gas which does not take part in reaction.

So, in that case partial pressure decreases, partial pressure of these molecules will decrease and as a result of which it is found that it follows when pressure is less, I mean partial pressure is in this region, so when partial pressure decreases this way. So, it is found to follow a linear trend, but while **you know** in high-pressure region it **it** is found to deviate significantly from linearity. So, this is one example where this Lindeman mechanism, **mechanism** this is also called lindemann-hinshelwood mechanism, in 1921 this was proposed.

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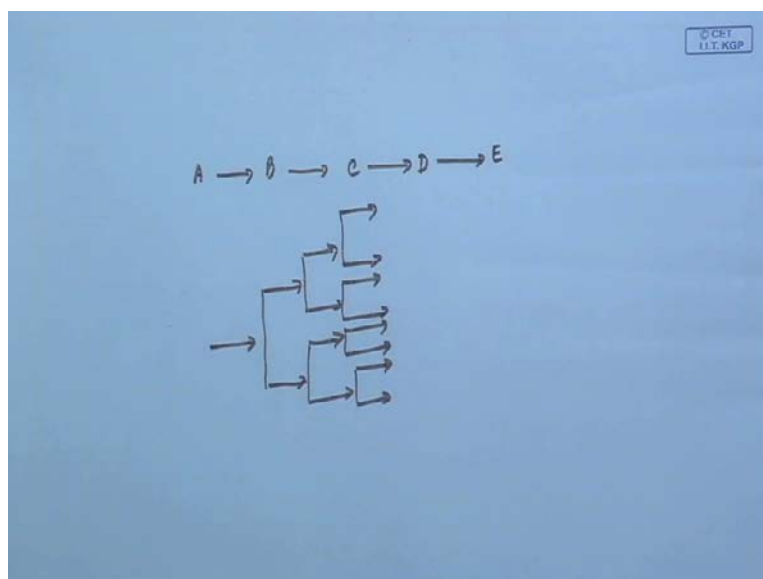
Complex reactions
Chain reactions

(a) $\text{CH}_3\text{CHO} \rightarrow \cdot\text{CH}_3 + \cdot\text{CHO}$ (Initiation)
(b) $\text{CH}_3\text{CHO} + \cdot\text{CH}_3 \rightarrow \text{CH}_4 + \text{CH}_3\text{CO}\cdot$ (Propagation)
(c) $\text{CH}_3\text{CO}\cdot \rightarrow \cdot\text{CH}_3 + \text{CO}$ (Propagation)
(d) $\cdot\text{CH}_3 + \cdot\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_3$ (Termination)

Two types of chain reaction:
↳ Straight chain reaction
↳ Branched chain reaction

Next, we will move onto chain reactions, chain reactions means a reaction which **you know which** is having a number of steps like one step, then another step, then another step, so which occurs in a chain.

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So, it is a sequential event, so like this step then another step then another step and so on. So, this is a **you know** typical schematic of a chain reaction like A to B then C then D, so **it is a it is a** it is like a consecutive reaction, but it is a complex one. It is not a very simple one, but it is a complex one, let us take one example that decomposition of

acetaldehyde producing **you know** this ethane, then methane and also carbon monoxide. So, **you know** CH_3CHO **you know** it produces first this CH_3 radical and CHO radical, this mechanism is proposed in this way and then the CH_3COCHO again reacts with another CH_3 radical producing C_2H_6 , that is this one snatches one hydrogen from here producing C_2H_5 radical and C_2H_4 , then C_2H_5 producing C_2H_5 dot and C_2O . So, these two steps are called propagation that is it is propagating; this chain reaction is being propagated. So, this is the starting point, so it is called the initiation reaction, initiation step that is this elementary step is initiation step. And here you see 2 C_2H_5 radicals they combine to form this ethane, so whatever C_2H_5 dot was produced, C_2H_5 radicals were produced in the initiation step and maybe in other steps they are basically consumed to produce ethane.

So, that is why it is called the termination as if this reaction is terminated over here, no further reaction should take place like that. So, now, two types of chain reactions maybe possible, one is **a** like I have drawn over here, so it is a straight chain reaction, another could be a branched chain reaction like starting point and then it is doing like this, then it is further branched like this and so on. And you see as time is passed by too many steps are coming into action, so as a result of which you see **you know** products initially if you start from here only two steps, here it is 1, 2, 3, 4, 5, 6, 7, 8, so it increases **you know** enormously. So, this type of situation is called the branching of chain, it is called the branching of chain, so it is branch chain, is branched, but this one is a straight chain reaction.

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The H₂ + Br₂ Reaction

- The overall rate for the reaction was established to be

$$\frac{d[\text{HBr}]}{dt} = \frac{k[\text{H}_2][\text{Br}_2]^{3/2}}{[\text{Br}_2] + k'[\text{HBr}]}$$

Now, let us take one example of this hydrogen plus bromine reaction producing H B r, H 2 plus Br 2 giving rise to H B r.

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The image shows a handwritten chemical equation and its corresponding rate law on a whiteboard. At the top, the reaction is written as $\text{H}_2 + \text{Br}_2 \rightarrow \text{HBr}$. Below it, the rate of production of HBr is given by the equation $\frac{d[\text{HBr}]}{dt} = \frac{k[\text{H}_2][\text{Br}_2]^{3/2}}{[\text{Br}_2] + k'[\text{HBr}]}$. A hand is visible at the bottom right, pointing to the denominator of the rate law equation.

So, it is found that rate of a production of H B r has got a very peculiar **you know** dependence on H 2 concentration, B r 2 concentration and also H B r. So, let us write that and we will try to find out how this is coming. So, **d** t of H D r, rate of production of H B r is equal to some constant H 2 B r 2 to the power 3 by 2 divided by B r 2 plus another constant k primed H B r. So, this reaction even if you write like this, **you know** if

you rearrange it, then k into H_2 , then Br_2 to the power half divided by $1 + k'$ into concentration of HBr divided by concentration of Br_2 . So, you see that this rate of production of HBr is proportional to the concentration of H_2 and **you know** it is Br_2 to the power half.

So, it is fractional order, **if if you** if you neglect this one, say if you neglect this one or maybe if you do not think right now **the** about the denominator, in the numerator you see that it has got a to the power half dependence, so fractional order with respect to Br_2 . So, that means, earlier I talked about **you know** zero order, first order, second order, third order and n th order, but here we are seeing that it is a fractional order, so order is an experimentally determined quantity and it can be fractional.

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Mechanism

- The mechanism was proposed independently by Christiansen and Herzfeld
- and by Michael Polyani

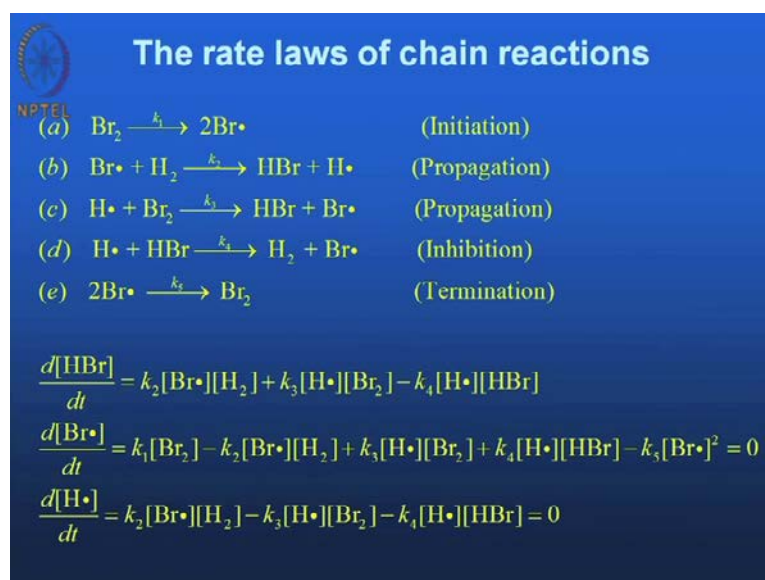
Mechanism	Rate Law
$Br_2 \rightarrow 2Br\cdot$	$v_1 = k_1 [Br_2]$
$Br\cdot + H_2 \rightarrow HBr + H\cdot$	$v_2 = k_2 [Br\cdot][H_2]$
$H\cdot + Br_2 \rightarrow HBr + Br\cdot$	$v_3 = k_3 [Br_2][H\cdot]$
$H\cdot + HBr \rightarrow H_2 + Br\cdot$	$v_4 = k_4 [H\cdot][HBr]$
$Br\cdot + Br\cdot \rightarrow Br_2$	$v_5 = k_5 [Br\cdot]^2$

So, it is an important insight, so let us look into the mechanism that was proposed independently by **you know** Michael polygamy and Christiansen and Herzfeld, so mechanism goes as **as** follows. So, **you know** Br_2 if you look into **the into** the slide you see first is Br_2 producing $2Br\cdot$, so it is the initiation step, so if the rate constant is k_1 for this process then for the first one rate **rate** is rate of production of this $2Br\cdot$ is k_1 times concentration of Br_2 , then there are other steps $Br\cdot$ plus H_2 producing HBr plus $H\cdot$, then $H\cdot$, this $H\cdot$ is used up to produce HBr and $Br\cdot$.

And then $H\cdot$ again reacts with HBr to produce H_2 plus $Br\cdot$, **you see** if you look into **look into the the** this scheme, I mean this expression, you will be seeing that this H

Br is in the denominator. So, if HBr increases, rate of production of this HBr will be reduced, so this maybe, maybe this can be regarded as that step which is responsible for the inhibition or it is acting as an inhibitor for the process. So, H₂ plus Br• it is producing H₂ plus Br•, so corresponding rate is like this and then it is the termination Br• plus Br•, so that is the back reaction of this producing this one, Br₂. So, the corresponding rate is this, so these are the rate laws and these are the corresponding elementary steps. So, since these are elementary steps, so, therefore the species which are involved in the elementary step can be directly involved, can be directly retained in the corresponding rate expression.

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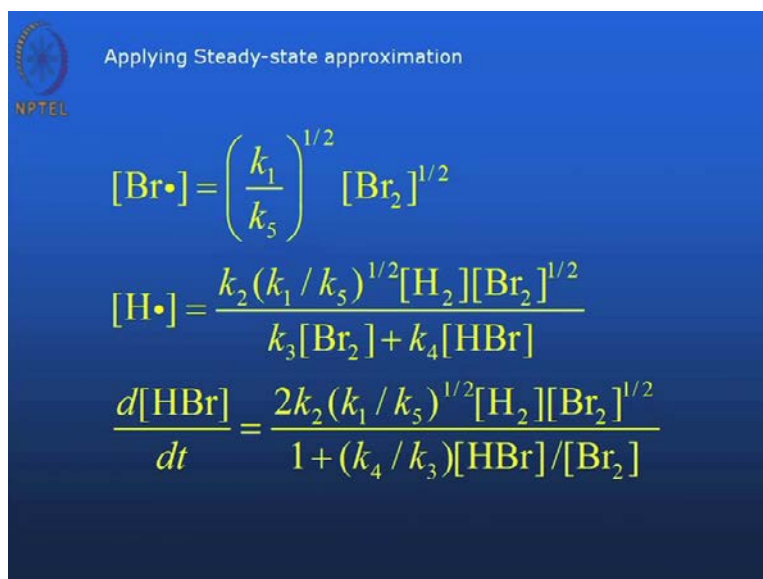


So, again what I told that this is initiation, as I told you this is your propagation, why propagation, because this reaction produces one H dot, because the active ingredient for the reaction to proceed further is the radicals. So, here the active ingredients will be your Br• and H dot, so this Br• produces another H dot and this H dot, again reacts with another bromine molecule to produce HBr and Br•. So, whatever Br• was involved was utilized in this k₂ step is again generated through k₃ step. So, these two are basically propagating this reaction, so reaction I mean the process remains alive because of these two propagation steps.

So, remember this initiation step requires a **a** homolytic cleavage of this B_r , B_r bond producing $B_r \cdot$. So, this homolytic cleavage maybe done various ways, maybe thermally or maybe photo chemically, so these specific situations we may discuss later on. Now, next is inhibition step, as I told you that in the rate equation, in the denominator you can see $1 H B_r$ concentration. So, when $H B_r$ concentration increases, so overall production of **you know** $H B_r$ is also reduced, because **you know** this $H B_r$ is again used up to produce H_2 and $B_r \cdot$. So, this is **some kind of this back to, this reaction** back of this reaction, back step of this reaction, backward reaction. So, that is why it is called the inhibition, it is acting **as an** as a kind of inhibition to the forward process and this is the termination step.

So, you know, what we should do is making steady-state approximation, applying steady-state approximation as I told you in **in** our last lecture, that we have to apply steady-state approximation to this active ingredients like active species which are responsible **for your** for the process to carry forward. So, therefore, **you know** this is $1 B_r \cdot$, so d/dt of $B_r \cdot$ is **is** this expression and d/dt of $H \cdot$ is this expression, how this is coming? So, this is coming like d/dt of B_r , so it is the rate of formation of $B_r \cdot$, so this is the first step, so $k_1 B_r^2$, then this $k_2 B_r \cdot H_2$ with a negative sign, because this is used up, then it is produced, $B_r \cdot$ is produced, that means it will be $k_3 H \cdot B_r^2$, $k_3 H \cdot B_r^2$. Then here $B_r \cdot$ is again produced, although this is an inhibition step, but it is $B_r \cdot$ produced, so, therefore $k_4 H \cdot H B_r$, so $k_4 H \cdot H B_r$ with a positive sign and it is the termination step. So, $B_r \cdot$ is **you know** used up, therefore k_5 with a negative sign into $B_r \cdot$ whole square.

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And you have to apply this equal to 0 for your steady-state approximation, in the same way $d[\text{H}\cdot]/dt$ will have this expression and you have to put this to 0 in order to have your steady-state approximation applicable. Now, overall **overall** rate of production of HBr , because we are interested in finding out the rate law for the production of HBr , so HBr is our product H_2 plus Br_2 producing HBr . So, $d[\text{HBr}]/dt$ will be equal to, so you just have to find out where this HBr is involved, so these are the three steps where HBr has been involved.

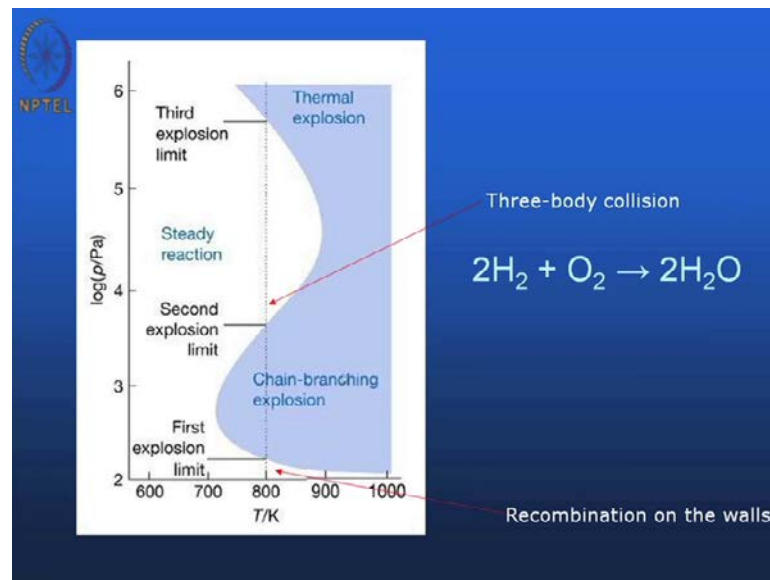
So, step B C and D these are the three steps where HBr has been involved, so here HBr is produced means so you have to write $k_2[\text{Br}\cdot][\text{H}_2]$ with a positive sign, so $k_2[\text{Br}\cdot][\text{H}_2]$. Here also it is produced, so that **that** should also be with plus $k_3[\text{H}\cdot][\text{Br}_2]$, but here it is **in** acting in opposite direction, so it will be minus $k_4[\text{H}\cdot][\text{HBr}]$. So, since these are all elementary steps you can directly put these concentration terms occurring in the left hand side, because **it is you know** it is **in it is** occurring from left to right. So, reaction is proceeding to the right, so your starting ingredient **should be** should be used in your rate expression. So, we have got three key equations of which the last two, this one and that one, these two should be equated to 0 because of this steady-state approximation. And **that** whatever **whatever** expressions for the concentration of $\text{H}\cdot$ and $\text{Br}\cdot$ that we should put in the first expression which is for the rate of production of HBr .

So, after a steady-state approximation is applied we can find directly that $B_r \dot{}$, concentration of $B_r \dot{}$ from steady state approximation will be k_1 divided by k_5 , k_5 whole to the power half into B_r^2 whole to the power half. $H \dot{}$, it will be a little complicated, because it involves many steps, but B_r you know $B_r \dot{}$ is a simple one equal to $H \dot{}$ is equal to k_2 times k_1 by k_5 to the power half times H^2 , then B_r^2 to the power half divided by divided by $k_3 B_r^2$ plus $k_4 H B_r$. So, if you plug in this, these two in the first expression which is for your which is for your rate of production of $H B_r$, so that is d t of $H B_r$, then it will be you know you you have to plug in these two onto the expression that i that that we have and we will be getting $2 k_2 k_1$ by k_5 to the power half $H^2 B_r^2$ to the power half divided by 1 plus k_4 by $k_3 H B_r$ by B_r^2 .

So, it is an example, which has I mean it is a it is a chain reaction, of course it is a radical reaction radical chain reaction of which one is initiation, another two is our propagation, the fourth one is inhibition and the fifth one is termination. So, considering all these and also invoking the steady-state approximation onto $H \dot{}$ and $B_r \dot{}$, which is a requirement of of retreatment of requirement while treating these complex reactions, so after after plugging in this respective expression, respective expressions to the expression of $H B_r$, that is the respective expressions for $H \dot{}$ and $B_r \dot{}$ to the expression of rate of production of $H B_r$ we got this one. This particular expression which says that the rate of production of $H B_r$ has got a fractional dependence, concentration dependence on B_r^2 and also as more of $H B_r$ is produced.

So, forward reaction is little bit inhibited as evident from the from the explosion, so what is meant by explosion? Explosion is, this can be you know thermal explosions, so rapid increase in reaction rate with temperature, which is called the thermal explosion or explosion may happen as a result of chain branching. So, chain branching when steps into the mechanism that will lead to a huge, maybe exponential increase in the number of chain carriers in the system that means as I showed to you like this, like this, so it is a huge increase. So, initially one, then two, two becomes four, four becomes eight and so on, so in it increases hugely and that leads to explosion, that leads to explosion. So, this is the schematic you know that it is a straight chain reaction, it is a branched chain reaction and leading to explosion. So, basically if you do a simple experiment that you fill the container with hydrogen gas and then you try to burn it with with a flame, then it will just you know explode.

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So, these productions of hydrogen, I mean water from **from** H_2 and O_2 through **you know** burning is an example of explosion, so this is a typical $\text{H}_2 + \text{O}_2$ producing $2\text{H}_2\text{O}$ kinds of **you know it is a it is a** situation, so it is the plot **plot** of p versus temperature. So, now, this is the region where chain branching and explosion happens and here thermal explosion happens. And in this pressure region it is a steady, **you you know** this is your steady reaction **ah** region and these are the three explosion limits, one is the first explosion limit, which is **in the in you know** in between **3** 2 to 3 Pascal, I mean $\log p$, where p **is retained in**, **you know** p is expressed in Pascal. So, 2 to 3 there is limit, then 3 to 4 one limit and there is in between 5 and 6 it is the third explosion limit. So, this corresponds to maybe a three-body collision and this correspond to recombination onto the walls.

Now, the **the** mechanism is like this that $\text{H}_2 + \text{O}_2$, this is the initiation step, $\text{H}_2 + \text{O}_2$ producing $2\text{OH}\cdot$, OH radical, then this $\text{OH}\cdot$ radical will again **you know** react with H_2 to produce a water and hydrogen, I mean single hydrogen, monohydrogen, hydrogen atom. So, this is the first process that is the propagation, then this $\text{H}\cdot$ once it is generated through this first propagation, **first propagation**, so it will react with O_2 to produce $\text{OH}\cdot$ **and $\text{OH}\cdot$** and O with two electrons. So, it is a slow, it is called the branching, but this process is slow.

Another step is fast and which is also branching is $O_2 + H_2$ producing OH and H , so it is with k_4 . And recombination at the wall H plus wall means it collides with the wall to produce hydrogen back, it is called the termination and this is one termination step. There could be another termination step that H plus O_2 producing HO_2 , well while m is another component, another molecule present there, molecule or maybe another entity.

So, producing this, this is also a termination, now what is the key step for this? So, we have to look into these two, so this is your termination step, this is one important step and this is the slow one, because these two are fast, this occurs very quickly with time it occurs very fast it does not take that much of time. Therefore, overall process will depend very much on the competition between this step c, step c and step e, that is the third and fifth step.

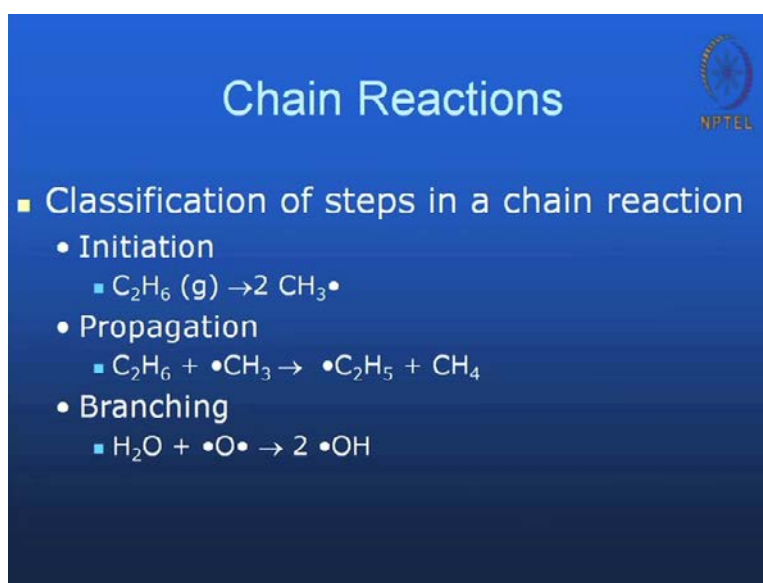
Now, when p is reducing that is under low-pressure condition, so step C is slow and step e is fast, so under low-pressure condition what is happening that this molecule, this oxygen molecule, since they are rarified under low pressure, means maybe some inert gas is present or maybe if pressure is low means the these gas molecules are rarified. So, the average distance between these molecules are more, therefore the probability of this collision, so this process will be less, so, therefore, it becomes slow, but this will be fast, because since this is occurring slowly, therefore these molecules will get chance to collide with the walls, therefore producing this.

So, termination will win, so it will be a no explosion situation, next is when p increases, what is happening, step C goes up, because naturally if this is reducing, whatever situation is happening over here should be reversed over here. So, when p increases step C tends to go up and step e tends to go down, why go down, because these oxygen molecules will get chance to collide with H dot. So, therefore, less number of H dot will remain in the reaction mixture to collide with the wall. So, what will happen that it will be an explosion situation, so that means branching will happen, this branching will take place. At the moment branching will take place means you will be getting enormous number of chain carriers. So, it will. So, here it is 4, then it will be 16 and so on, it will increase very rapidly like an exponential function, therefore this will lead to explosion. p is still higher, what will

happen, **that** in that case maybe step f **that is the** that is the last step shown over here as the termination step, **this will** this will be very important under that condition.

So, this will be important means these will be used up, that is this hydrogen dots will be scavenged by O₂ with the help of another molecule or another entity m. So, it is another termination step, so it will be again nonexplosive. When p is very **very** high, go back to this slide very **very** high above third explosion limit, so where H₂O₂ dot, this whatever H₂O₂ dot is produced in this termination step because this is predominating in the high-pressure region. So, this will again react with H₂ producing **this will react with H₂ producing** H₂O and OH dot, so OH dot means this situation. So, it is again an explosive situation, I hope that this explains this particular representation of H₂ plus O₂ producing 2 H₂O. So, branching of chain leads to explosion can be easily understood by taking this water formation from H₂ plus O₂.

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Chain Reactions

- Classification of steps in a chain reaction
 - Initiation
 - $C_2H_6(g) \rightarrow 2 CH_3\cdot$
 - Propagation
 - $C_2H_6 + \cdot CH_3 \rightarrow \cdot C_2H_5 + CH_4$
 - Branching
 - $H_2O + \cdot O\cdot \rightarrow 2 \cdot OH$


So, as I told you, as I mentioned in the earlier slides that initiation propagation branching, so these are the typical steps in chain reaction. So, chain reaction must have this initiation, a typical example is C₂H₆ gas producing 2 C H₃ dot, **then propagation,** then propagation. Propagation means this is propagated, that is C H₃ dot plus C₂H₆ producing another radical and C H₄ is produced, so this will continue. Branching, as usual this is a branching situation, so this is branching; this is one example of branching.

Retardation, as I told you that if more of H B r is produced, more of H B r is produced means it is a retardation, **that is that is that is** that will retard the reaction.

Termination, when 2 say B r dot or maybe 2 C H 3 C H 2 dot are there, are combining **they will** they will produce one nonracial species that means **it is** it is a termination step. Inhibition means that will act as an inhibitor, this is similar to retardation, so a chain reaction will have initiation, propagation, termination, retardation, branching and maybe inhibition. Now, let us move onto polymerization kinetics, so what do you mean by a polymer, all of you heard about **you know** molecules, say H 2, say maybe water, maybe oxygen. So, these are all **you know** examples of a single molecule, I mean if you have water, means **in a** in a glass of water you will be finding that everywhere you will be getting monomer of H 2 O, maybe they are a little bit associated because of hydrogen bonding, but that is not a true chemical linkage.

Even if you go to say hydrogen gas **you will be** if we have a chance to look into this gas molecules, although it is not possible, because **it is** we know gas molecules are too small to be detectable by our eyes, we should find the, means, **if we** if we look into, we should find that every molecule will be H 2. So, these are all examples of **you know** monomers. Now, **if we say** move from monomer to a situation that two molecules, say **say** some anhydride like acetic acid, acetic anhydride.

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Polymerization Kinetics

- Chain polymerization
 - Activated monomer attacks another monomer, chemically forms bond to the monomer, and then the whole unit proceeds to attack another monomer
- Stepwise polymerization
 - A reaction in which a small molecule (e.g., H₂O) is eliminated in each step

So, if you take out water, from two molecules of acetic acid you will be generating acetic anhydride, which is in true sense a dimer of, you will be generating acetic anhydride, which is a true sense of a **in true sense a** dimer of acetic acid. So, it is the case of dimer. In the same way **same way** if you keep on adding one unit after another, there is one unit, then another unit like **like** brickwork to produce to **to** generate a huge building. So, you will be generating a **huge you know** huge molecule, so which is nothing but it will become a dimer, trimer, tetramer, pentamer and so on, ultimately it will be an **I mean n means n** number of monomer combination, which is called the number or which is also called as polymer, that is poly monomer is called the polymer.

Like a protein is a biopolymer, so it consists of 20 **you know** naturally occurring amino acids, so if you look into any protein like **you know** hemoglobin, it is also a **you know** metallic protein, it contains **you know** a metal metallic prosthetic group, that is iron to prosthetic group plus which is embedded this iron to prosthetic group, is embedded within **you know** a polymeric framework, which is called the protein backbone or protein matrix. So, this protein matrix is consisting of a combination of this, a specific combination, which is called a sequence, a specific combination of these monomers. So, protein is a biopolymer.

And also in day-to-day life like plastic or maybe **you know** we call polythene, it is also a polymer, so it is polyethylene. So, polythene is a polymer, plastic it is also another polymer, so **you know** these are all called polymers. So, polymerization, if we look into polymerization kinetics, so the process by which this polymer is generated is called the polymerization. So, polymerization kinetics we have to look into since we deal with in this particular series of lectures, the rate process.

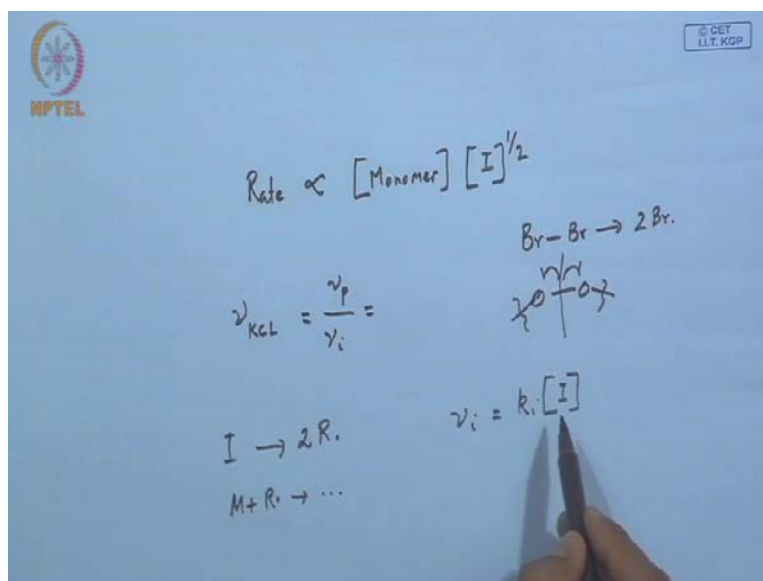
So, one is called the chain polymerization and the second one is called the stepwise polymerization or polymerization, so then what is called a chain polymerization. Now, it is basically **you know you can call** you can say like this an activated monomer attacks another monomer or one activated monomer reacts with another monomer and forms a chemical linkage, a chemical bond with the second monomer, thereby producing a dimer. Then this whole dimer is again acting as a reactant to attack the third monomer **to producing to to** produce a trimer and so on.

So, in this way monomer becomes a dimer, dimer becomes a trimer, trimer becomes a tetramer and it will continue for long time. And if you allow the reaction to occur for long time then you will be ending up with a situation that is you will be able to generate a giant molecule having n monomers, they are chemically linked with one another which is called a polymer. So, **it is it is called a** this process is called a chain polymerization, that is this reaction occurs in a chain of sequences one after another, **one after another.**

What happens in case of stepwise polymerization? Now, in this case, **the reaction** the reaction where this stepwise polymerization is occurring that is a sequential polymerization is occurring that is one after another, **so** in steps. So, in this case small molecules like water gets eliminated **from the** from the reaction mixture or from reaction **from from you know from the reaction** medium. So, A plus another B producing **a poly I mean** a dimer say a B plus water or maybe a small molecule, it is called the stepwise polymerization. Now, **now** chain polymerization, **is it it it** generally requires a chain initiator, like I **I** told you that like this $H_2 + Br_2$ reaction, that initially you need to generate $2 Br \cdot$, $2 Br$ radicals.

So, that is your **your** initiation step and that radical, that $Br \cdot$ radical is used up to do further propagation step. So, in this case also for chain polymerization reaction now this requires **you know** some **some** initiator which initiates your reaction. So, in this case it has been found that this reaction rate is **is** first order in monomer and to the power half in initiator.

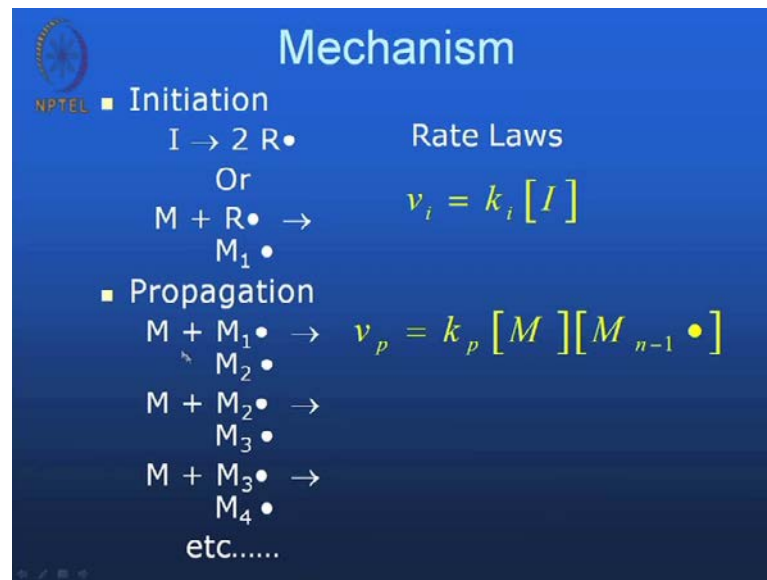
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So, your rate is proportional to your monomer and initiator I to the power half. So, then we **we** would like to define one quantity which is called the kinetic chain length, which is called ν_{KCL} , ν kinetic chain length, it is nothing but the measure of the efficiency of the chain propagation reaction. How efficiently **how efficiently** this chain is propagated, because propagation is very important **for the** for further processing like if you do not have **you know a very you know** long propagation, if it does not propagate for long time then **you know** longer molecules cannot be formed, that is the molecules having **having** huge chain length will be difficultly formed.

So, this is defined in this way that is ν_p divided by ν_i , which is nothing but the number of monomer units consumed in the numerator divided by the number of active centers produced, active centre means the centers like a radical centre maybe an active centre or the centre which is active for doing further reaction. So, this ratio is called the kinetic chain length. Now, let us come to **you know this mechanism of** this **a** general mechanism for this, what is that? Now, initiator, initiator I producing 2 $\text{r} \cdot$, maybe 2 radicals, because generally **you know** like $\text{Br} \cdot$, so if you initiate then it will be generating 2 $\text{Br} \cdot$ or maybe say peroxide, say like this, something is there, something is also there. So, if you do a homolytic cleavage, then you will be generating two radical centres over here, that is why 2 $\text{r} \cdot$ or it maybe $\text{m} + \text{r} \cdot$ producing another radical. So, initiation rate is your k_i times concentration of i, remember, this is your elementary step, it is not the overall rate, it is the rate for the elementary step.

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So, next come to propagation, that monomer, monomer plus monomer 1, monomer 1 means m 1 maybe. So, producing something m 2, monomer 2, I mean m 2, m 2 means **it is** it is another monomer is combined with m 1, then m plus m 2 producing m 3, m plus m 3 producing m 4 in this way. So, v_p or v_p is equal to k_p , so rate constant times, since two species are involved, so therefore one monomer concentration will be there and one n minus 1 mer. So, **if this reaction**, if a reaction is producing nth nether, I mean a polymer with n number of monomers therefore for that reaction you can write your rate expression, which is equal to some constant times monomer into the concentration of m n minus 1 dot.

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Mechanism (contd..)

- Termination
$$M + M_3 \bullet \rightarrow M_4 \bullet$$
$$v_t = k_t [M \bullet]^2$$

Note – Not all the initiator molecules produce chains
Define ϕ = fraction of initiator molecules that produce chains

$$\Rightarrow \frac{d[M \bullet]}{dt} = 2\phi k_i [I]$$

There is a termination step also, that m plus m 3 maybe m 4, which is a termination step, it may be something else also, it is just a just a you know representation. So, rate of termination is k termination times say m dot square, because 2 m dot, 2 m dot, 2 m dot is giving rise to you know another product. So, therefore, you may put a dot over here, maybe and you may you may remove this dot, so because it is termination, means two radicals must combine.

So, here this dot may be somehow somehow moved over here, so anyway say you you may put a dot over here or maybe 1 m dot, another m dot producing m 2, that may be another thing. So, important thing that not all initiator molecules produce chains it is very important point and phi is the fraction of another thing, we are we are using another quantity phi the fraction of initiator molecule that produces chain. That means, important concept that you have to we have to invoke over here that any initiator may not lead to chain reaction or may not lead to further propagation of a chain.

And also another point is that, that hundred percent you know initiator molecules are not used up to produce chains, maybe some fraction is lost, so to account for that fraction you have to put a quantity like here, this one, k i I, so you put 2 phi k i I d d t of m dot. So, it takes into account of you know this probability of producing a chain, so in terms of kinetic chain length you know you have to write in terms of k t and k p, so k t in terms of k t and in terms of k p you have to write. So, what you can write?

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Kinetic Chain Length

- kinetic chain length in terms of k_t and k_p

$$v_{KCL} = \frac{k_p [M] [M \bullet]}{2 k_t [M \bullet]^2}$$
$$= \frac{k_p [M] [I]^{1/2}}{2 (\phi k_i k_t)^{1/2}}$$

So, in that case, **in terms of** if you want to write in terms of k_t and k_p you will be getting this expression, if you put the appropriate numbers over here, appropriate expression over here, you will be generating, you will be getting this expression, that your v_{KCL} kinetic chain length will be like, it is a first order in m and half order, in I initiator, concentration of the initiator.

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Stepwise Polymerization


- A classic example of a stepwise polymerization – nylon production.
$$\text{NH}_2\text{-(CH}_2\text{)}_6\text{-NH}_2 + \text{HOOC-(CH}_2\text{)}_4\text{COOH} \rightarrow$$
$$\text{NH}_2\text{-(CH}_2\text{)}_6\text{-NHOC-(CH}_2\text{)}_4\text{COOH} + \text{H}_2\text{O}$$
- After many steps
$$\text{H-(NH-(CH}_2\text{)}_6\text{-NHOC-(CH}_2\text{)}_4\text{CO)}_n\text{-OH}$$

Now, we will come to stepwise polymerization. A classic example of a stepwise polymerization is **you know** nylon production, so, now, let us take this example. So, n H

2 C H 2 whole 6 n H 2 and you know, this is basically the formation of C O n H, it is it is you know a peptide bond formation, not it should not be, it is an amide bond formation. So, this peptide bond, I mean amide bond is there in proteins kind of peptide bond formation. So, this n H 2 reacts with this one, so, therefore producing this 4 C H 2 continuing this one and 6 C H 2 continuing this one, they are they are you know condensing to produce ah condensing to produce this one plus water.

So, after many steps what is happening, after many steps it will be n number of you know this whole whole unit, n number of whole unit of which in one side there will be n H 2 and the other side there will be C O O H. So, this side will be called as C O carboxyl terminus, carboxyl related carboxyl related terminus or carboxyl terminus and this side is amino terminus.

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The Rate Law (contd..)


- Suppose, $[A] = [-COOH]$
- **A** can be taken as any generic terminal group for the polymer undergoing condensation
- **One** -OH for each -COOH

$$v_{poly} = -k_{poly} [-OH][A]$$

$$= -k_{poly} [A]^2$$

Now, rate law, suppose A is equal to concentration of C, I mean concentration of C O H. So, A can be taken as any generic terminal group for polymer undergoing condensation. So, rate of polymer formation will be this unit and that unit, so this will be basically, this will go as a square, minus sign is simply because of you know something is used up or whether something is generated.

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The Rate Law (contd..)


- If the rate constant is independent of the molar mass of the polymer

$$\begin{aligned} [-COOH]_t &= \frac{[-COOH]_o}{1 + k_{poly}t[-COOH]_o} \\ &= \frac{[A]_o}{1 + k_{poly}t[A]_o} \end{aligned}$$

So, if the rate constant is independent of molar mass of the polymer then you can express this as this one. So, what we have learnt today in **in** this lecture, so let us go back **that** it is a complex reaction, we have started with types of **complex reaction you know** complex chain reaction, we talked about chain reaction. Then we have taken H₂ plus Br₂ reaction and why it is a fractional order with respect to Br₂ we have also explained it using this mechanism. Then we moved onto **you know** explosion, then we moved onto this branching reaction, I mean branching of chain which leads to explosion.

We have taken a classic example of H₂ plus O₂ producing H₂O and the mechanism is also **you know** I talked about in details and the factors that affect this process whether **you know** explosion will take place or not that we can **you know** explain very well. Now, **then we** then we talked about **this you know** basic **you know** characteristics of chain reactions and then we started with polymerization kinetics. And there are two types of kinetics, one is chain polymerization, another is stepwise polymerization. And chain polymerization we talked about in terms of kinetic chain length, we have also tried to talk about a little in terms of mechanism and then kinetic chain length, how this can be calculated, that is also talked about.

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The H₂ + Br₂ Reaction

- The overall rate for the reaction was established to be

$$\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{3/2}}{[Br_2] + k'[HBr]}$$

And finally we came to the conclusion that your overall rate that is kinetic chain length is first order in monomer concentration and half order in **you know** initiator concentration. So, in our next lecture, **we will focus probably that will be, you know the last lecture probably I am not sure, I have to think of anyway, but probably that will be the last lecture for you know complex reaction, then** we will move onto **I mean move onto** theory of reaction rates. So, we will have that in the next lecture, that is complex reaction continued, so I hope **I hope** in the next lecture we should be able to complete complex reaction. So, till then have nice time; thank you.