Polymer Reaction Engineering
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Lecture – 24
Multiple Reaction System - III

Welcome to the third segment of multiple reaction system under the head of polymer reaction engineering. Now, let us have a look at about that what we studied previously.

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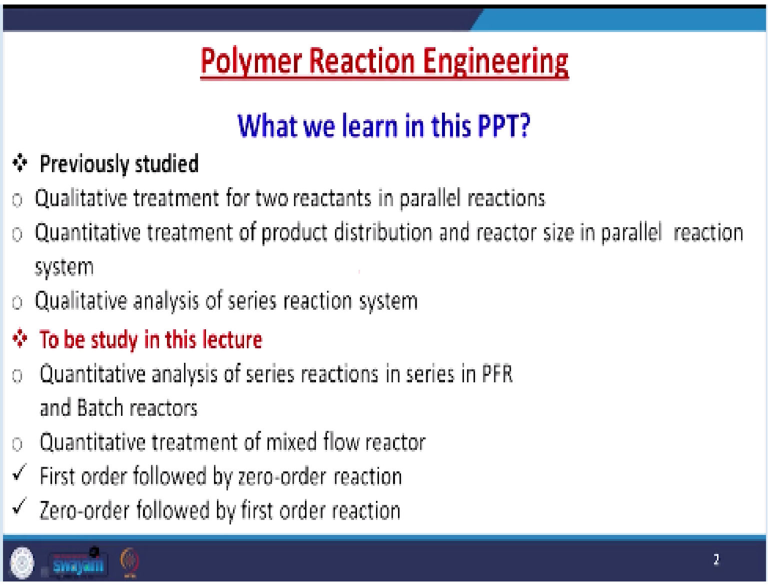

Polymer Reaction Engineering

What we learn in this PPT?

- ✣ Previously studied
  - ○ Qualitative treatment for two reactants in parallel reactions
  - ○ Quantitative treatment of product distribution and reactor size in parallel reaction system
  - ○ Qualitative analysis of series reaction system
- ✣ To be study in this lecture
  - ○ Quantitative analysis of series reactions in series in PFR and Batch reactors
  - ○ Quantitative treatment of mixed flow reactor
  - ✓ First order followed by zero-order reaction
  - ✓ Zero-order followed by first order reaction

We had a discussion about the qualitative treatment of 2 reactants in parallel reaction system. Now, here we discuss about the 2 reactants, both are reacting in parallel reactions profile. Then we perform the quantitative treatment of product distribution and a reactive size in parallel reaction system. We discussed about the qualitative analysis of a series reaction system.

In this particular lecture, we are going to discuss the quantitative analysis of a series reaction in series and PFR and batch reactors both. We will perform the quantitative treatment methodology of a mixed flow reactor. We will discuss about the first order followed by zero order reaction. We will have a discussion about the zero-order followed by the first order reaction.

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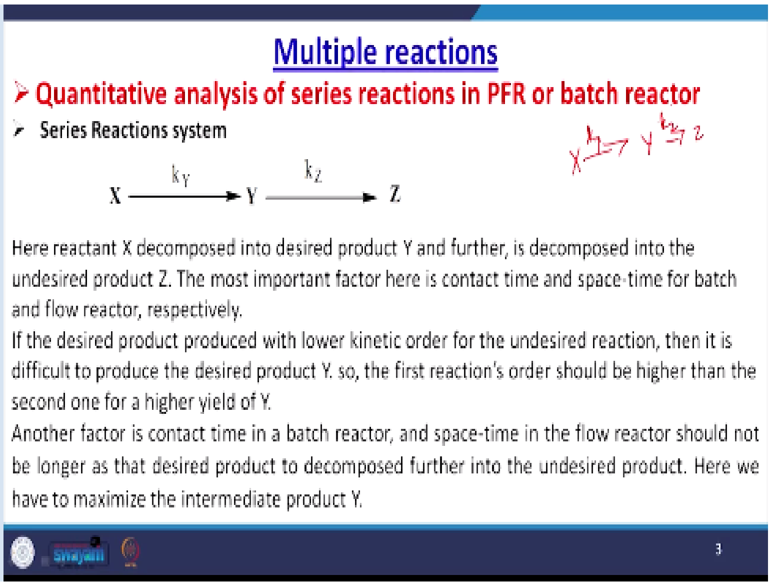

Multiple reactions

- **Quantitative analysis of series reactions in PFR or batch reactor**
  - Series Reactions system

$X \xrightarrow{k_1} Y \xrightarrow{k_2} Z$

$$X \xrightarrow{k_Y} Y \xrightarrow{k_Z} Z$$

Here reactant X decomposed into desired product Y and further, is decomposed into the undesired product Z. The most important factor here is contact time and space-time for batch and flow reactor, respectively.

If the desired product produced with lower kinetic order for the undesired reaction, then it is difficult to produce the desired product Y. so, the first reaction's order should be higher than the second one for a higher yield of Y.

Another factor is contact time in a batch reactor, and space-time in the flow reactor should not be longer as that desired product to decomposed further into the undesired product. Here we have to maximize the intermediate product Y.

So, let us have a look about the quantitative analysis of a series reaction in PFR or batch reaction. Now, as you recall that we had a discussion about the series reaction system, where we were having X is converted into Y is converted into Z with the independent rate constants as we are representing over here. Now, this if we go for the elaborative manner, then we can say that the X is decomposed into the desired product Y.

And further it is decomposed into the undesired product set. The most important factor here is the contact time and the space time for batch and flow reactor respectively. Now, if the desired product produced with a lower kinetic order for the undesired reaction, then it is difficult to produce the desired product Y. So, the first reactions order should be higher than the second one for a higher yield of Y.

Now, another factor is the contact time in a batch reactor, the space time in the flow reactor, this should not be longer as the desired product to decompose further into the undesired product. So, you should not give more time to grab this particular aspect. Now, this particular thing should keep into mind while we design the reaction protocol, while we design the size of the reactor.

Now, here we have to maximise the intermediate product Y because this is the desired one. We should not promote the formation of undesired one. So, that is why you need to adjust the space time and a contact time booth accordingly.

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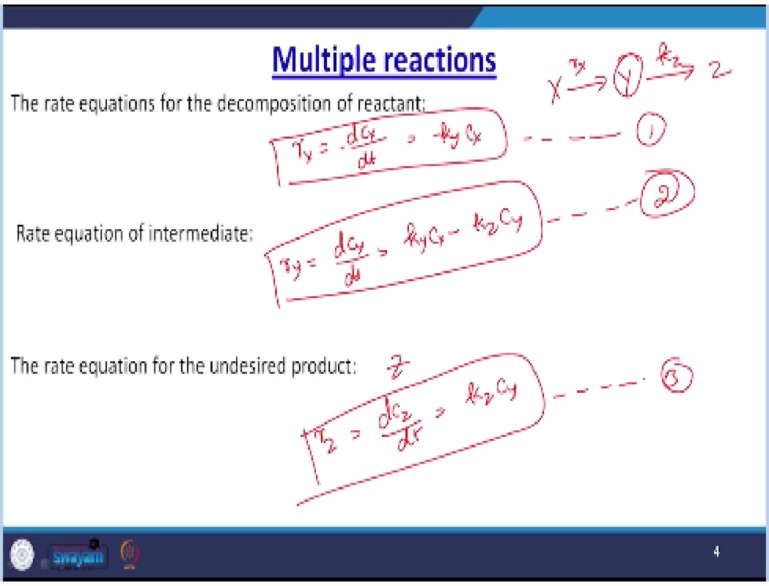

Multiple reactions

$X \xrightarrow{r_x} Ⓨ \xrightarrow{k_z} Z$

The rate equations for the decomposition of reactant:

$\boxed{r_y = \frac{dC_x}{dt} = -k_y C_x}$ - - - - ①

Rate equation of intermediate:

$\boxed{r_y = \frac{dC_y}{dt} = k_yC_x - k_zC_y}$ - - - ②

The rate equation for the undesired product: Z

$\boxed{r_z = \frac{dC_z}{dt} = k_zC_y}$ - - - - ③

Now, when we talk about this the rate equation for the decomposition of a reactant which we discussed in this slide. Now, here the rate equation for the decomposition of a reactant X can be termed as r_X is equal to dC_X dt is equal to – k_YC_X. Now, this may be termed as equation number 1. Then you can say that this is r x. Similarly, if I write the rate equation for intermediate that is Y. Then it can be represented as r_Y is equal to dC_Y upon dt that is the concentration of y.

Now, since, it is constantly being formed as well as constantly being consumed, then we can write that that k_Y C_X - k_Y C_Y that is equation number 2 and we can write this case Z. Now, since here we experienced the formation of undesired product Z, then the rate equation for the undesired product can be written as r_Z is equal to C dC_Z upon dt. This is equal to k_Z C_Y and you can say that this equation is equation number 3.

Rate equation for the decomposition of reactant

$$r_X = \frac{\mathrm{dC}_X}{\mathrm{dt}} = -k_Y C_X$$

Rate equation of intermediate:

$$r_Y = \frac{\mathrm{dC}_Y}{\mathrm{dt}} = k_Y C_X - k_{YZ} C_Y$$

The rate equation for the undesired product:

$$r_Z = \frac{\mathrm{dC}_Z}{\mathrm{dt}} = k_Z C_Y$$

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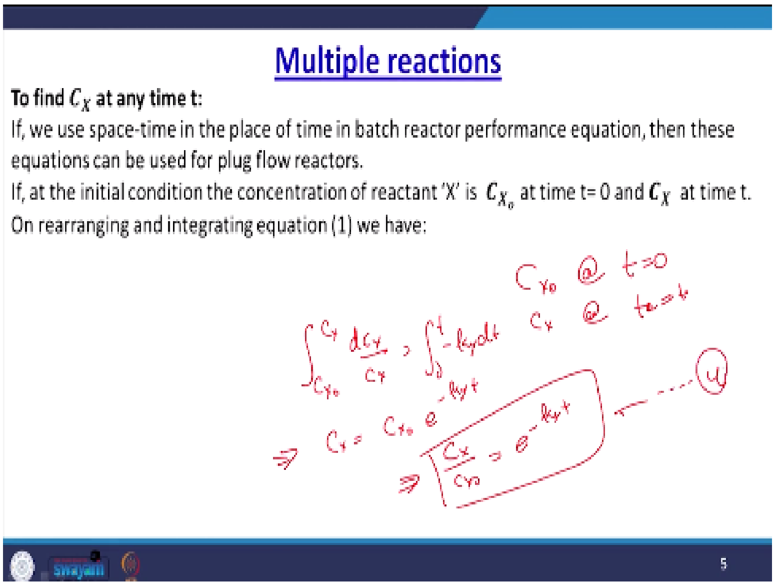

Multiple reactions

To find C_X at any time t:

If, we use space-time in the place of time in batch reactor performance equation, then these equations can be used for plug flow reactors.

If, at the initial condition the concentration of reactant 'X' is C_{X_o} at time t= 0 and C_X at time t.

On rearranging and integrating equation (1) we have:

C_{X0} @ $t=0$

C_X @ $t=t$

$$\int_{C_{X0}}^{C_X}\frac{dC_X}{C_X} = \int_0^t -k_Y dt$$

$$\Rightarrow C_X = C_{X0}\, e^{-k_Y t}$$

$$\Rightarrow \boxed{\frac{C_X}{C_{X0}} = e^{-k_Y t}} \leftarrow ④$$

Now, sometimes we need to find out the concentration of X at any time. So, if we use the space time in place of time in the batch reactor performance equation, then these equations can be used for plug flow reactor too. So, if at the initial concentration or initial condition of the concentration of the reactants X is C_X at time C_{X0} at time t is equal to 0 and C_X at time t is equal to t.

So, if we rearrange and integrate the equation, which we discussed in this slide, then we may have C_{X0} C_X dC_X upon C_X. This is 0 to t - k_Y dt or it is represented as C_X /C_{X0} is equal to e to the power – k_Y t or C_X upon C_{X0} is equal to e to the power – k_Y t. Let us say that this is equation number 4.

If at the initial condition the concentration of reactant X $\boldsymbol{C_{X_o}}$ at time t= 0 and $\boldsymbol{C_X}$ at time t.

$$\int_{C_{X_o}}^{C_X} \frac{dC_X}{C_X} = \int_o^t -k_Y\, dt$$

On solving the above equation we get:

$$\frac{C_X}{C_{X_o}} = e^{-k_Y t} \qquad \text{Or} \qquad C_X = C_{X_o} e^{-k_Y t} \qquad (4)$$

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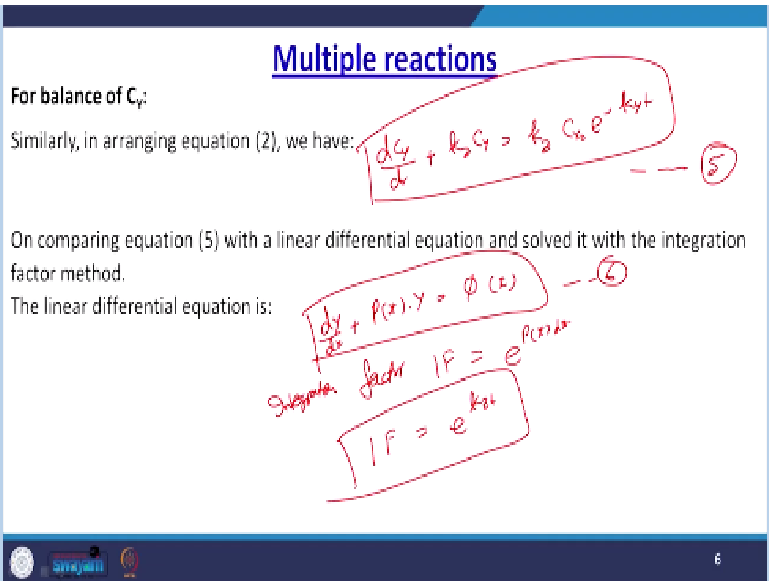

Multiple reactions

For balance of C_Y:

Similarly, in arranging equation (2), we have: $\boxed{\frac{dC_Y}{dt} + k_Z C_Y = k_Z C_{X_0} e^{-k_Y t}}$ --- ⑤

On comparing equation (5) with a linear differential equation and solved it with the integration factor method.

The linear differential equation is: $\boxed{\frac{dy}{dx} + P(x)\cdot Y = \phi(x)}$ --- ⑥

Integration factor $IF = e^{\int P(x)dx}$

$\boxed{IF = e^{k_Z t}}$

Now, if we talk about the balance of C_Y that is remember this is the intermediate. So, we can rearrange this equation number 2 which we represented over here. If we rearrange this equation, then we may have dC_Y dt + k_Z C_Y and that is k_Z C_{X0} e to the power – k_Y t. This can be represented as equation number 5. Now, if we compare the equation 5 with a linear differential equation and solved it with the integration factor method.

$$\frac{dC_Y}{dt} + k_Z\, C_Y = k_Z C_{X_o} e^{-k_Y t} \qquad (5)$$

Then the linear differential equation can be represented as dy over dx + P(X)Y is equal to phi X that is equation number 6. Now, integration factor you can write IF can be written as e to the power P(X) dx. So, integration factor for equation number 5 if we try to write that may become integration factor e to the power k_Z t.

On comparing equation (5) with a linear differential equation and solved it with the integration factor method.

The linear differential equation is:

$$\frac{dY}{dX} + P(X)Y = Q(X) \qquad (6)$$

Integration factor is:

$$\mathrm{I.F} = e^{\int P(X)d(X)}$$

So, the integration factor for equation (5) is:

$$\mathrm{I.F} = e^{k_Z t}$$

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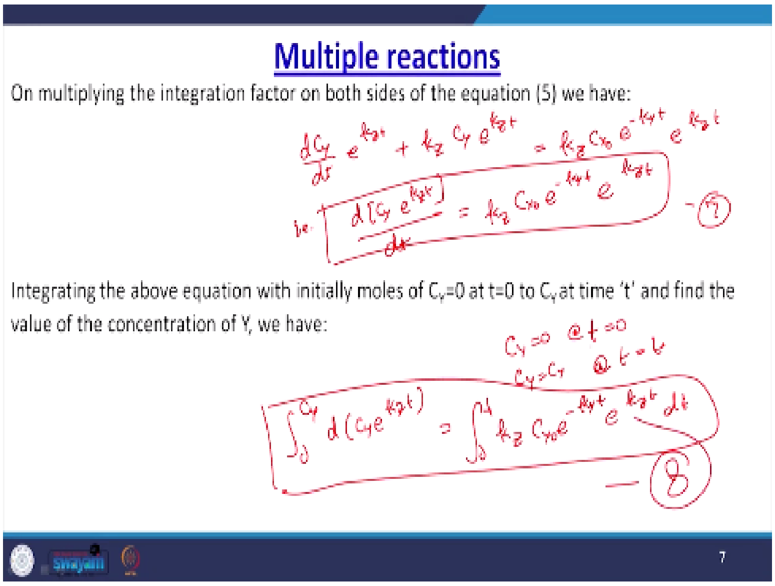

Multiple reactions

On multiplying the integration factor on both sides of the equation (5) we have:

$$\frac{dC_Y}{dt} e^{k_Z t} + k_Z C_Y e^{k_Z t} = k_Z C_{X_0} e^{-k_Y t} e^{k_Z t}$$

$$\text{i.e.} \quad \boxed{\frac{d[C_Y e^{k_Z t}]}{dt} = k_Z C_{X_0} e^{-k_Y t} e^{k_Z t}} \quad -⑦$$

Integrating the above equation with initially moles of C_Y=0 at t=0 to C_Y at time 't' and find the value of the concentration of Y, we have:

$C_Y = 0$ @ $t = 0$
$C_Y = C_Y$ @ $t = t$

$$\boxed{\int_0^{C_Y} d(C_Y e^{k_Z t}) = \int_0^t k_Z C_{X_0} e^{-k_Y t} e^{k_Z t} dt} \quad -⑧$$

Now, if we multiply this integration factor on both sides of the equation 5, then we may have dC by dt e to the power k_Z t + k_Z C_Y e to the power k_Z t is equal to k_Z C_{X0} e to the power – k_Y t e to the power k_Zt. Now, that is d Cy e k_Zt upon dt, this is equal to k_Z C_{X0} e to the power – k_Y t e to the power k_Zt. You can write this as equation number 7. Now, upon integrating this equation with the initial moles of Y with respect to that at time t is equal to 0; C_Y will be 0at time t is equal to 0 and C_Y is equal to C_Y at time t is equal to t.

And then we need to find the value of concentration of y. So, we may have this 0 to C_Y d C_Y e to the power k_Z t is equal to 0 to t, k_Z C_{X0} e to the power – k_Yt e to the power k_Z t dt. You may say that this is equation number 8.

On multiplying the integration factor on both sides of the equation (5)

$$\frac{dC_Y}{dt}.e^{k_Z t} + k_Z C_Y.e^{k_Z t} = k_Z C_{X_o} e^{-k_Y t}.e^{k_Z t}$$

i.e.

$$\frac{d(C_Y.e^{k_Z t})}{dt} = k_Z C_{X_o} e^{-k_Y t}.e^{k_Z t} \qquad (7)$$

Integrating the above equation with initially moles of Y are not formed and dividing with integration factor to find the value of the concentration of Y so,

$$\int_0^{C_Y} d(C_Y . e^{k_Z t}) = \int_0^t k_Z C_{X_o} e^{-k_Y t} . e^{k_Z t}\, dt \qquad (8)$$

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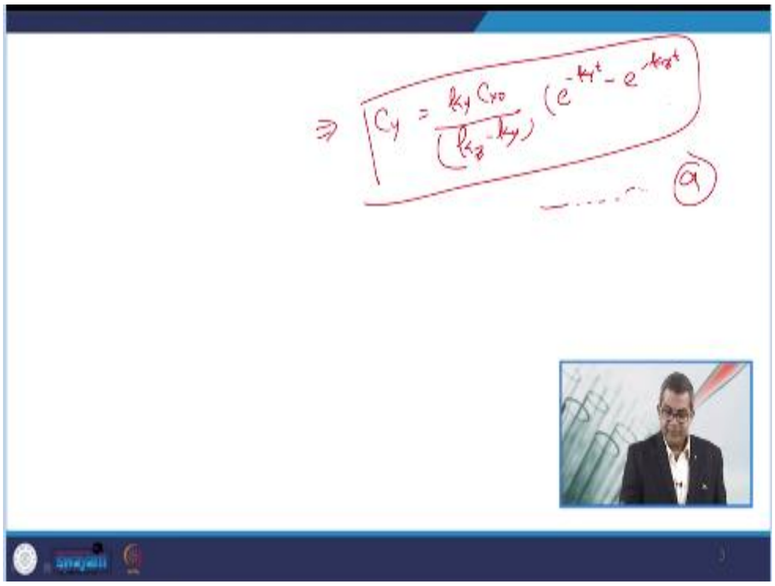

$$\Rightarrow \boxed{C_Y = \frac{k_Y C_{X0}}{(k_Z - k_Y)} (e^{-k_Y t} - e^{-k_Z t})} \quad ⑨$$

This can be rearranged and can be written as C_Y is equal to k_Y C_{X0} upon k_Z – k_Y into e to the power – $k_Y t$ – e to the power $k_Z t$. Now, you can write it as equation number 9.

$$C_Y = \frac{k_Y C_{X_o}}{(k_Z - k_Y)} (e^{-k_Y t} - e^{-k_Z t}) \qquad (9)$$

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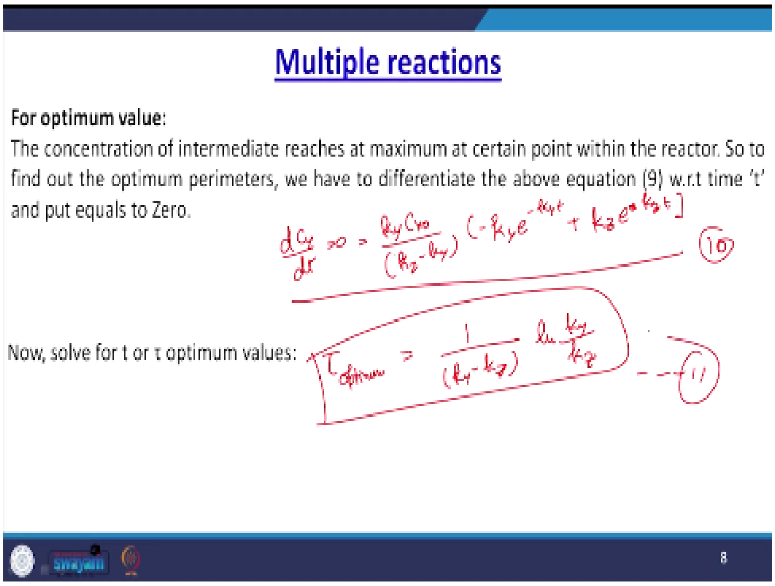

Multiple reactions

For optimum value:

The concentration of intermediate reaches at maximum at certain point within the reactor. So to find out the optimum perimeters, we have to differentiate the above equation (9) w.r.t time 't' and put equals to Zero.

$$\frac{dC_Y}{dt} = 0 = \frac{k_Y C_{Y0}}{(k_Z - k_Y)} (-k_Y e^{-k_Y t} + k_Z e^{-k_Z t}] \quad ⑩$$

Now, solve for t or τ optimum values:

$$\boxed{\tau_{optimum} = \frac{1}{(k_Y - k_Z)} \ln \frac{k_Y}{k_Z}} \quad ⑪$$

Now, if sometimes, we are always looking for the optimum value; now, the optimum value when we talk about the optimum value, the concentration of intermediate reaches at maximum in a certain point within the reactor. So, to find out the optimum parameters or perimeter, we have to differentiate the equation number 9 which we discussed with respect to time and put equal to the 0.

So, in that case, we can write this as dC_Y upon dt is equal to 0 and this is k_Y C_{X0} upon k_Z – k_Y – k_Y e to the power – k_Yt + k_Z e to the power – this kz, this is not – t. Now, this may be termed as equation number 10. Now, if we solve for t for tau optimum value, in that case that tau optimum that is 1 upon k_Y – k_Z lnk_Y upon k_Z that may become the equation number 11.

$$\frac{dC_Y}{dt} = 0 = \frac{k_Y C_{X_o}}{(k_Z - k_Y)}\left(-k_Y e^{-k_Y t} + k_Z e^{-k_Z t}\right) \qquad (10)$$

Now solve for t or τ optimum values:

$$t_{\text{opt.}} = \frac{1}{(k_Y - k_Z)} \ln \frac{k_Y}{k_Z} \qquad (11)$$

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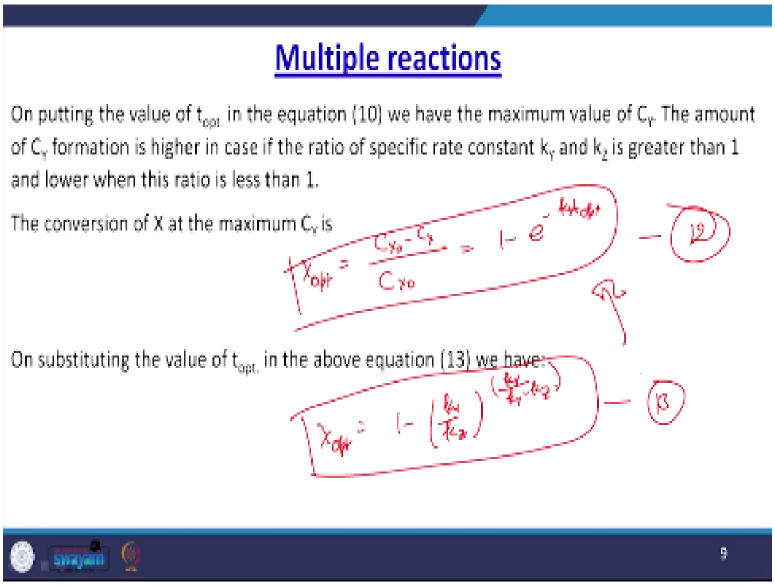

Multiple reactions

On putting the value of $t_{opt.}$ in the equation (10) we have the maximum value of C_Y. The amount of C_Y formation is higher in case if the ratio of specific rate constant k_Y and k_Z is greater than 1 and lower when this ratio is less than 1.

The conversion of X at the maximum C_Y is

$$\chi_{opt} = \frac{C_{Y_0} - C_Y}{C_{Y_0}} = 1 - e^{-k_Y t_{opt}} \quad — ⑫$$

On substituting the value of $t_{opt.}$ in the above equation (13) we have:

$$\chi_{opt} = 1 - \left(\frac{k_Y}{k_Z}\right)^{\left(\frac{k_Y}{k_Y - k_Z}\right)} \quad — ⑬$$

Now, if we put the value of this tau optimum to the equation in the previous equation 10, we have the maximum value of C_Y. So, the amount of C_Y formation is higher in case of the ratio of a specific rate constant k_Y and k_Z is greater than 1 and the lower when the ratio is less than 1. So, when we try to write the conversion of X at the maximum C_Y. So, we can write the mathematical equation X optimum that is equal to C_{X0} – C_X upon C_{X0} that is equal to 1 – e to the power – k_Yt optimal.

And this you can represent as equation number 12. Now, if we substitute the value of tau optimum in this particular equation, we may have this X optimum that is equal to 1 – k_Y upon k_Z to the power k_Y upon k_Y – k_Z that is the equation number 13.

The conversion of X at the maximum C_Y is

$$\chi_{\text{opt.}} = \frac{C_{X_o} - C_X}{C_{X_o}} = 1 - e^{-k_Y t_{\text{opt.}}} \qquad (12)$$

On substituting the value of $t_{opt.}$ in the above equation we have

$$\chi_{opt.} = 1 - \left(\frac{k_Y}{k_Z}\right)^{\frac{k_Y}{k_Y - k_Z}} \qquad (13)$$

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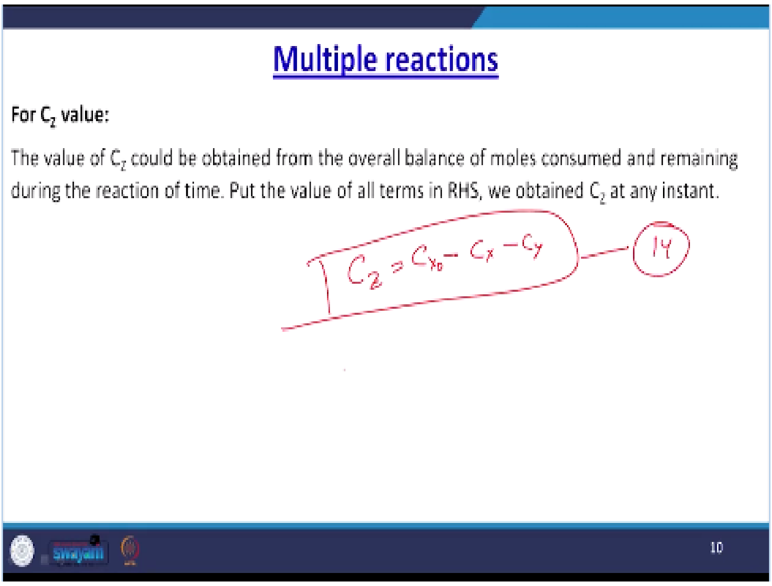

Multiple reactions

For C_z value:

The value of C_z could be obtained from the overall balance of moles consumed and remaining during the reaction of time. Put the value of all terms in RHS, we obtained C_z at any instant.

$$\boxed{C_Z = C_{X_0} - C_X - C_Y} \quad (14)$$

Now, sometimes you may be interested to find out the value of Z with respect to the concentration and that is sometimes referred to as C_Z. So, the value of C_Z, this can be obtained from the overall balance of moles consumed and remaining during the reaction of time. Now, you can put the value of all in terms of right-hand side, we obtain the value of C_Z at any instance.

So, let us put in the mathematical form that is C_Z is equal to C_{X0} – C_X – C_Y. This is quite obvious that is the concentration of X that is start then concentration after time t and then concentration of Y that is the intermediate after time t. So, we can put this as equation number 14.

$$C_Z = C_{X_o} - C_X - C_Y \qquad (14)$$

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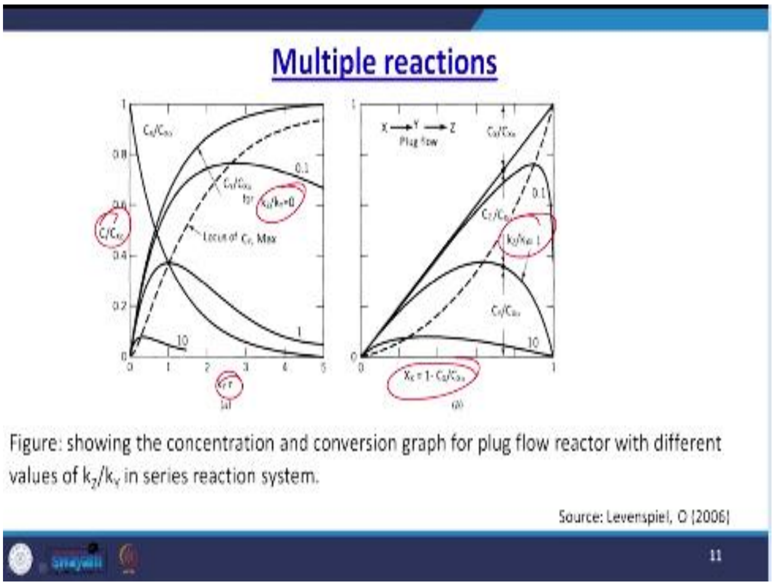

Multiple reactions

Figure: showing the concentration and conversion graph for plug flow reactor with different values of k_Z/k_Y in series reaction system.

Source: Levenspiel, O (2006)

Now, if we try to plot this thing and we represent with respect to the k_Y tau and X. You can see the behaviour of your flow or reactor etcetera, then you will find different things that is related to C upon C_{X0} and you see that at start, the concentration and conversion graph of PFR with a different value of k_Z and k_Y in series reaction systems. So, you can see that here you can have the values of this one like k_Z upon k_Y is equal to 0 and k_Z upon k_Y is equal to 1.

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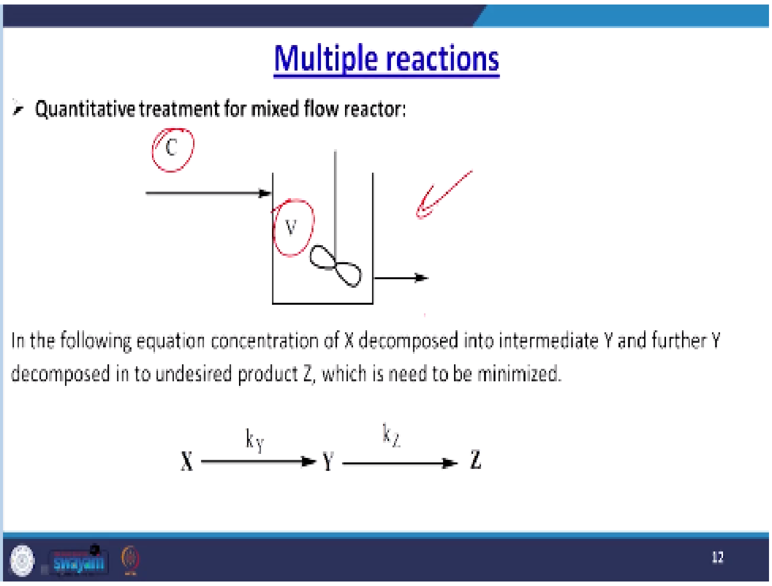

Multiple reactions

- Quantitative treatment for mixed flow reactor:

In the following equation concentration of X decomposed into intermediate Y and further Y decomposed in to undesired product Z, which is need to be minimized.

$$X \xrightarrow{k_Y} Y \xrightarrow{k_Z} Z$$

Now, let us have a look about the quantitative treatment for mixed flow reactor. Now, here we have discussed about this the mixed flow reactor. Now, here you are having then reactant which is coming into this reactor system having the concentration C, this reactor is having the volume V and it is the s-type of reactor or mixing type of reactor. Now, again we are coming back to our original equation for this one that is the equation concentration of X decomposes into the intermediate Y.

And further Y is decomposed in the undesired product Z, which is, which as per the requirement, it needs to be minimised in due course of time.

$$X \xrightarrow{k_Y} Y \xrightarrow{k_Z} Z$$

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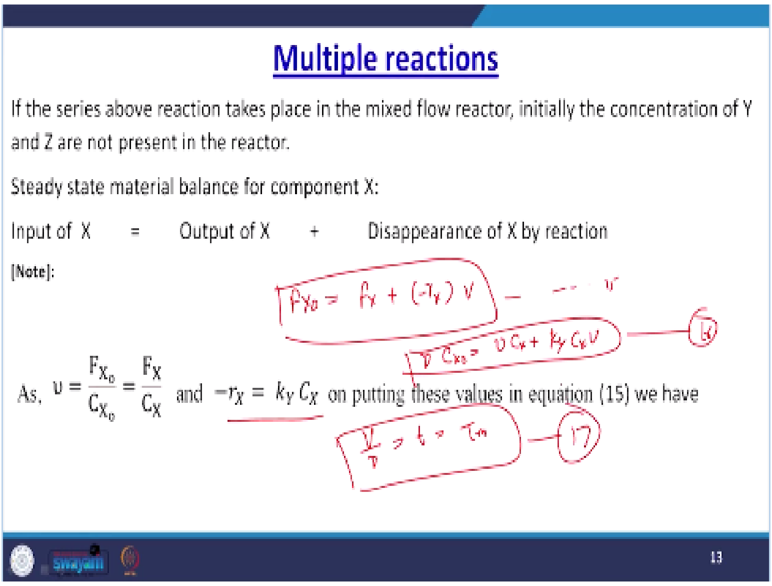

Multiple reactions

If the series above reaction takes place in the mixed flow reactor, initially the concentration of Y and Z are not present in the reactor.

Steady state material balance for component X:

Input of X = Output of X + Disappearance of X by reaction

[Note]:

$$\boxed{F_{X_0} = F_X + (-r_X)\,V} \text{ --- 15}$$

$$\boxed{\nu C_{X_0} = \nu C_X + k_Y C_X V} \text{ --- ⑯}$$

As, $\nu = \frac{F_{X_0}}{C_{X_0}} = \frac{F_X}{C_X}$ and $\underline{-r_X = k_Y C_X}$ on putting these values in equation (15) we have

$$\boxed{\frac{V}{\nu} = t = \tau_m} \text{ --- ⑰}$$

So, in that case, if the series of above reaction takes place in a mixed flow reactor, initially the concentration of Y and Z are not present in the reactor. So, initially only X is present. The concentration of X is present. So, in other words, we can say, if we perform the steady state material balance for component X, that is the input of X is equal to output of X plus disappearance of X by reaction.

So, we can write the steady state material balance equation for X and that is F_{X0} is equal to F_X plus since it is being consumed in due course of time or disappearing due course of time that is that is why we are putting – sign over here and that is this is the equation number 15. Now, if we put this value into the previous equation, then we may have like nu C_{X0} is equal to nu C_X + k_Y C_X V. Now, this is equation number 16.

So, here nu is equal to F_{X0} upon C_{X0} is equal to F_X upon C_X and – r_X is equal to k_Y C_X and if you put this all values in the previous equation and rearrange this then we may have this V upon nu is equal to t this is equal to tau m. This is my next equation. Now, here as I evident that volume is V volume of the reacting fluid, it is represented as a metre cube, then nu is the volumetric flow rate of reacting fluid.

Steady state material balance for component X:

Input of X = Output of X + Disappearance of X by reaction

$$(F_{X_o}) = (F_X) + ((-r_X)V)$$

As $\upsilon = \frac{F_{X_o}}{C_{X_o}} = \frac{F_X}{C_X}$ and $-r_X = k_Y\, C_X$ on putting these values in equation (16) we have

$$\upsilon C_{X_o} = \upsilon C_X + k_Y\, C_X V \qquad (16)$$

$$\frac{V}{\upsilon} = t = \tau_m \qquad (17)$$

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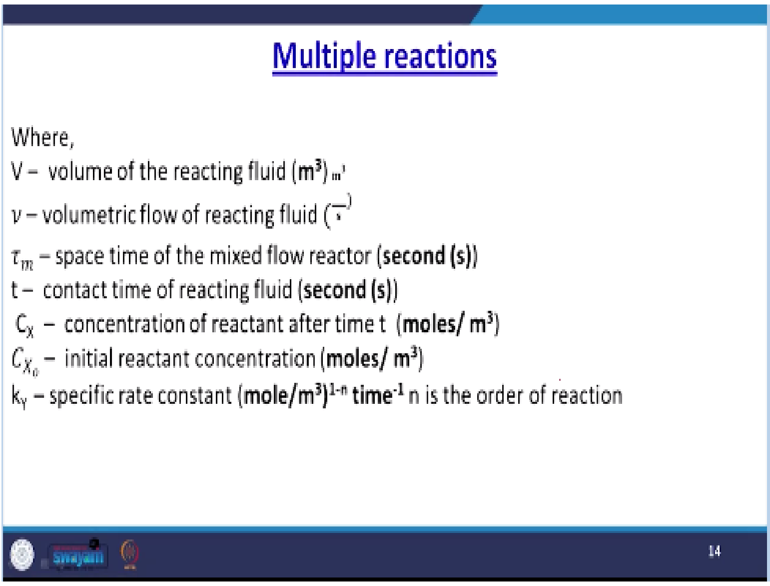

Multiple reactions

Where,

V – volume of the reacting fluid (**m^3**) $_{m^3}$

ν – volumetric flow of reacting fluid ([illegible])

τ_m – space time of the mixed flow reactor (**second (s)**)

t – contact time of reacting fluid (**second (s)**)

C_X – concentration of reactant after time t (**moles/ m^3**)

C_{X_0} – initial reactant concentration (**moles/ m^3**)

k_Y – specific rate constant (**mole/m^3)$^{1-n}$ time^{-1}** n is the order of reaction

This is the units are always represented as the second inverse. Then tau is the space time of the mixed flow reactor; then t is the contact time of the reacting fluids; C_X is the concentration of the reactant after time t and C_{X0} is the initial reactant concentration and k_Y is the specific rate constant and n is the order of the reaction.

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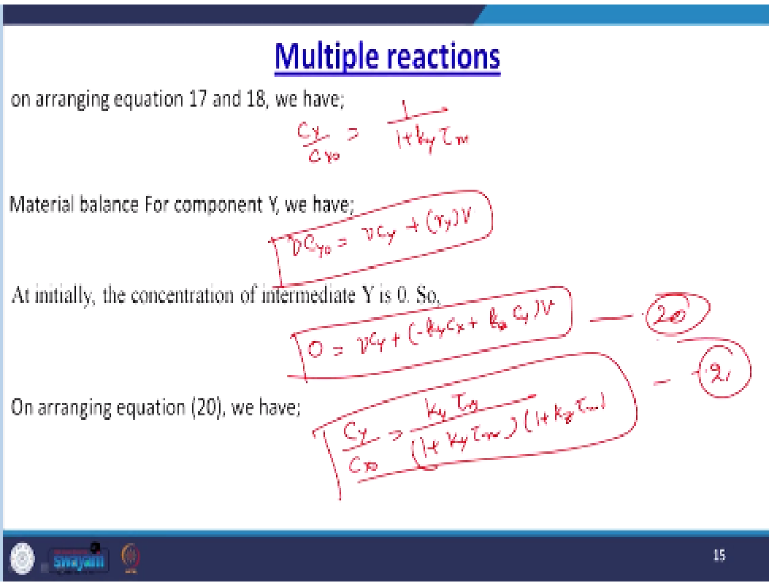

Multiple reactions

on arranging equation 17 and 18, we have;

$$\frac{C_Y}{C_{Y0}} = \frac{1}{1+k_Y\tau_m}$$

Material balance For component Y, we have;

$$\boxed{\nu C_{Y0} = \nu C_Y + (r_Y)V}$$

At initially, the concentration of intermediate Y is 0. So,

$$\boxed{0 = \nu C_Y + (-k_Y C_X + k_Z C_Y)V} \quad \text{— (20)}$$

On arranging equation (20), we have;

$$\boxed{\frac{C_Y}{C_{X0}} = \frac{k_Y\tau_m}{(1+k_Y\tau_m)(1+k_Z\tau_m)}} \quad \text{— (21)}$$

15

Now, if we rearrange the things of equations 17 and 18 in the previous slides which we discussed, then we may have this equation the C_X upon C_{X0} is equal to 1 upon 1 + k tau m and material balance equation, if we try to write the material balance for component Y, we may have nu C_{Y0} is equal to nu C_Y + r because r, the sign of this r_Y is putting positive because it is being consumed in due course of time.

Now, at initially the concentration of intermediate Y is 0 because at time t is equal to 0 and when reaction proceeds, then it acquires some values. So, in that case, we can put like this 0 is equal to nu C_Y plus – k_Y C_X + k_Z C_Y V. Now, if we rearrange this equation that is referred to as equation number 20. Now, if we rearrange this equation, we may have C_Y upon C_{X0} is equal to k_Y tau m upon 1 + k_Y tau m into 1 + k_Z tau m that you can write as equation number 21.

on arranging equation 16 and 17 we have

$$\frac{C_X}{C_{X_o}} = \frac{1}{1+k_Y\,\tau_m} \qquad (18)$$

For component Y, the material balance equation gives

$$\upsilon C_{Y_o} = \upsilon C_Y + (r_Y)V \qquad (19)$$

As initially, the concentration of intermediate Y is 0. So,

$$0 = \upsilon C_Y + (-\,k_Y\,C_X + k_Z C_Y)V \qquad (20)$$

On arranging equation (20) we have

$$\frac{C_Y}{C_{X_o}} = \frac{k_Y\,\tau_m}{(1+k_Y\,\tau_m)(1+k_Z\,\tau_m)} \qquad (21)$$

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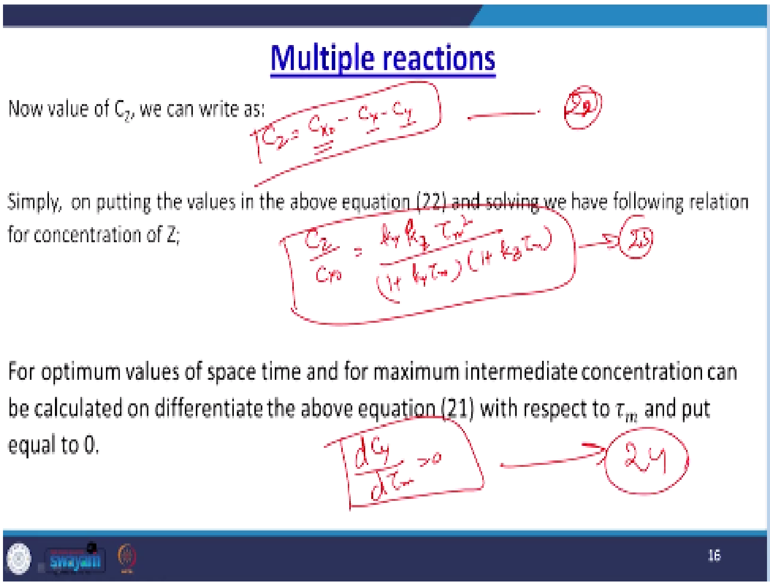

Multiple reactions

Now value of C_Z, we can write as: $C_Z = C_{X_0} - C_X - C_Y \longrightarrow (22)$

Simply, on putting the values in the above equation (22) and solving we have following relation for concentration of Z; $\frac{C_Z}{C_{X_0}} = \frac{k_Y k_Z \tau_m^2}{(1+k_Y\tau_m)(1+k_Z\tau_m)} \longrightarrow (23)$

For optimum values of space time and for maximum intermediate concentration can be calculated on differentiate the above equation (21) with respect to τ_m and put equal to 0. $\frac{dC_Y}{d\tau_m} = 0 \longrightarrow (24)$

So, by this way we can put all these equations in things. Now, if we try to calculate the value of Cz. Now, we can write this thing like Cz is equal to $C_{X0} - C_X - C_Y$. Now, it is quite obvious because we have already initiated this thing that this is the initial concentration of X, then over the period of time the concentration of see, X became Cx. And then during this course of time the Cy is formed and it is further decomposing that is why we are putting negating sign over here.

Now, in putting the values in this, let us say, this is equation number 22. Now, if we put the value of values in equation 22 and we solve, we can have the following relations like Cz upon C_{X0} is equal to k_Y k_Z tau m squared upon 1 + k_Y tau m into 1 + k_Z tau m. Now, this you can termed as equation number 23.

Now, for optimum value of space time and for the maximum intermediate concentration, this can be calculated by the differentiating this equation 21, the previous equation with respect to tau and you can put it to the 0. Then in that case, this maximum intermediate equation may become like dC_Y upon d tau m that is equal to 0. So, you can say that this is equation number 24.

Now Cz, can be calculated as:

$$C_Z = C_{X_o} - C_X - C_Y \tag{22}$$

Simply, on putting the values in the above equation (23) and solving we have following relation for concentration of Z;

$$\frac{C_Z}{C_{X_o}} = \frac{k_Y\, k_Z\, \tau^2{}_m}{(1+k_Y\,\tau_m)(1+k_Z\,\tau_m)} \tag{23}$$

For optimum values of space time and for maximum intermediate concentration can be calculated on differentiate the above equation (22) with respect to τ_m and put equal to 0.

i.e.

$$\frac{dC_Y}{d\tau_m} = 0 \qquad (24)$$

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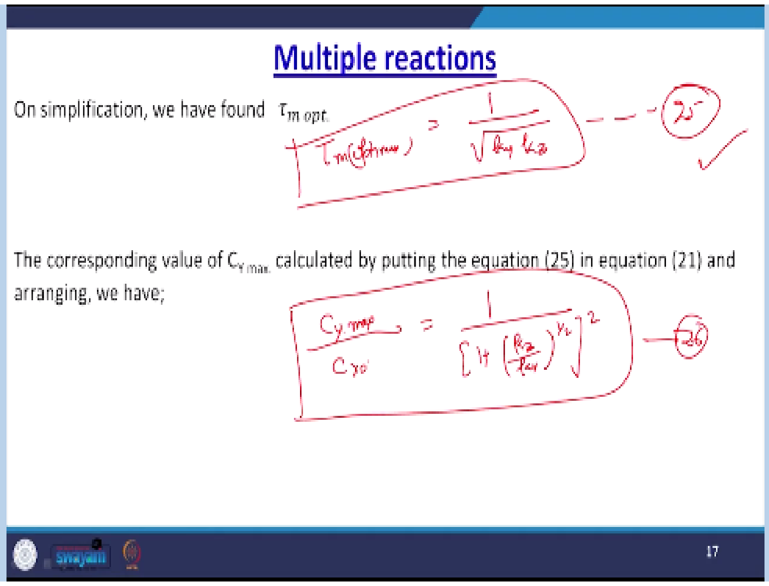

Multiple reactions

On simplification, we have found $\tau_{m\ opt.}$

$$\boxed{\tau_{m(optimum)} = \frac{1}{\sqrt{k_Y k_Z}}} \text{ - - - } ⑳\!\!\!\!\quad (25) \checkmark$$

The corresponding value of $C_{Y\ max.}$ calculated by putting the equation (25) in equation (21) and arranging, we have;

$$\boxed{\frac{C_{Y\ max}}{C_{X0}} = \frac{1}{\left[1+\left(\frac{k_Z}{k_Y}\right)^{1/2}\right]^2}} \longrightarrow (26)$$

Now, if we simplify all these equations, we can find tau m optimum. Now, this tau m optimum that can be represented as 1 upon square root of k_Y k_Z that you can say that question number 25. Now, if put the corresponding values of C_Y maximum, this can be calculated by putting the equation 25, this equation in equation the previous equation where we will be finding out our maximum optimum tau optimum.

And if we rearrange all those things, then we may get this C_Y maximum upon C_{X0} that is equal to 1 upon 1 + k_Z k_Y to the power half. Now, this you can termed as equation number 26.
On simplification, we have found $\tau_{m\ opt.}$

$$\tau_{m\ opt.} = \frac{1}{\sqrt{k_Y\, k_Z}} \qquad (25)$$

The corresponding value of $C_{Y\ max.}$ calculated by putting the equation (25) in equation (22) and arranging, we have

$$\frac{C_{Y,\ max}}{C_{X_O}} = \frac{1}{\left[1+\left(\frac{k_Z}{k_Y}\right)^{\frac{1}{2}}\right]^2} \qquad (26)$$

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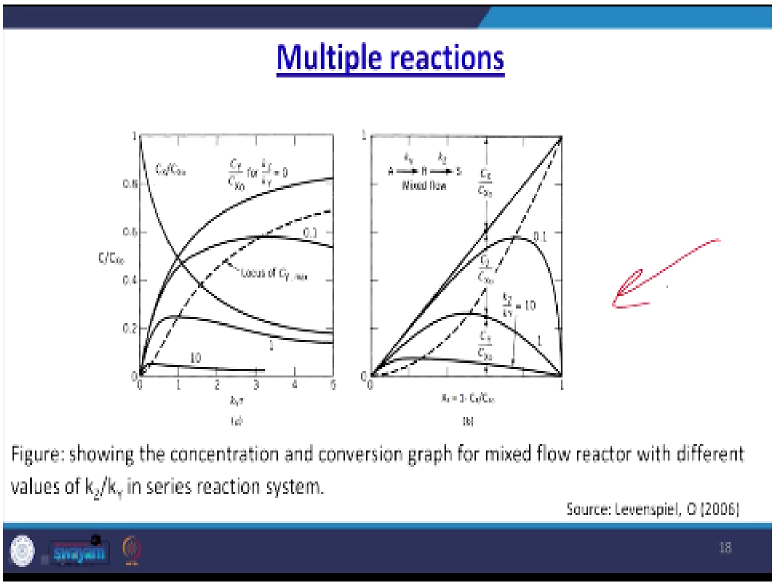

Multiple reactions

Figure: showing the concentration and conversion graph for mixed flow reactor with different values of k_Z/k_Y in series reaction system.

Source: Levenspiel, O (2006)

Now, you can easily plot these concentration and conversion graph for mixed flow reactant with the different values of k Z over k Y in series reaction system and you may see that these are the standard graphs, graphs which we have requested from Levenspiel.

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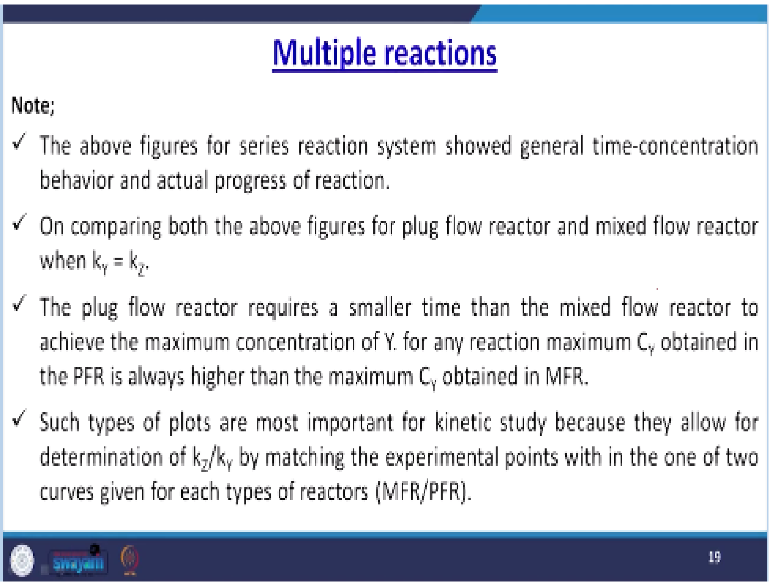

Multiple reactions

Note;

- ✓ The above figures for series reaction system showed general time-concentration behavior and actual progress of reaction.
- ✓ On comparing both the above figures for plug flow reactor and mixed flow reactor when $k_Y = k_Z$.
- ✓ The plug flow reactor requires a smaller time than the mixed flow reactor to achieve the maximum concentration of Y. for any reaction maximum C_Y obtained in the PFR is always higher than the maximum C_Y obtained in MFR.
- ✓ Such types of plots are most important for kinetic study because they allow for determination of k_Z/k_Y by matching the experimental points with in the one of two curves given for each types of reactors (MFR/PFR).

Now, if we take about these figures for series reaction system, then shows the general time concentration behaviour and actual progress of reaction. Now, if we compare these figures for plug flow reactor and the mixed flow reactor when k_Y is equal to k_Z. The plug flow reactor requires a smaller time than the mixed flow reactor to achieve the maximum concentration of Y.

For any reaction maximum, concentration of Y can be opt in the PFR which is always higher than the maximum C_Y opt in mixed flow reactor. So, these types of plots are most important for the kinetic study because they allow for the determination of k_Z over k_Y by matching the experimental point or validating those points within the one, 2 curves given in each type of reactor like the either MFR or PFR in this thing.

Now, if we talk about the first order followed by the zero-order reaction that is quite evident in different type, because people may say that we are discussing these 2 reactions.

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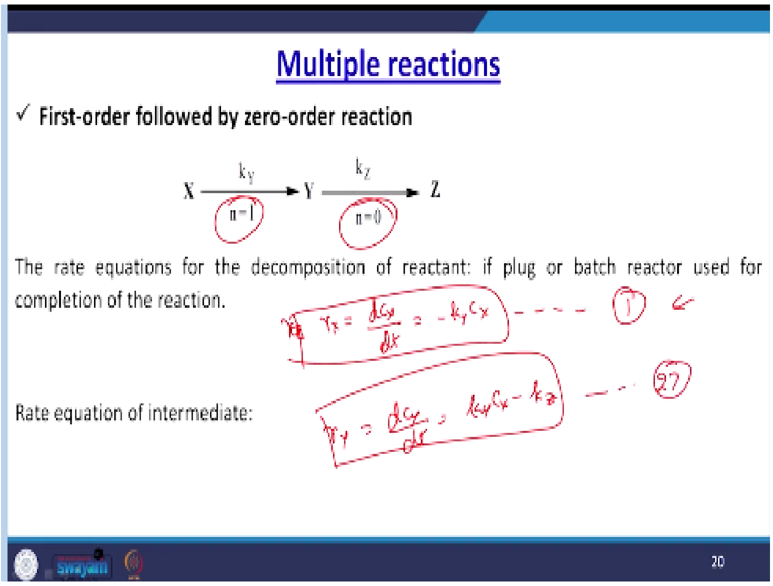

Multiple reactions

✓ First-order followed by zero-order reaction

$$X \xrightarrow[n=1]{k_Y} Y \xrightarrow[n=0]{k_Z} Z$$

The rate equations for the decomposition of reactant: if plug or batch reactor used for completion of the reaction.

$$r_X = \frac{dC_X}{dt} = -k_Y C_X \quad ---- ①$$

Rate equation of intermediate:

$$r_Y = \frac{dC_Y}{dt} = k_Y C_X - k_Z \quad --- ②$$

There are 2 reactions indeed. One is that X is converting into Y. And the second one is that Y is converting into Z in respect to that whether anyone is the desired and second one is the undesired one. So, these are 2 reactions and sometimes you may experience that the order of both the reactions are different, like here we are going to discuss this thing that first order followed by the zeroth order.

Here, you are having this first order reaction and here you are having this zeroth order reaction. Then we try to find out (( )) (24:53), we try to write the rate equation for the decomposition of reactant. Now, if plug or batch reactor used for the completion of the reaction, in that case, r_X is equal to dC_X upon dt – k_Y C_X that you may say that equation number 1.

And if we write the rate equation for the intermediate, then it may be r Y is equal to dC_Y upon dt that is k_Y C_X – k_Z that is equation, this was my question number 1 and this is if you take into the sequence, then it may become the equation number 27.

$$X \xrightarrow[n=1]{k_Y} Y \xrightarrow[n=0]{k_Z} Z$$

The rate equations for the decomposition of reactant: if plug or batch reactor used for completion of the reaction.

$$r_X = \frac{dC_X}{dt} = -k_Y C_X \qquad (1)$$

Rate equation of intermediate:

$$r_Y = \frac{dC_Y}{dt} = k_Y C_X - k_Z \qquad (27)$$

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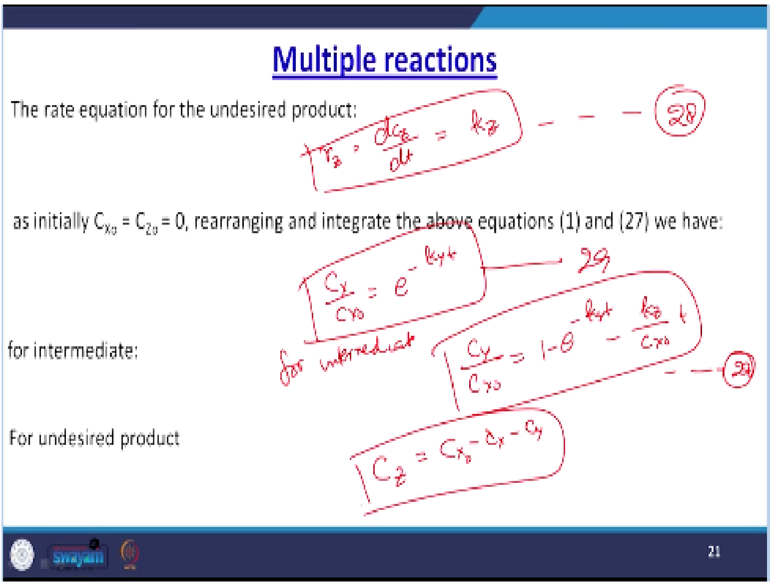

Multiple reactions

The rate equation for the undesired product: $\boxed{r_Z = \frac{dC_Z}{dt} = k_Z}$ – – – ㉘

as initially $C_{X_0} = C_{Z_0} = 0$, rearranging and integrate the above equations (1) and (27) we have:

$\boxed{\frac{C_X}{C_{X0}} = e^{-k_Y t}}$ —— 29

for intermediate:

for intermediate $\boxed{\frac{C_Y}{C_{X0}} = 1 - e^{-k_Y t} - \frac{k_Z}{C_{X0}} t}$ – – ㉙

For undesired product

$\boxed{C_Z = C_{X_0} - C_X - C_Y}$

So, the rate equation for undesired product, again it can be written down like this r_Z is equal to dC_Z upon dt is equal to k_Z. Now, you can write that equation number 28. Now, as initially the C_{X0} is equal to C_{Z0} is equal to 0. So, rearranging and integrating this equation number 1 which we discussed and this is equation number 27, then in that case C_X upon C_{X0} will become e to the power – k_Yt that you can say that equation number 29.

Now, for intermediate, you can write C_Y upon C_{X0} is equal to 1 – e to the power – k_Y t – k_Z upon C_{X0} t that you can say that is equation number 29. Now, sometimes, it is quite obvious to write the equation for undesired product. So, for undesired product, you may write C_Z is equal to C_X – C_{X0} – C_X – C_Y, this equation is we have already discussed.

The rate equation for the undesired product:

$$r_Z = \frac{dC_Z}{dt} = k_Z \qquad (28)$$

as initially $C_{Xo} = C_{Zo} = 0$, rearranging and interate the above equations (1) and (27) we have:

$$\frac{C_X}{C_{X_o}} = e^{-k_Y t} \qquad (29)$$

for intermediate:

$$\frac{C_Y}{C_{X_o}} = 1 - e^{-k_Y t} - \frac{k_Z}{C_{X_o}} t \qquad (30)$$

For undesired product

$$C_Z = C_{X_o} - C_X - C_Y$$

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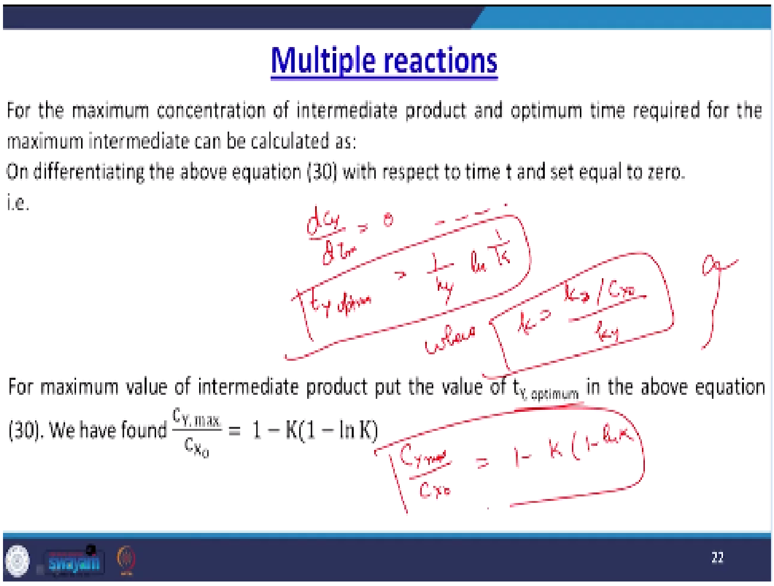

Multiple reactions

For the maximum concentration of intermediate product and optimum time required for the maximum intermediate can be calculated as:

On differentiating the above equation (30) with respect to time t and set equal to zero.

i.e.

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

$$\boxed{t_{Y\,optimum} = \frac{1}{k_Y} \ln \frac{1}{K}}$$

where $\boxed{K = \frac{k_Z / C_{X0}}{k_Y}}$

For maximum value of intermediate product put the value of $t_{Y,\,optimum}$ in the above equation (30). We have found $\frac{C_{Y,max}}{C_{X_0}} = 1 - K(1 - \ln K)$

$$\boxed{\frac{C_{Y\max}}{C_{X0}} = 1 - K(1 - \ln K}$$

So, if we differentiate these equations and for the maximum concentration of the intermediate because, we are always claiming that my intermediate product is my desired product and optimum time required for the maximum intermediate, this can be calculated by differentiating this equation which we discussed previously with respect to t and Z equal to 0, then in that case dC_Y upon d tau m that is equal to 0 that is a different set of equation.

Now, if we solve this one, then we may have t Y optimum that is equal to 1 upon k_Y ln 1 upon K and where k is equal to k_Z upon C_{X0} upon k_Y. Now, for maximum value of intermediate product put the value of t or tau Y optimum in the above equation, this is equation number 30, which we discussed previously. So, we may find the value of C_Y maximum on C_{X0} that is equal to 1 – k 1 – ln k. So, this is the desired equation which we are looking for.
On differentiating the above equation (30) with respect to time t and set equal to zero.

i.e.

$$\frac{dC_Y}{d\tau_m} = 0 \qquad (32)$$

We have get

$$t_{Y,opti} = \frac{1}{k_Y} \ln \frac{1}{K} \qquad (33)$$

Where,

$$K = \frac{\frac{k_Z}{C_{X_o}}}{k_Y}$$

For maximum value of intermediate product put the value of $t_{Y,\ optimum}$ in the above equation (30). We have found

$$\frac{C_{Y,\ max.}}{C_{X_o}} = 1 - K(1 - \ln K) \qquad (34)$$

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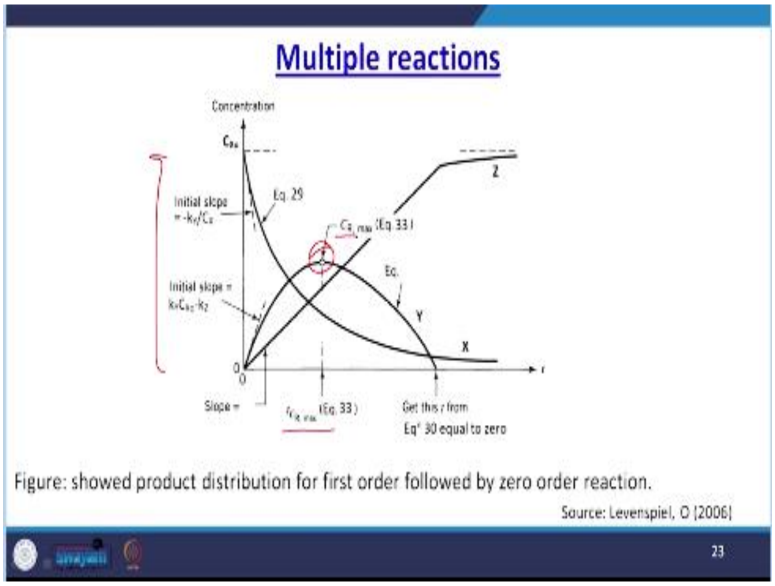

Multiple reactions

Figure: showed product distribution for first order followed by zero order reaction.

Source: Levenspiel, O (2006)

Now, if we plot the product distribution for first order followed by the zeroth order, you can see here we have plotted this t C_R maximum and this is the concentration profile, you can see that initially, we are having this with the help of this equation 33 that a C_R maximum and if you follow this previous equation 29, then you see that this curve is approaching to the minimum value.

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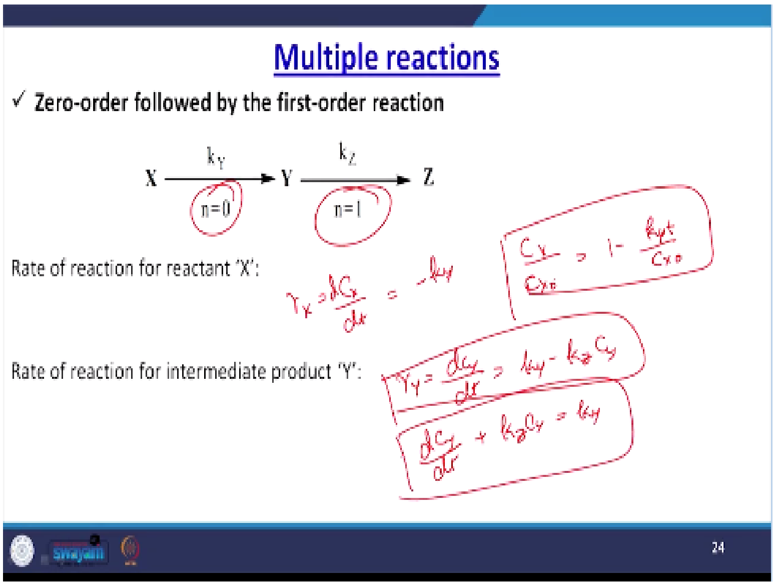

Multiple reactions

- ✓ Zero-order followed by the first-order reaction

$$X \xrightarrow[n=0]{k_Y} Y \xrightarrow[n=1]{k_Z} Z$$

Rate of reaction for reactant 'X':

$$r_X = \frac{dC_X}{dt} = -k_Y$$

$$\boxed{\frac{C_X}{C_{X0}} = 1 - \frac{k_Y t}{C_{X0}}}$$

Rate of reaction for intermediate product 'Y':

$$\boxed{r_Y = \frac{dC_Y}{dt} = k_Y - k_Z C_Y}$$

$$\boxed{\frac{dC_Y}{dt} + k_Z C_Y = k_Y}$$

Now, sometimes the other aspect or other things that is that sometimes you may experience this thing that zero-order followed by the first order. So, here you see that this is the zeroth order and this one is the first order. So, the rate of a reaction of reactant X, this can be put forward like this r_X is equal to dC_X upon dt is equal to – k_Y. And similarly, if we try to solve it, then it can become the C_X upon C_{X0} is equal to 1 – k_Y t upon C_{X0}.

Now, for intermediate product to Y, if we try to write this, then r_Y is equal to dC_Y upon dt that is equal to $k_Y - k_Z C_Y$ and this can be represented as dC_Y upon dt + $k_Z C_Y$ is equal to k_Y. Now, if we see that a rate of a reaction of undesired product, it is quite obvious, because we have to follow these series.

$$\mathbf{X} \xrightarrow[n=0]{k_Y} \mathbf{Y} \xrightarrow[n=1]{k_Z} \mathbf{Z}$$

rate of reaction for reactant X

$$r_X = \frac{dC_X}{dt} = -k_Y \qquad (35)$$

For intermediate product

$$r_Y = \frac{dC_Y}{dt} = k_Y - k_Z C_Y \qquad (36)$$

or

$$\frac{dC_Y}{dt} + k_Z C_Y = k_Y$$

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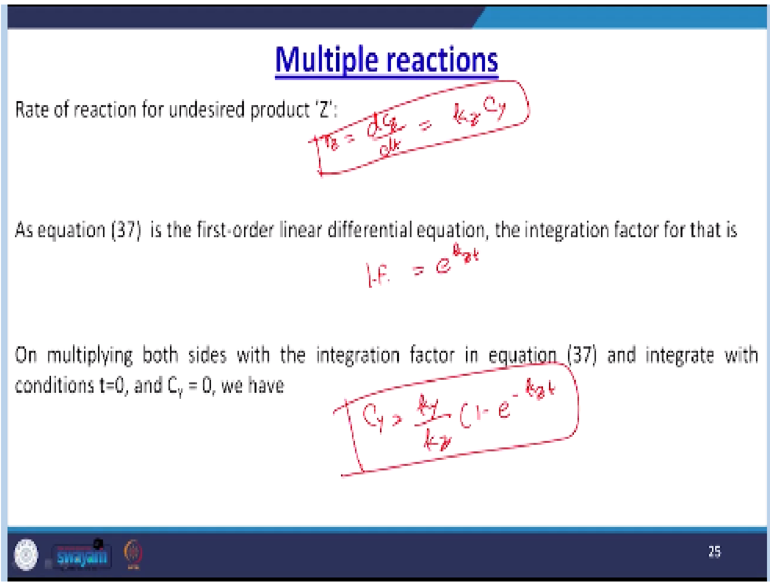

Multiple reactions

Rate of reaction for undesired product 'Z':

$$\boxed{r_Z = \frac{dC_Z}{dt} = k_Z C_Y}$$

As equation (37) is the first-order linear differential equation, the integration factor for that is

$$\text{I.F.} = e^{k_Z t}$$

On multiplying both sides with the integration factor in equation (37) and integrate with conditions t=0, and $C_Y = 0$, we have

$$\boxed{C_Y = \frac{k_Y}{k_Z}(1 - e^{-k_Z t})}$$

Then it can be put forward as r_Z is equal to dC_Z over dt, then $k_Z C_Y$. Now, if we integrate this equation and found the integration factor, then IF the integration factor can be written as e to the power k_Z t. now, if we multiply both the side with the integration factor in the previous this, previous equation, then we may have this C_Y is equal to k_Y k_Z into 1 – e to the power – k_Z t.

For undesired product

$$r_Z = \frac{dC_Z}{dt} = k_Z C_Y \qquad (37)$$

As equation (37) is the first-order linear differential equation, the integration factor for that is

$$\text{IF} = e^{k_Z}\,t \qquad (38)$$

On multiplying both sides with the integration factor in equation (37) with IF and integrate with conditions t=0, and C_Y = 0, we have

$$C_Y = \frac{k_Y}{k_Z}(1 - e^{-k_Z t})$$

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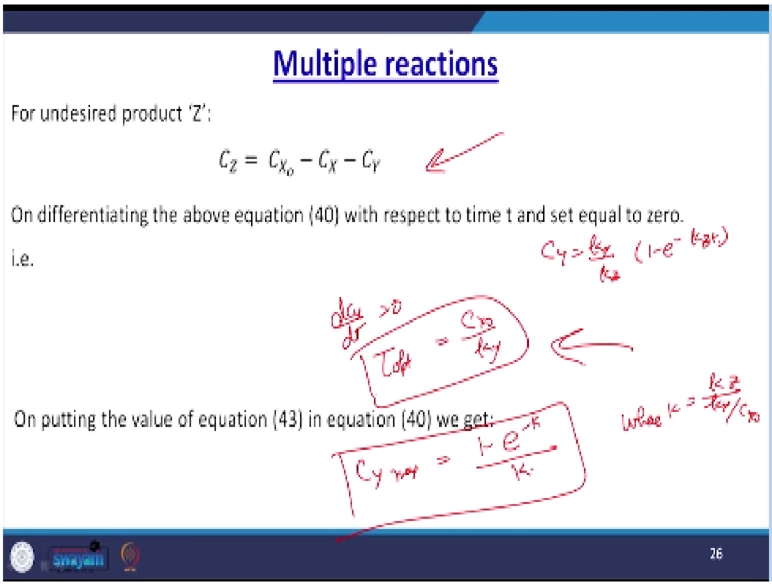

Multiple reactions

For undesired product 'Z':

$$C_Z = C_{X_0} - C_X - C_Y$$

On differentiating the above equation (40) with respect to time t and set equal to zero.

i.e.

$$C_Y = \frac{k_Y}{k_Z}(1 - e^{-k_Z t})$$

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

$$\boxed{\tau_{opt} = \frac{C_{X_0}}{k_Y}}$$

On putting the value of equation (43) in equation (40) we get:

$$\boxed{C_{Y\,max} = \frac{1 - e^{-K}}{K}}$$

where $K = \frac{k_Z}{k_Y / C_{X_0}}$

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Now, if we talk about the undesired product profile, you are always having this particular equation with Y that is C_Z is equal to C_{X0} – C_X – C_Y. Now, if you differentiate this equation the previous equation, then with respect to t and Z or put forward equal to 0, then it may become, this equation we are talking about the C_Y is equal to k_Y upon k_Z 1 – e to the power k_Z t.

Now, if we differentiate this equation with respect to t and put equal to the 0, then dC_Y upon dt is equal to 0. Now, if we solve this particular equation, then we may have a t optimum tau optimum is equal to C_{X0} upon k_Y. So, if we put the all the values in this equation, we may have C_Y maximum that is equal to 1 – e to the power – k upon k where k is equal to k_Z upon k_Y upon C_{X0}. So, this is my final equation which I am looking for.

For undesired product:

$$C_Z = C_{X_o} - C_X - C_Y \qquad (40)$$

On differentiating the above equation (39) with respect to time t and set equal to zero.

i.e.

$$\frac{dC_Y}{dt} = 0 \qquad (41)$$

We have :

$$t_{optimum} = \frac{C_{X_o}}{k_Y} \qquad (42)$$

On putting the value of equation (41) in equation (39) we get:

$$C_{Y,max} = \frac{1-e^{-K}}{K} \qquad (43)$$

Where,

$$K = \frac{k_Z}{\frac{k_Y}{C_{X_o}}}$$

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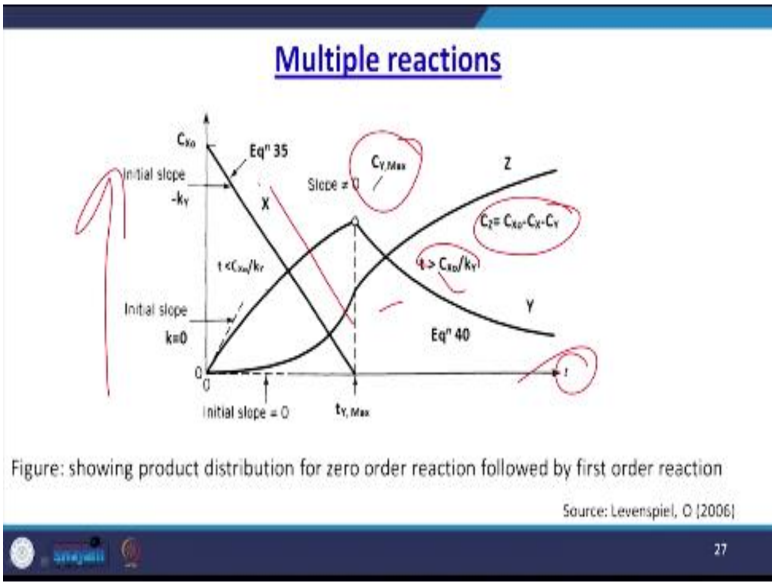


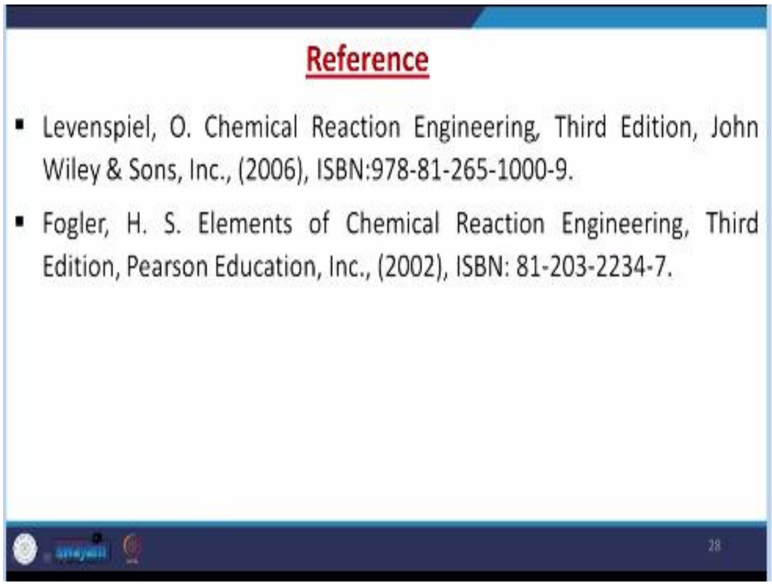
Multiple reactions

Figure: showing product distribution for zero order reaction followed by first order reaction

Source: Levenspiel, O (2006)

Now, if we try to plot this thing with respect to the time and concentration, so, you can see that we are obtaining product distribution for zero order reaction. Now, you see that with the help of our previous equation, which we developed, you can find these 2 curves which are quite evident that what kind of a different product profiling, you may have in this type of a reaction where zero order is followed by the first order reaction.

(Refer Slide Time: 33:26)



Reference

- Levenspiel, O. Chemical Reaction Engineering, Third Edition, John Wiley & Sons, Inc., (2006), ISBN:978-81-265-1000-9.
- Fogler, H. S. Elements of Chemical Reaction Engineering, Third Edition, Pearson Education, Inc., (2002), ISBN: 81-203-2234-7.

Now, in this particular chapter, we have discussed about the different configuration, a special emphasis was given to the various reaction sequences, zero order followed by a first order and then first order followed by the zeroth order. And again, for your convenience, we have enlisted couple of references for further reading. Thank you very much.