Chemical Reaction Engineering 1
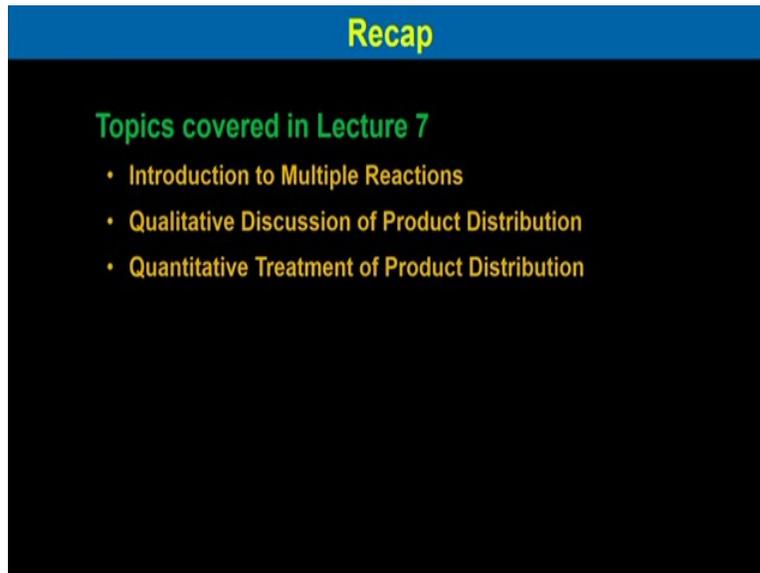**Professor Bishnupada Mandal**
Department of Chemical Engineering
Indian Institute of Technology Guwahati
Lecture 18
Design for Series Reactions

Welcome to the 8 lecture of module 4. In this module we are discussing reactor design, before going to this lecture let us have brief recap on our previous lecture.
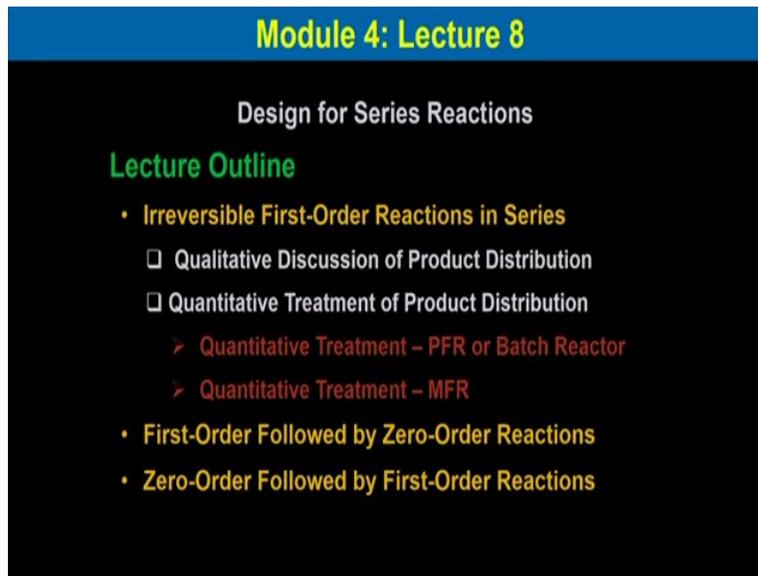
(Refer Slide Time: 0:42)

In our previous lecture we have mainly considered introduction to multiple reactions. And then we have considered quantitative (qualitative) discussion of product distribution for parallel reaction, and quantitative treatment of product distribution for parallel reactions. And we have seen how to optimize the product distribution by different ways of contacting the reactants.

In this lecture we will start with multiple reactions and since, we have discussed in the last lecture parallel reaction, here we will introduce to the multiple reactions in series. The brief lecture outline irreversible first order reaction in series and under which we will considered qualitative discussion of product distribution, then quantitative treatment of the product distribution, then we will do the quantitative treatment for two different categories, one is PFR or batch reactor, and secondly the quantitative treatment for the mixed flow reactor. And finally we will call cover first order followed by zero order reaction and zero order followed by first order reactions. So let us start with irreversible first order reaction in series.

(Refer Slide Time: 2:35)
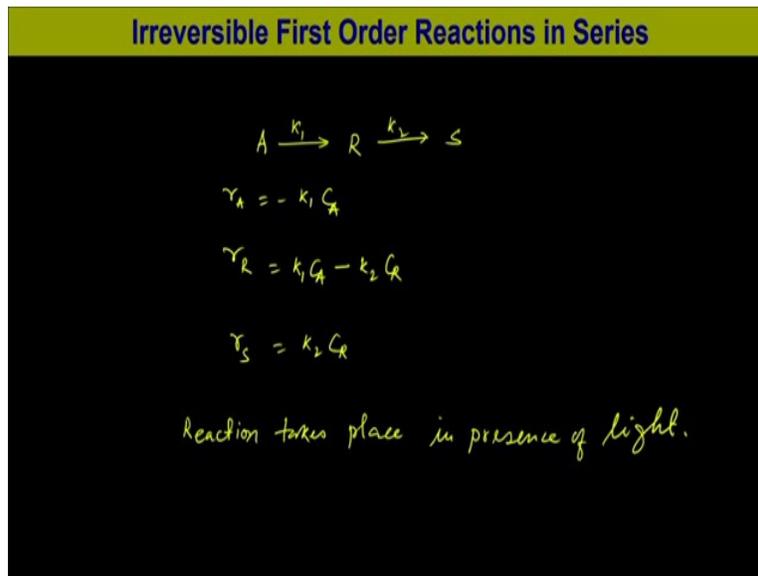
So, if you consider $A \xrightarrow{k_1} R \xrightarrow{k_2} S$, and if you write the rate of reactions for each step, for each

species we can write $r_A = -k_1 C_A$, $r_R = k_1 C_A - k_2 C_R$ and for S, $r_S = k_2 C_R$. And assume

that this reaction takes place in presence of light, so reaction takes place in presence of light. So

as soon as we put off the light, their reaction will not occur.

(Refer Slide Time: 4:38)
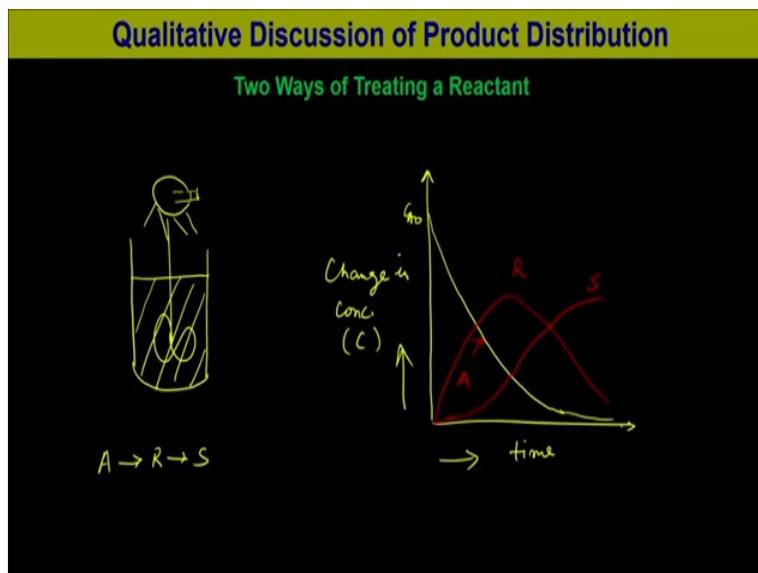
We can treat the product distribution in two ways, one we can take a CSTR and it is start and we have a light source, so light will fall and we have reaction will start so our reaction is $A \rightarrow R \rightarrow S$. Now, how this product distribution will change? As soon as the light will fall, the concentration of A will decrease, so reaction will start. So, if we plot the distribution of the product or the concentration change versus the time, so time for the exposure of the light to this reactants or to this content.

So A will react and or dissociate and form product R, so the concentration of A gradually changes starting from a certain value, so this is C_{Ao}, so this is change in concentration of A. Now as soon A formed R, so the concentration of R will increase, and then after a certain time when the concentration of A is low the formation of R would be low, so R would decrease.

So this is the profile for R and as the initial concentration of R was low the formation of S was also low, so S will start like this and it will slowly increases depending on the presence of R. So this is the concentration profile for R, this is the concentration profile for S. So during this time of exposure of the light to this reactant content the concentration profile change for all species A, R and S would look like this.

(Refer Slide Time: 8:27)
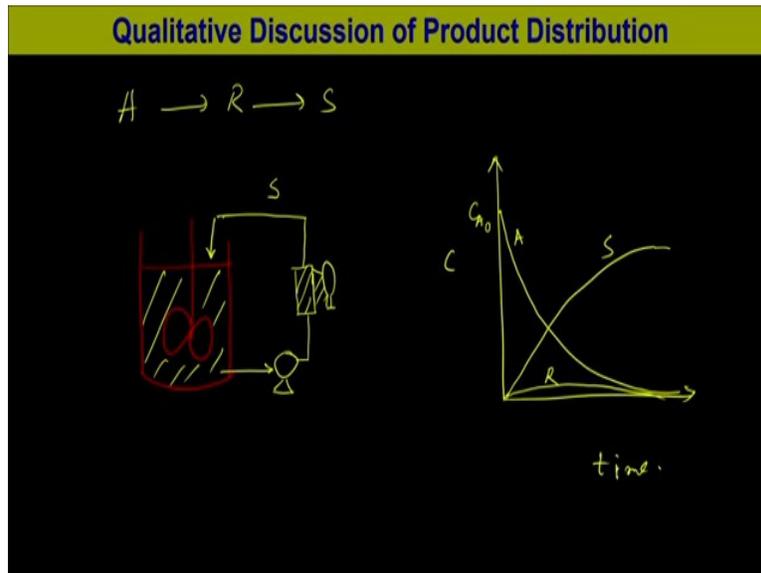
Now, if we treat this system in a different way we take a CSTR and then the content of the reactant is taken out and it is pumped through another cell where the light is put on, so light

source is over here and then it is recycled back to this. So, if we plot the concentration profile for this we can see this is C and time. So this exposure time to this light is such that all the reactant which is passed through this cell is completely converted to R.

So, the reactant content which are pumped through this cell and the time of exposure in is such that the all the reactant is converted to the final product S. So in this time of exposure $A \rightarrow R \rightarrow S$, so this the product which is returned to this content is only S and all the time A and S is returned and A is converted to S, so the product concentration of S will increase concentration of A will decrease and what we will find the concentration over here.

So, C_A will start from C_{Ao} and it will come down. So this is the variation of A and then S will increase, so this is the formation of S and with 0 or very negligible formation of presence of R. So this is R, that means the way we contact we can control the formation of the intermediate. So intermediate formation we can control by different way of reacting the initial reactants.

(Refer Slide Time: 12:28)
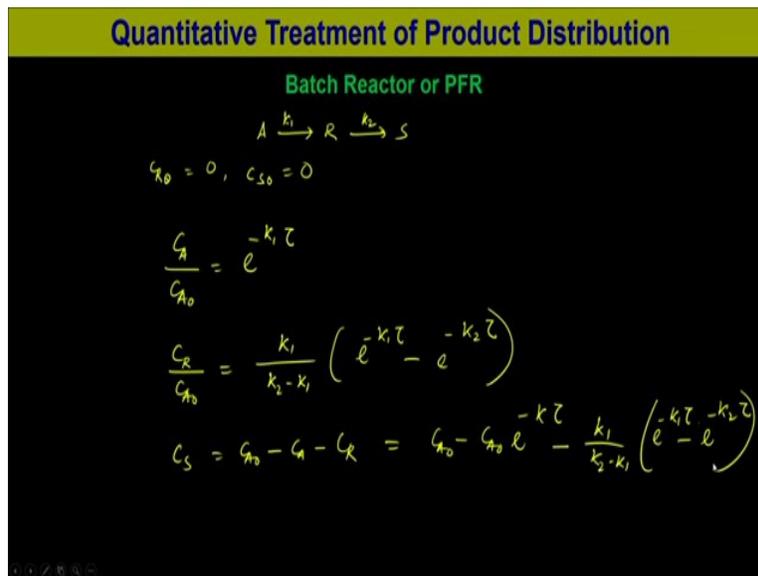
Now, let us do the quantitative treatment of product distribution and we will first consider batch reactor, this is unimolecular type of reactions, the first order reaction in series. So $A \xrightarrow{k_1} R \xrightarrow{k_2} S$,

So assumptions here is $C_{Ro} = 0$, $C_{So} = 0$, so we can use the space time and the reaction time we can use interchangeably for the batch reactor and PFR.

So we can write for the first reaction A to R we can write $\dfrac{C_A}{C_{Ao}} = e^{-k_1\tau}$ for the intermediate

product R,

we can write $\dfrac{C_R}{C_{Ao}} = \dfrac{k_1}{k_2 - k_1}\left(e^{-k_1\tau} - e^{-k_2\tau}\right)$.

And for the final product S, we can obtain $C_S = C_{Ao} - C_A - C_R$.

So, if we substitute here C_A from this would be, $C_{Ao} - C_{Ao}e^{-k_1\tau} - \dfrac{k_1}{k_2 - k_1}\left(e^{-k_1\tau} - e^{-k_2\tau}\right)$.

(Refer Slide Time: 15:30)

We can maximize the concentration of the intermediate as we did before, so we differentiate the

equation your $\dfrac{C_R}{C_{Ao}} = \dfrac{k_1}{k_2 - k_1}\left(e^{-k_1\tau} - e^{-k_2\tau}\right)$.

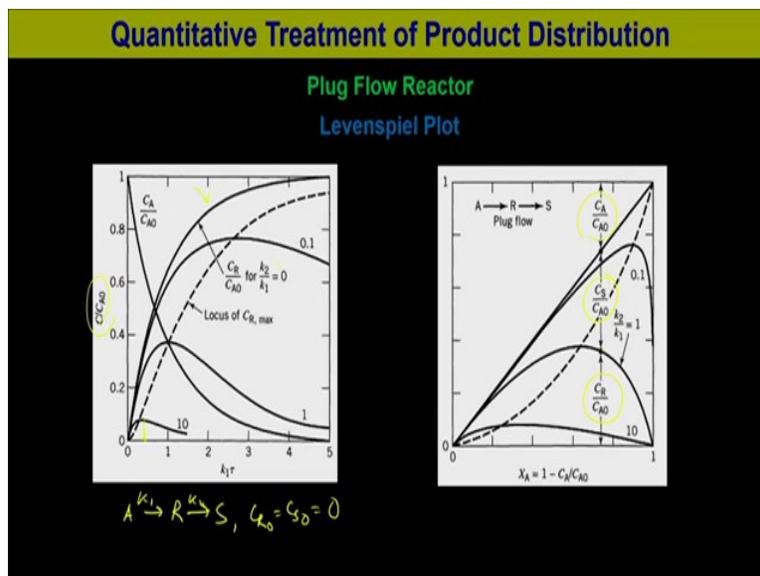So, if we differentiate this and set it to 0 $\dfrac{dC_R}{d\tau} = 0$, we would obtained

$\tau_{P,opt} = \dfrac{1}{k_{\log mean}} = \dfrac{\ln\left(k_2 / k_1\right)}{k_2 - k_1}$. So this we have already done while bringing the single reaction

for the PFR in our analysis of the Kinetic data for batch reactor or PFR. Now, if this optimum tau

in this relation, then we would obtain $\dfrac{C_{R,\max}}{C_{Ao}} = \left(\dfrac{k_1}{k_2}\right)^{k_1 / (k_2 - k_1)}$

(Refer Slide Time: 17:35)

Now this can be seen, the product distribution can be seen graphically for a plug flow reactor, if

you look into the Levenspiel plot, over here the concentration ratio $\dfrac{C}{C_{Ao}}$, so concentration of

each species versus $k_1\tau$ is plotted over here at different $\dfrac{k_2}{k_1}$ ratio and you can see that the

product so this is for $A \xrightarrow{k_1} R \xrightarrow{k_2} S, C_{Ro} = C_{So} = 0$. So this is you can see how the $\dfrac{C_R}{C_{Ao}}$ can be

varied or can be changed with respect to $\dfrac{k_2}{k_1}$. So if we change $\dfrac{k_2}{k_1}$ from say 1, 2, above 1 so then

the ratio the C_R variation should be small and for $\dfrac{k_2}{k_1} = 0$, so this is the curve

for $\dfrac{k_2}{k_1} = 0$. Now, the time dependent plot is shown over here and you can see the relative

product distribution for a particular conversion, so you can see for $\dfrac{k_2}{k_1} = 1$, this is the 45 degree

diagonal and from here this is the product distribution, this is $\dfrac{C_R}{C_{Ao}}$, this one and this is from
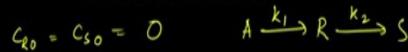
diagonal to this is distance is $\dfrac{C_S}{C_{Ao}}$, and $\dfrac{C_A}{C_{Ao}}$, so this is at particular conversion how the product

distribution we can get for a plug flow reactor where the reaction is happening into in a series

reaction.

(Refer Slide Time: 20:23)

Now, let us look into the mix flow reactor, in a mixed flow reactor let us develop the concentration time curve and we start with no reactant or product presents no intermediates or product present that means $C_{Ro} = C_{So} = 0$. Now, if we do the material balance at steady state input would be equal to output plus disappearance due to the reaction.

So for reactant A we can write $F_{Ao} = F_A + (-r_A)V$, or $vC_{Ao} = vC_A + k_1 C_A V$ for first order reaction $A \xrightarrow{k_1} R \xrightarrow{k_2} S$. So now, we know that $\dfrac{V}{v} = \tau_m = \bar{t}$. So, if we rearrange this relation this would be, so this would be $vC_{Ao} = C_A(v + k_1 V)$.

So we can write from here $vC_{Ao} = C_A(v + k_1 V)$. So from here we can write $\dfrac{C_A}{C_{Ao}} = \dfrac{v}{(v + k_1 V)}$,.

So now, this we can rearrange, this would be equal to $\dfrac{1}{1 + k_1 \dfrac{V}{v}}$. So then, this we can write

$\dfrac{C_A}{C_{Ao}} = \dfrac{1}{1 + k_1 \tau_m}$ and this $\dfrac{V}{v} = \tau_m$, so we can put τ_m.

(Refer Slide Time: 24:50)

Now, if we do the material balance for R component R, we can write $vC_{Ro} = vC_R + (-r_A)V$.

Or we can write $C_{Ro} = 0$, at the as we have assumed. So, $0 = vC_R + (-k_1C_A + k_2C_R)V$. So

now, if we use this $\dfrac{C_A}{C_{Ao}} = \dfrac{1}{1 + k_1 \tau_m}$, if we use this and if is simplify this, this would be

$$\frac{C_R}{C_{Ao}} = \frac{k_1 \tau_m}{(1 + k_1 \tau_m)(1 + k_2 \tau_m)}.$$

(Refer Slide Time: 26:56)

Quantitative Treatment of Product Distribution

Mixed Flow Reactor

$$C_A + C_R + C_S = C_{Ao} = \text{constant}.$$

$$\frac{C_S}{C_{Ao}} = \frac{k_1 k_2 \tau_m^2}{\left(1 + k_1 \tau_m\right)\left(1 + k_2 \tau_m\right)}$$

Now, we have calculated C_A concentration profile for A, and concentration profile for R. Now we have to find out the concentration profile for S, either we do the material balance or we can do by simply noting the total concentration remains constant. So, simply at any time $C_A + C_R + C_S = C_{Ao}$ which is constant. So from this if we substitute C_A and

$\dfrac{C_S}{C_{Ao}} = \dfrac{k_1 k_2 \tau_m^2}{\left(1 + k_1 \tau_m\right)\left(1 + k_2 \tau_m\right)}$. So the, we obtain the 3 concentration profiles for the 3

component which are in series.

(Refer Slide Time: 28:32)

Quantitative Treatment of Product Distribution

Mixed Flow Reactor

$$\frac{C_R}{C_{Ao}} = \frac{k_1 \tau_m}{\left(1 + k_1 \tau_m\right)\left(1 + k_2 \tau_m\right)} \qquad \left(\frac{dC_R}{d\tau_m}\right) = 0$$

$$\frac{dC_R}{d\tau_m} = 0 = \frac{C_{Ao} k_1 \left(1 + k_1 \tau_m\right)\left(1 + k_2 \tau_m\right) - C_{Ao} k_1 \tau_m \left[k_1 \left(1 + k_2 \tau_m\right) + \left(1 + k_1 \tau_m\right)k_2\right]}{\left(1 + k_1 \tau_m\right)^2 \left(1 + k_2 \tau_m\right)^2}$$

$$\tau_{m,opt} = \frac{1}{\sqrt{k_1 k_2}}$$

$$\frac{C_{R,max}}{C_{Ao}} = \frac{1}{\left(\sqrt{k_2/k_1} + 1\right)^2}$$

Now, we can optimize the intermediate by differentiating the equation $\dfrac{C_R}{C_{Ao}}$. This equation

concentration profile and we put $\dfrac{dC_R}{d\tau_m} = 0$.

So, if we do so we would obtain $\dfrac{C_R}{C_{Ao}} = \dfrac{k_1 \tau_m}{\left(1 + k_1 \tau_m\right)\left(1 + k_2 \tau_m\right)}$.

So, we can differentiate it would be

$$\frac{dC_R}{d\tau_m} = 0 = \frac{C_{Ao} k_1 \left(1 + k_1 \tau_m\right)\left(1 + k_2 \tau_m\right) - C_{Ao} k_1 \tau_m \left[k_1 \left(1 + k_2 \tau_m\right) + \left(1 + k_1 \tau_m\right) k_2\right]}{\left(1 + k_1 \tau_m\right)^2 \left(1 + k_2 \tau_m\right)^2}.$$

And if we simplify this we would obtain $\tau_{m,opt} = \dfrac{1}{\sqrt{\left(k_1 k_2\right)}}$ and then if we can substitute this in
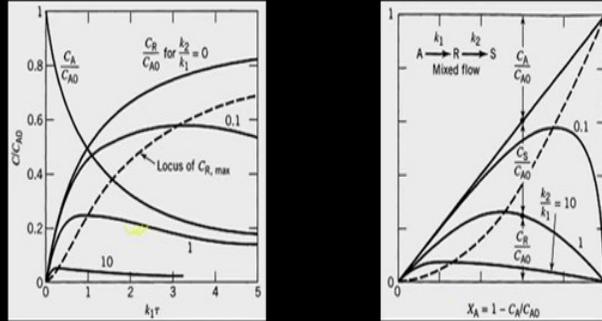
this relation τ_m then we would obtain $\dfrac{C_{R,\max}}{C_{Ao}} = \dfrac{1}{\left(\sqrt{k_2 \big/ k_1} + 1\right)^2}$.

(Refer Slide Time: 31:56)

So, the typical concentration profile can be seen in the Levenspiel plot where the variation of

$\dfrac{k_2}{k_1}$ with respect to product distribution and time can be seen over here in this case and the

relative concentration for mix flow reactor for a series reaction can be seen at different $\dfrac{k_2}{k_1}$

values at a different conversion level.
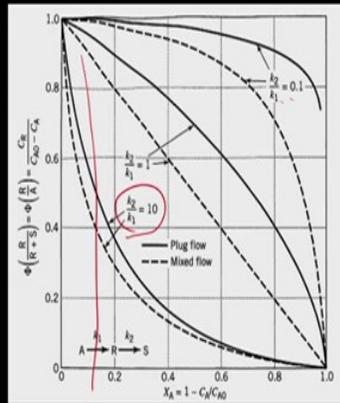
(Refer Slide Time: 32:34)

Now, if we consider quantitative treatment of the product distribution for PFR and MFR. If we compare among these two we can see from the Levenspiel plot that the ratio fractional yield

$$\phi\left(\frac{R}{R+S}\right) = \phi\left(\frac{R}{A}\right) = \frac{C_R}{C_{Ao} - C_A}$$ versus conversion plot over here. This plot clearly shows that

the fractional yield of R is always higher for PFR than MFR.

So the dotted line, the dotted line shown over here R for the mixed flow reactor and the solid line

is for the plug flow reactor and at any point if we consider for this for $\frac{k_2}{k_1} = 1$, so for any save

point 8 if we consider the conversion level for this, the conversion level for MFR is lower. The

second thing is that if $\frac{k_2}{k_1}$ is much smaller as we can see $\frac{k_2}{k_1}$ is small in this case or smaller

means it is smaller than unity, design for a high conversions.

So for high conversion is better compared to the low conversion. If $\frac{k_2}{k_1}$ is greater than unity the
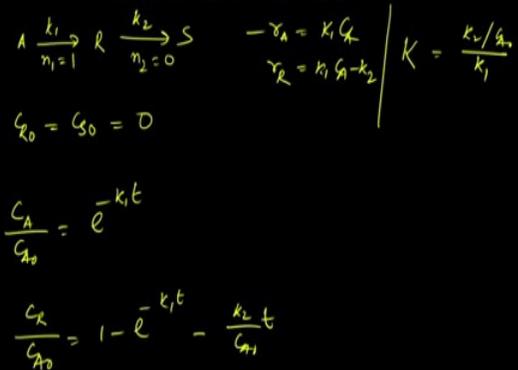
fractional yield drops sharply, so which is the case for $\frac{k_2}{k_1}$ is 10. So in this case the yield

fractional yield drops sharply in this region with a very small change in conversion, so we need to design for a small conversion. But at the same time it would be helpful if we want to avoid the undeserved product S designed for small conversion of A per pass, separate R and then recycle the unused reactant A. So it would help to maximize the intermediate product or the desired product.
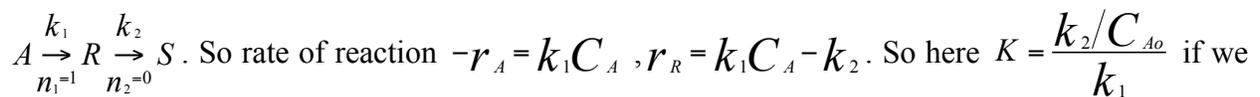
(Refer Slide Time: 35:28)

First-Order Followed by Zero-Order Reaction

Now, let us consider first order reaction followed by zero order reaction. So for a typical case of

$$A \underset{n_1=1}{\overset{k_1}{\rightarrow}} R \underset{n_2=0}{\overset{k_2}{\rightarrow}} S$$. So rate of reaction $-r_A = k_1 C_A$, $r_R = k_1 C_A - k_2$. So here $K = \dfrac{k_2/C_{Ao}}{k_1}$ if we
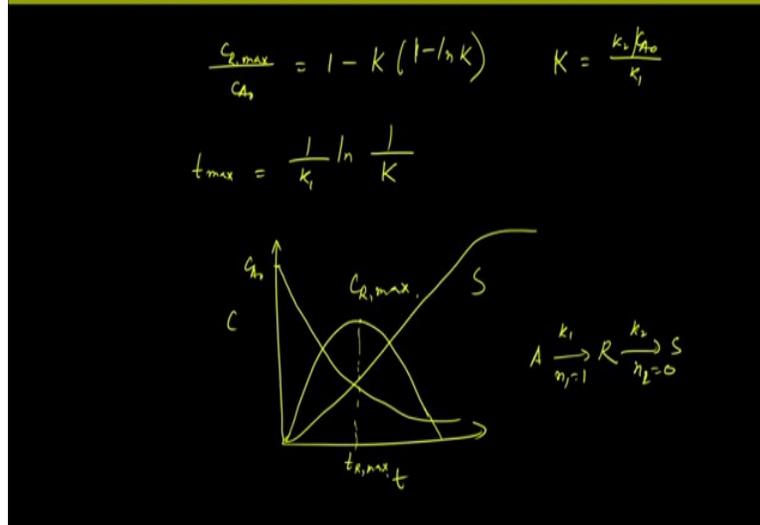
define so and if we start with $C_{Ro} = C_{So} = 0$, no RN is present. In that case we can, the first one

would be concentration profile we can derive $\dfrac{C_A}{C_{Ao}} = e^{-k_1 t}$, and for the second reaction we can

write $\dfrac{C_R}{C_{Ao}} = 1 - e^{-k_1 t} - \dfrac{k_2}{C_{Ao}} t$.
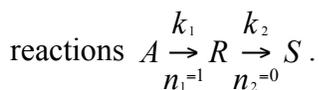
(Refer Slide Time: 37:30)

So the maximization of C_R can be obtained by differentiating and setting it to 0. The C_R

equation, then we can write $\dfrac{C_{R,max}}{C_{Ao}} = 1 - k(1 - \ln K)$, where K is given as $\dfrac{k_2/C_{Ao}}{k_1}$ and

$t_{max} = \dfrac{1}{k_1} \ln \dfrac{1}{K}$. The concentration profile if we plot concentration versus time for this zero order

or first order followed by the zero order reaction, we can get the concentration of A that is C_{Ao}

will drop, then concentration of R will increase.

So, this is for maximum, this is $C_{R,max}$ and this is the $t_{R,max}$, then the concentration of S which

is zero order reactions it will vary like this and become constant. So this is S, so this is for series

reactions $A \underset{n_1=1}{\overset{k_1}{\rightarrow}} R \underset{n_2=0}{\overset{k_2}{\rightarrow}} S$.

(Refer Slide Time: 40:21)
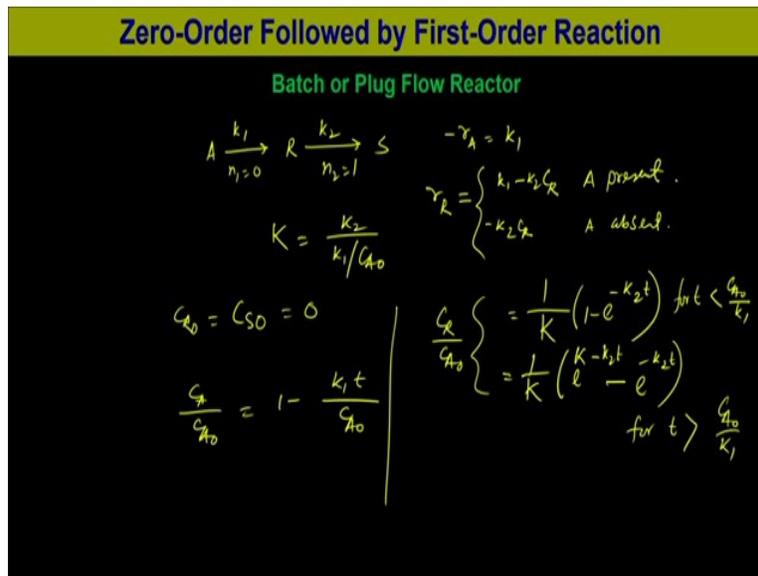
Now, let us consider batch or plug flow reactor, where zero order followed by first order

reaction. So, the reaction like this, $A \xrightarrow[n_1=0]{k_1} R \xrightarrow[n_2=1]{k_2} S$. So, rate of reaction first one is $-r_A = k_1$ and

second is formation of $r_R = k_1 - k_2 C_R$ when A is present and it would be $-k_2 C_R$ when A is
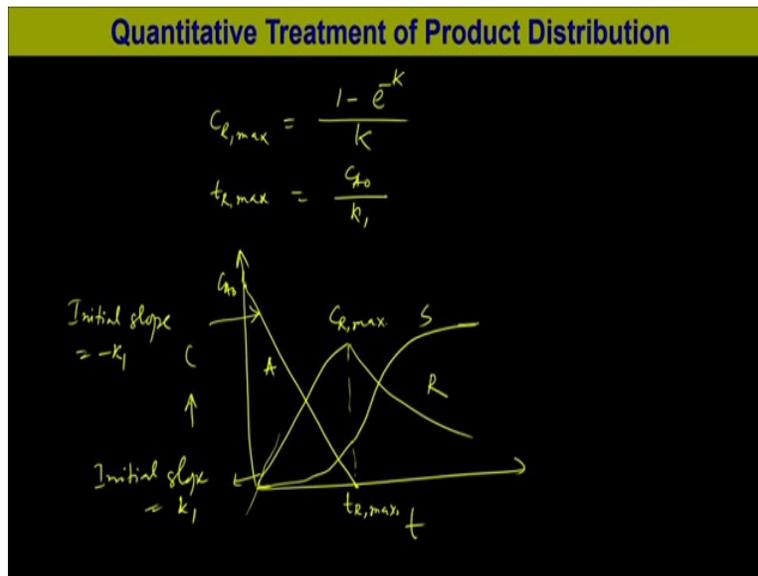
absent. And $K = \dfrac{k_2/C_{Ao}}{k_1}$.

With the same concept $C_{Ro} = C_{So} = 0$ and if we start integrating the rate equation first one it

would give $\dfrac{C_A}{C_{Ao}} = 1 - \dfrac{k_1 t}{C_{Ao}}$.

Now, $\dfrac{C_R}{C_{Ao}}$ this would be equal to $\dfrac{1}{K}\left(1 - e^{-k_2 t}\right), t < \dfrac{C_{Ao}}{k_1} 1,$

and this would be $\dfrac{1}{K}\left(e^{K-k_2 t} - e^{-k_2 t}\right), t > \dfrac{C_{Ao}}{k_1}.$

Now, the maximum concentration of C_R can be obtained by differentiating and setting it to 0

that is intermediate. So, $C_{R,\max}$ would be equal to $\dfrac{1-e^{-K}}{K}$ and $t_{R,\max} = \dfrac{C_{Ao}}{k_1}$. Now, if we look

into the concentration profile. So this is concentration, this is time. So the concentration of A that

is C_{Ao} it falls sharply to a 0 value. Where, at this time the concentration of R would be

maximum.

So this is the concentration for R then R will drop like this. The concentration of S would slowly

increase, and it reaches like this. So this is for S, this is for R, this is for A. So, slope of this line

is initial slope is equal to $-k_1$ and initial slope for this is also k_1. This is $C_{R,\max}$ and this would

be $t_{R,\max}$. So this is how the concentration profile of different component in a series reaction can

change from different order of the reaction.

(Refer Slide Time: 46:22)

So, thank you very much for attending this lecture and we will continue our discussion on reactor design in the next lecture.