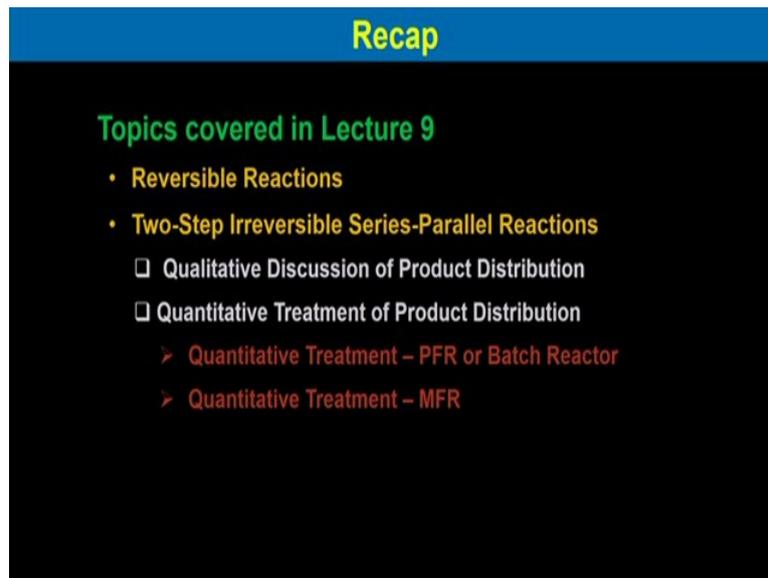


Chemical Reaction Engineering I
Professor Bishnupada Mandal
Department of Chemical Engineering
Indian Institute of Technology, Guwahati
Lecture 20
Denbigh Reactions and Their Special Cases

Welcome to the 10th 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.

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In the last lecture, we have considered reversible reaction and we have seen the product distribution for our special cases of first order reversible reactions both in series as well as parallel arrangements. Then we have considered two-step irreversible series-parallel reactions and in this case we have analyzed the series parallel reaction in terms of qualitative discussion and quantitative treatment.

In qualitative discussion, we have mainly considered three different ways of contact between the reactants and three cases are adding b into (i a) container containing a then adding a containing b and both a and b added simultaneously and we have seen the product distribution. Then we have treated the quantitative treatment of product distribution both for plug flow reactor or batch reactor and also the mix flow reactor and we have seen the product distribution changes how they changes graphically.

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Module 4: Lecture 10

Denbigh Reactions and Their Special Cases

Lecture Outline

- The Denbigh Reactions and
- Their Special Cases

In this lecture, we will consider Denbigh reactions and their special cases and this is the brief outline of our lectures the Denbigh reaction and their special cases.

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Denbigh Reactions and Their Special Cases

$$\begin{array}{c}
 A \xrightarrow{k_1} R \xrightarrow{k_3} S \\
 \searrow^{k_2} \quad \swarrow_{k_4} \\
 T \quad \quad U
 \end{array}$$

$$\begin{aligned}
 -r_A &= k_{12} C_A \\
 r_R &= k_1 C_A - k_{34} C_R \\
 r_S &= k_3 C_R \\
 r_T &= k_2 C_A \\
 r_U &= k_4 C_R
 \end{aligned}$$

$$\begin{aligned}
 k_{12} &= k_1 + k_2 \\
 k_{34} &= k_3 + k_4
 \end{aligned}$$

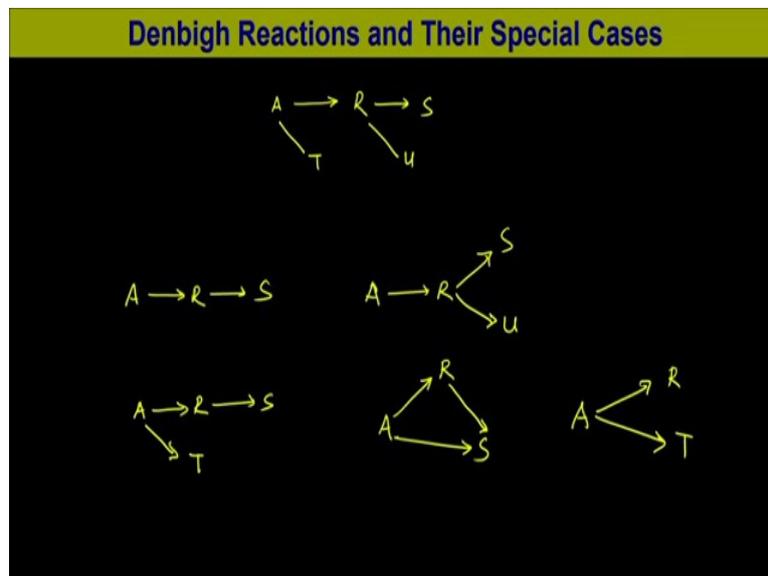
$$\begin{aligned}
 C_{A0} + C_{R0} + C_{S0} + C_{T0} + C_{U0} \\
 = C_A + C_R + C_S + C_T + C_U
 \end{aligned}$$

Denbigh reaction is kind of general reactions which Denbigh in 1958 who is the first Scientist to treat a general kind of Chemical Reactions to solve the product distribution. The reaction is like this A producing R and forming S, A is forming T and R is forming U and let the rate constants for these reactions are k 1, k 2, k 3 and k 4. The rate of the reactions for these we can write $-r_A = k_{12} C_A$ where $k_{12} = k_1 + k_2$.

We can write $r_R = k_1 C_A - k_{34} C_R$ here $k_{34} = k_3 + k_4$; $r_S = k_3 C_R$; $r_T = k_2 C_A$ and $r_U = k_4 C_R$. So, these are the rate of the reactions and for this general series-parallel reaction and with the condition that $C_{A0} + C_{R0} + C_{S0} + C_{T0} + C_{U0}$ that these are the initial concentration is sum of these would remain constant throughout the reactions.

So, it would be $C_A + C_R + C_S + C_T + C_U$. So, these general reactions were solved and obtained the concentration profile or the product distribution by Denbigh, this general reaction can be written in different schemes reaction schemes.

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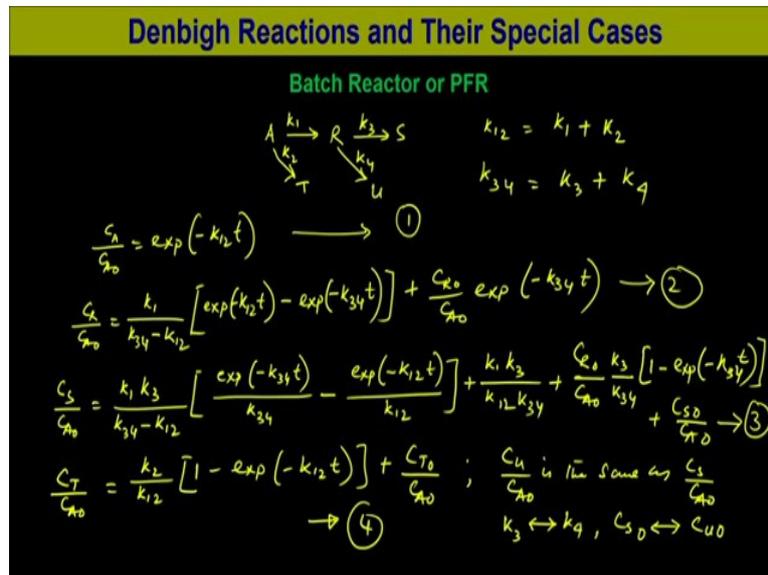


So, the reaction is A to R to S, T and U. So, this can be written as A to R to S this series reactions depending on the rate constant values between A to T, R to U and A to R and R to S this can be also written as A to R to S to U or it can be A to R to S and to T it can also be considered as close reactions of like this. So, A to R, R to S and A to S this can be A to R and to T so can be considered as parallel reactions such way. So, several scheme can be considered based on this general reaction schemes. So, all these reactions are of first order and solution of this does not involve much complication mathematically.

So, this can be solve but though these reaction schemes solving analytically is a bit tedious but it is not so complex. So, the treatment of this we will not present here the detail balance equations it can be obtained which we have discussed earlier over the last few lectures and

which can be applied and can be solve to get the concentration (profile) and we can just list down the equations which can be solved and obtained.

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Now, if you considered batch reactor or plug flow reactor the integration of the performance equations gives us the concentration profile for this general reactions A to R to S this is T and this is U, (k₁, k₂) k₁, k₂, k₃, k₄. Now, the concentration profile of A can be written as

$$\frac{C_A}{C_{A0}} = \exp(-k_{12}t) \text{ where } k_{12} = k_1 + k_2, \quad \frac{C_R}{C_{A0}} = \frac{k_1}{k_{34} - k_{12}} \left[\exp(-k_{12}t) - \exp(-k_{34}t) \right] + \frac{C_{R0}}{C_{A0}} \exp(-k_{34}t)$$

say this is equation 1, this is equation 2 here $k_{34} = k_3 + k_4$.

Now, if we write for concentration profile of .

$$\frac{C_S}{C_{A0}} = \frac{k_1 k_3}{k_{34} - k_{12}} \left[\frac{\exp(-k_{34}t)}{k_{34}} - \frac{\exp(-k_{12}t)}{k_{12}} \right] + \frac{k_1 k_3}{k_{12} k_{34}} + \frac{C_{R0} k_3}{C_{A0} k_{34}} \left[1 - \exp(-k_{34}t) \right] + \frac{C_{S0}}{C_{A0}} \rightarrow 3$$

Now, similarly we can also obtain $\frac{C_{T0}}{C_{A0}} = \frac{k_2}{k_{12}} \left[1 - \exp(-k_{12}t) \right] + \frac{C_{T0}}{C_{A0}} \rightarrow 4$

. So, these are the know concentration profile for batch reactor for these general reactions.

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Denbigh Reactions and Their Special Cases

Batch Reactor or PFR

Special Case: $C_{R0} = C_{S0} = C_{T0} = C_{U0} = 0$

$C_R = f(C_A)$

$$\frac{C_R}{C_{A0}} = \frac{k_1}{k_{12} - k_{34}} \left[\left(\frac{C_A}{C_{A0}} \right)^{k_{34}/k_{12}} - \frac{C_A}{C_{A0}} \right] \rightarrow (5)$$

$$\frac{C_{R,max}}{C_{A0}} = \frac{k_1}{k_{12}} \left(\frac{k_{12}}{k_{34}} \right)^{k_{34}/(k_{34}-k_{12})} \rightarrow (6)$$

at $t_{max} = \frac{\ln(k_{34}/k_{12})}{k_{34} - k_{12}} \rightarrow (7)$

Now, if we want to find out the maximum concentration of the intermediate R we can consider special case where $C_{R0} = C_{S0} = C_{T0} = C_{U0} = 0$. So, the expression which we have derived for R that is $C_R = f(C_A)$. So, we can write

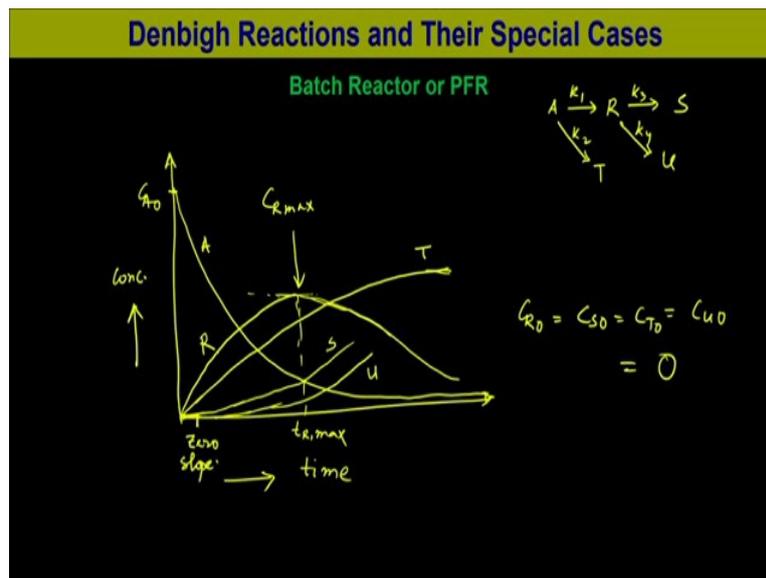
$$\frac{C_R}{C_{A0}} = \frac{k_1}{k_{12} - k_{34}} \left[\left(\frac{C_A}{C_{A0}} \right)^{\frac{k_{34}}{k_{12}}} - \frac{C_A}{C_{A0}} \right] \rightarrow 5$$

So, this is we can differentiate this relation and then we can obtain

$$\frac{C_{R,max}}{C_{A0}} = \frac{k_1}{k_{12}} \left(\frac{k_{12}}{k_{34}} \right)^{\frac{k_{34}}{k_{34}-k_{12}}} \rightarrow 6 \text{ we can put this value to obtain. So, the maximum time can be}$$

obtained at $t_{max} = \frac{\ln\left(\frac{k_{34}}{k_{12}}\right)}{k_{34} - k_{12}} \rightarrow 7$. Now, these equations can be seen graphically the concentration distribution or the product distribution.

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So, if we plot this is concentration and this is time so for the reactions A to R to S forming T, R forming U so k_1 , k_2 , k_3 and k_4 . So, we can see the concentration distribution of A, A will be continuously decrease. So, A will start at a concentration C_{A0} and we will drop whereas for R since it is intermediates it increases and then decreases so there is a point of maxima here. So, this is time $t_{R, \max}$ and this is the concentration $C_{R, \max}$ as far the equations we have derived and the concentration of t will also increase because it is not dissociating so concentration of t also will increase and will look this.

So, this is for concentration of A, this is concentration of R, this is concentration of T. Similarly U concentration of U and A is initially would be less because R is the intermediate which is forming and then dissociating S and U. So, concentration at the initially S and U would be very close or very close to 0 and so it is concentration for S will be very less and then you know it will increase.

Similarly for U, so this is for S and this is for U so initially this is the range of the zero slope for S and U. So, this concentration profile is obtained based on the condition of the Denbigh reactions of general kind for plug flow reactor with the conditions

$C_{R0} = C_{S0} = C_{T0} = C_{U0} = 0$. So, this is how we can obtain the concentration profile for a batch reactor.

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Example 1

Chemical A reacts to form R ($k_1 = 6 \text{ hr}^{-1}$) and R reacts away to form S ($k_2 = 3 \text{ hr}^{-1}$). In addition R slowly decomposes to form T ($k_3 = 1 \text{ hr}^{-1}$). If a solution containing 1.0 mol/liter of A is introduced into a batch reactor, how long would it take to reach $C_{R,\max}$ and what would be $C_{R,\max}$?

Solution

$$\begin{array}{c}
 A \xrightarrow{k_1 = 6 \text{ hr}^{-1}} R \begin{cases} \xrightarrow{k_2 = 3 \text{ hr}^{-1}} S \\ \xrightarrow{k_3 = 1 \text{ hr}^{-1}} T \end{cases} \\
 k_{32} = k_3 + k_2 \\
 = 1 \text{ hr}^{-1} + 3 \text{ hr}^{-1} \\
 = 4 \text{ hr}^{-1}
 \end{array}$$

$$\frac{C_{R,\max}}{C_{A0}} = \left(\frac{k_1}{k_{32}} \right)^{k_{32} / (k_{32} - k_1)} = \left(\frac{6}{4} \right)^{4 / (4 - 6)} = 0.444$$

$$\Rightarrow C_{R,\max} = 0.444 \times C_{A0} = 0.444 \times 1 \frac{\text{mol}}{\text{lit}} = 0.444 \frac{\text{mol}}{\text{lit}}$$

Let us take an example to see how we can obtain the concentration profile. Say we have say chemical A reacts to form R with a rate of rate constants 6 hour inverse and R reacts away to form S with k_2 is equal to 3 hour inverse. In addition R slowly decomposes to form T with k_3 is equal to 1 hour inverse. If a solution containing 1 mole per liter of A is introduced into a batch reactor how long would it take to reach $C_{R,\max}$ and what would be $C_{R,\max}$?

So, we have to calculate the T max for C R reaching maximum concentration and also $C_{R,\max}$, so let us solve this. So, the reaction can be written as A forming R with a rate of reactions k_1 is 6 hour inverse so k_1 is equal to 6 hour inverse and then it is forming S with say k_2 is equal to 3 hour inverse and it is R is again dissociating to T with k_3 is equal to 1 hour inverse.

So, this is given and we have derived the $C_{R,\max}$ equations if we write that equation that is

$$\frac{C_{R,\max}}{C_{A0}} = \frac{k_1}{k_{32}} \left(\frac{k_{12}}{k_{34}} \right)^{\frac{k_{34}}{k_{34} - k_{12}}}$$

Now, if we substitute the values, $k_{32} = k_3 + k_2$ so which is equal to 1 hour inverse plus 3 hour inverse so which is 4 hour inverse.

Now, if we substitute it would be $\left(\frac{6}{4}\right)^{\frac{4}{4-6}} = 0.444$. Now, from this we calculate

$C_{R,\max} = 0.444C_{A0}$, C_{A0} is 1 mole per liter so if we substitute this point 0.444 into 1 mole per liter which is equal to 0.444 mole per liter so we can calculate the C R max.

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Example 1

Chemical A reacts to form R ($k_1 = 6 \text{ hr}^{-1}$) and R reacts away to form S ($k_2 = 3 \text{ hr}^{-1}$). In addition R slowly decomposes to form T ($k_3 = 1 \text{ hr}^{-1}$). If a solution containing 1.0 mol/liter of A is introduced into a batch reactor, how long would it take to reach $C_{R,\max}$ and what would be $C_{R,\max}$?

Solution

$$t_{R,\max} = \frac{\ln(k_{32}/k_1)}{k_{32} - k_1} = \frac{\ln(4/6)}{(4 - 6)} = 0.2027 \text{ hr.}$$
$$= 12.2 \text{ min.}$$

Now, we have to calculate a $t_{R, \max}$. So, the equation for $t_{R, \max}$ is $t_{\max} = \frac{\ln\left(\frac{k_{32}}{k_1}\right)}{k_{32} - k_1}$. Now,

if we substitute this would be $\frac{\ln\left(\frac{4}{6}\right)}{4 - 6} = 0.2027$ this is hour and we can convert it to minutes

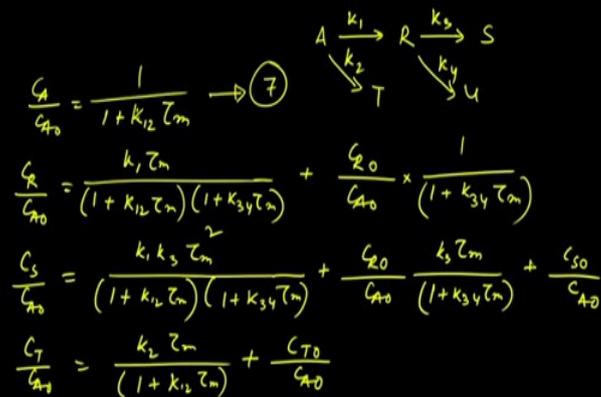
which is 12.2 minute. So, alternatively we can have the concentration profile and from graph

we can calculate C_R by $C_{A0} \max$. So, this way we can get the maximum concentration of R and the maximum time $t_{R, \max}$ to attain the concentration $C_R \max$.

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The Denbigh Reactions and Their Special Cases

Mixed Flow Reactor



Now, if we consider mixed flow reactor the performance equation for mixed flow reactor we can write for this general reactions of A to R to S, T and U this is k 1, k 2, k 3, k 4. So, the

concentration profile for A in a mixed flow reactor would be $\frac{C_A}{C_{A0}} = \frac{1}{1 + k_{12}\tau_m}$ say this is

equation 7 and then

$$\frac{C_R}{C_{A0}} = \frac{k_1\tau_m}{(1 + k_{12}\tau_m)(1 + k_{34}\tau_m)} + \frac{C_{R0}}{C_{A0}(1 + k_{34}\tau_m)}$$

For concentration profile of S,

$$\frac{C_S}{C_{A0}} = \frac{k_1 k_3 \tau_m^2}{(1 + k_{12}\tau_m)(1 + k_{34}\tau_m)} + \frac{C_{R0}}{C_{A0}(1 + k_{34}\tau_m)} + \frac{C_{S0}}{C_{A0}}$$

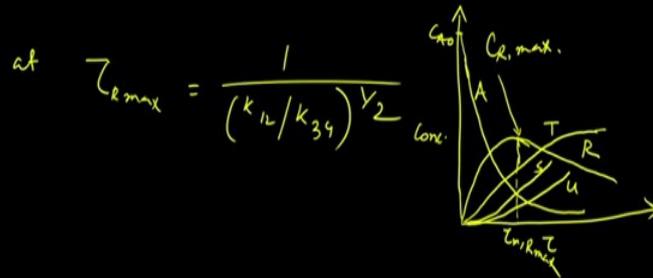
$$\frac{C_T}{C_{A0}} = \frac{k_2\tau_m}{(1 + k_{12}\tau_m)} + \frac{C_{T0}}{C_{A0}}$$

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The Denbigh Reactions and Their Special Cases

Mixed Flow Reactor

$$\frac{C_{R,max}}{C_{A0}} = \left(\frac{k_1}{k_2}\right) \times \frac{1}{\left[\left(\frac{k_{34}}{k_{12}}\right)^{1/2} + 1\right]^2}$$



So, at the optimum if we wanted to maximize C R. So, we can obtain

$$\frac{C_{R,max}}{C_{A0}} = \left(\frac{k_1}{k_2}\right) \times \frac{1}{\left[\left(\frac{k_{34}}{k_{12}}\right)^{1/2} + 1\right]^2}$$

be at the maximum time $t_{R,max}$ or for C S t R we can write

$$t_{R,max} = \frac{1}{\left(\frac{k_{12}}{k_{34}}\right)^{1/2}}$$

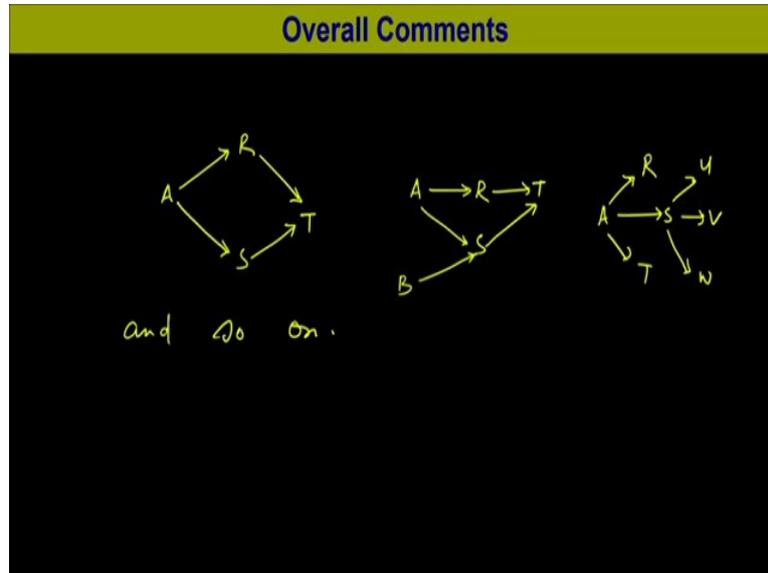
this concentration profile can be seen graphically and we can so the graphical presentation of this.

So, if we plot the concentration profile for mixed flow reactor concentration versus tau say we will get similar observation like in plug flow the concentration change C_{A0} and will drop suddenly here the concentration drop is very fast because of C S t R. So, with a sort time A will decrease R will increase to a maxima and then it will decrease so this time is tau m, R max and this is the concentration for C R max.

So, this is concentration profile for R, this is concentration profile for A, T will also increase so this is for T and S and U initially very less so then S will be like this and then U so

concentration of S and concentration profile of U. So, this is how the concentration profile would change in case of the mixed flow reactor.

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Now, this general reactions which was considered overall for multiple reactions this can be lead to direct analysis of different schemes of like this A to R to T to S and S to T it can be of even further different types A to R to T and it is forming S, S forming T and also S is forming from B this can be viewed as A to S to V and each producing by products R, T, U, W and so on.

So, analysis careful analysis of the product distribution for different concentration versus time curve will give how the product distribution will change for different kind of reactions. So, with this we conclude our Isothermal reactor design and for single and multiple reactions. In the next lecture, we will consider the temperature and pressure effect for the reactions where the kinetic parameters the k influences because of the temperature and pressure as well as the product distribution. So, thank you very much for attending this lecture.