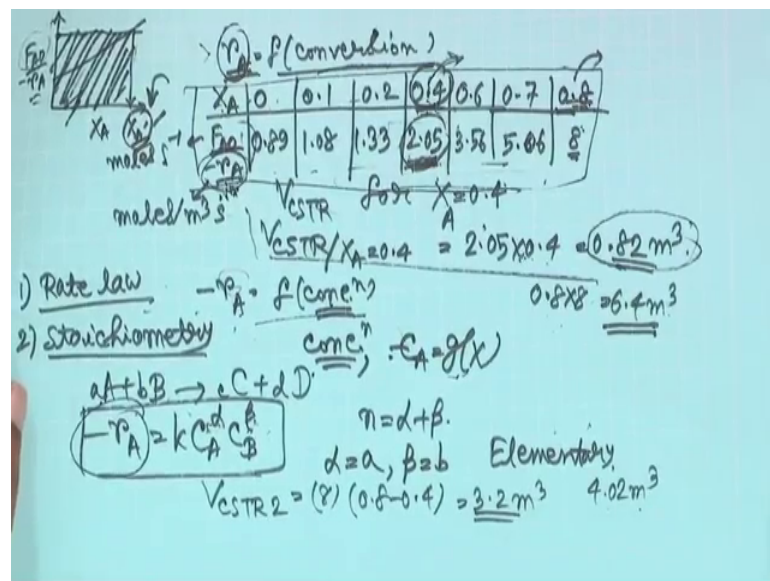


Principles of Polymer Synthesis
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Lecture – 24
Design of Chemical Reactors (Contd.)

Welcome back again to this class on principles of polymer synthesis, in continuation of the theme of this week we will keep talking about the design principle of chemical reactor, so this is lecture number 24. The topic continues to be the how to design the chemical reactors and the basic principle they are off. So, we left you at the end of the last class on the concept of Levenspiel plot and how to determine the volume of CSTR for a particular conversion. So, we will start right from there in this class.

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So, as I told F_{A0} by minus r_A is there, this is the volume that is required to get that conversion, so your design will tell you.

So, if you want a particular conversion for that particular reaction, what is the volume of c s t r, you have to go, you have got to you, so if you plot all these things and then you can get that area. So, flow rate you decide this r_A , I was telling that it is r_A you have to find as a function of conversion, we will come to that in a little while.

So, before that, let us do a simple problem. So, let us say you have this particular table. So, for all the different conversion values your FA_0 by minus r_A , this value is given 1.08, then 0.2 is 1.33, 0.4 2.05 and then 0.6, 0.7 all these values are given, 3.56, 5.06 and then 0.8, it is 8.

So, the question is, so this FA_0 by minus r_A FA_0 is in unit is moles per second; remember, this is the molar flow rate in and r_A is basically moles per meter cube per second, so this is in per meter cube. Now, if you say the question is here, what is the volume of CSTR necessary I am not just writing V_{CSTR} for a conversion of 40 percent? So, you find out the value of FA_0 by minus r_A at that point 2.05 and then you multiply with this because that is the area of the corresponding rectangle.

So, what is the V_{CSTR} for X_A equals to 0.4, it is 2.05 into 0.4, which is nothing but 0.82 meter cube. So, that is that, but let us now come back to this original question, how do you find? How can you derive if it plot like this I mean this data? In order to get that, you need to know the rate of the reaction as a function of conversion, then only with different conversion values you can have these values and then this becomes easy.

So, in order to get your things right, like your rate as a function of conversion, there are different steps involved. First, you need to find the rate law. So, rate law will give you the rate of disappearance of A as a function of concentration of different species and that is where the, comes the question of expressing all the concentrations in terms of the conversion after.

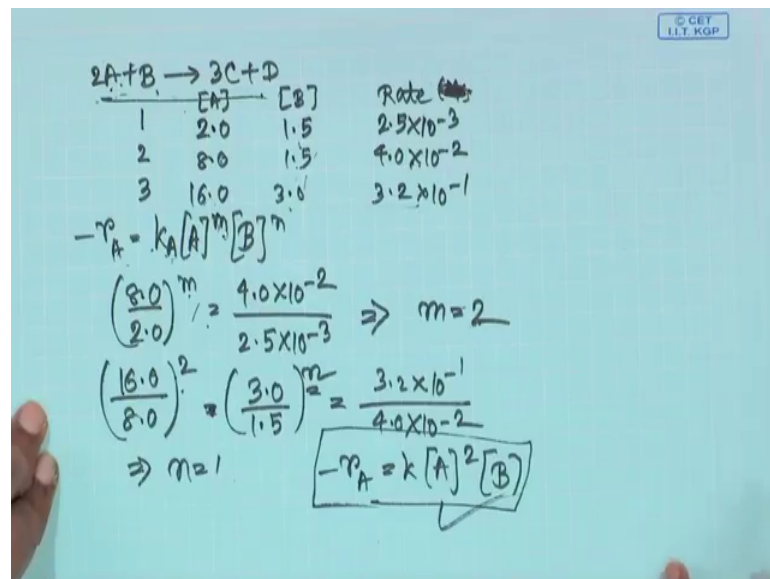
So, the second part is the part what you call as stoichiometry, in this step what you do is that you find concentration say let us say C_A , concentration as a function of conversion. So, it constitutes 2 parts, your target is having the rate as a function of conversion. So, to start with you derive the rate law, which tells you the rate as a function of concentration. Secondly, you look at the stoichiometry, which basically tells you how the concentration varies as a function of conversion. So, once you know these 2 things, you also know how the rate varies as a function of conversion.

So, let us say you have a reaction, which is say aA plus bB , again plus cC plus dD , the same general scheme I am saying. So, the rate is this minus r_A equals to the rate constant into concentration of A to the power alpha into concentration of B to the power beta. Now, these coefficients alpha and beta what is the overall order of the reaction?

Overall order is alpha plus beta. Now, if alpha equals to a and beta equals to b, then your reaction basically so your rate law. So, this is your rate law, then your rate law is basically an elementary rate law, these are some of the terminologies that that you should be aware of.

So, this alpha and beta will give you the order of the reaction. Now, alpha need not necessarily be equal to a, beta need not necessarily be equals to b, then the rate law is not elementary and this, the rate is experimentally determinable. So, I am going to give you a simple problem now, which will tell you how to determine the rate law to start with. As you see we are developing things step by step, apparently it has nothing to do it is reactor design, but ultimately we will see these knowledge is necessary, brick by brick only we will construct the concept. So, let us go into the problem then.

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Let say, we are considering a reaction 2A plus B equal to 3 C plus D, question is you are trying to find the rate law. So, in order to find the rate law for these, what you will do is that you will vary the concentration of 1 of the components and keep the concentration of the other component constant and you look at the rate. Let us say, you have done 3 experiments, 3 experiments you have done and in each of these experiments there are certain concentrations of A and B that you start with, the rate is say I do not talk about the unit here; we do not need to talk about the unit here let us say this is 2 molar 1.5

molar and then the rate you can experimentally determine 2.5×10^{-3} moles per second you can say also.

Now, this is 8 you can say moles per second rate of disappearance or a appearance. So, 4×10^{-2} you see it will vary the concentration of A, you keep the concentration of B constant; this is a technique through which you can determine the order of the reaction and also the rate law ultimately. So, this is 16×10^{-3} , now, you vary both and is 3.2×10^{-1} .

Now, rate is this k_a , so rate constant, let say rate of disappearance of A. So, $A^m B^n$, so you need to find out this m and n, then it will give you the rate law. How the rate varies as a function of concentration? This is the first step; this gives you the rate law.

So, what you do? You divide this rate by this rate, then the concentration of B will go. So, if you divide that then it will be 8×10^{-3} divided by 2×10^{-2} equal to your k_a also will go because 2 equations both have the k_a equal to this; divided by this which is 4×10^{-2} divided by 2.5×10^{-3} . So, if you work it out your m will come out as 2.

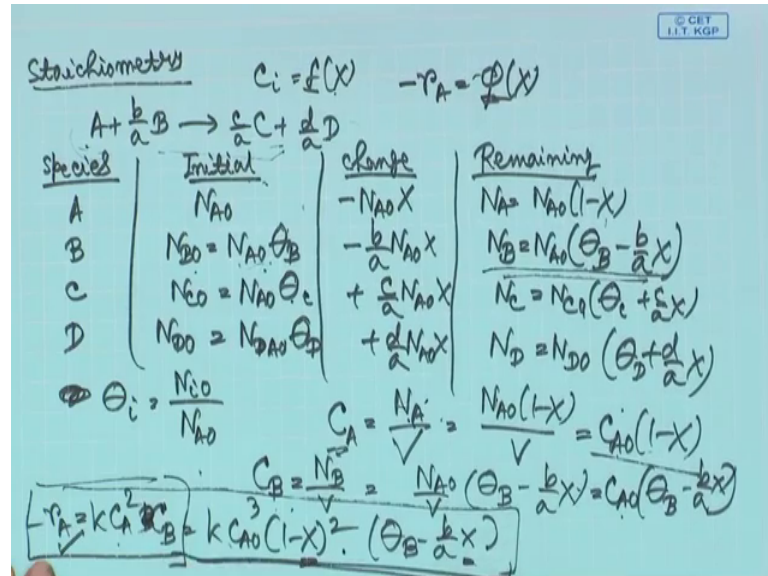
So, now, I have determined what is the value of m and correspondingly now you can take any other 2 rates and thus divide say this by this, then that will be 16×10^{-3} divided by 8×10^{-2} square, of course, now because you know the value of m and that will be equal to 3×10^{-1} multiplied by to the power n, this does not cancel out anymore, because they are not equal, multiplied this equals to 3.2×10^{-1} divided by 4×10^{-2} the power minus 2.

So, from here you have to find the value of n, n actually is 1 you can find out that. So, the rate law it becomes $r_A = k_a A^2 B$, it turns out to be an elementary rate law, it need not be, but it turns out to be. So, that is a way of determining the rate law.

So, you have now, accomplished the first step, that means, finding out the rate law that is the rate as a function of concentration, the second step is to find out the concentration as a function of conversion, then only you have a complete picture of how the rate varies

with conversion and then you can construct this kind of table, conversion versus FA0 by minus r A, that table you can construct.

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So, the second step we call as stoichiometry. So, we are trying to find out the concentration of ith species as a function of the conversion and then we will combine this information in the rate law and we will get r A as a function of x, I am putting a different function because this is not exactly the same here. So, that is why I am putting a different function there.

Now, let us consider a batch reactor, let us say you are doing a reaction A plus b by a B again the same reaction, you can construct what we call as a stoichiometric table for that. So, ultimately for this particular reaction, let us say we already know the rate law, we can find out the rate law independently. So, for the batch reactor, how the rate will vary with conversion that we can find out. So, the species let us say we construct the stoichiometric table here. So, here is species; here the species.

So, this is the initial concentration of the species, this is the change in the concentration the table and this is the remaining whatever amount is there. So, for species A, initial concentration is NA0, again we are considering the conversion of a basis of A, so change is NA0 into X. Now, these things the table that we are constructing, we have already talked about some of these things, when we say it we are trying to express the

concentration of different species in terms of the conversion. So, the same concept comes back here. So, all the concepts are interrelated.

As you see, we are bringing things up brick by brick step by step. So, remaining how much N_{A0} into $1 - x$, I am just writing x here you are assuming you already know x is in terms of A . So, what about B ? B is N_{B0} equals to N_{A0} into say θ_B , where your θ_i for the i th species it is defined as N_{i0} initial concentration of that species divided by initial concentration of A .

So, basically N_{B0} equals to N_{A0} into N_{B0} divided by N_{A0} . So, that N_{B0} divided by N_{A0} is θ_B that actually simplifies the system. So, change is minus b by a ; into N_{A0} into X , we have already discussed this before and N_B is equal to N_{A0} into θ_B minus b by a , into X , θ_B is N_{A0} divided by N_{B0} .

So, correspondingly your C is N_{C0} equals to N_{A0} into θ_C define what is θ_i , this is plus c by a because it is being generated into N_{A0} into x and your N_C is N_{C0} into θ_C plus c by a into X and your for species D , you will have N_{D0} equals to N_{A0} into θ_D plus d by a , I mean this is the this different table, the different column like this. Plus d by a N_{A0} into X and N_D equals to N_{D0} into θ_D plus d by a ; into X .

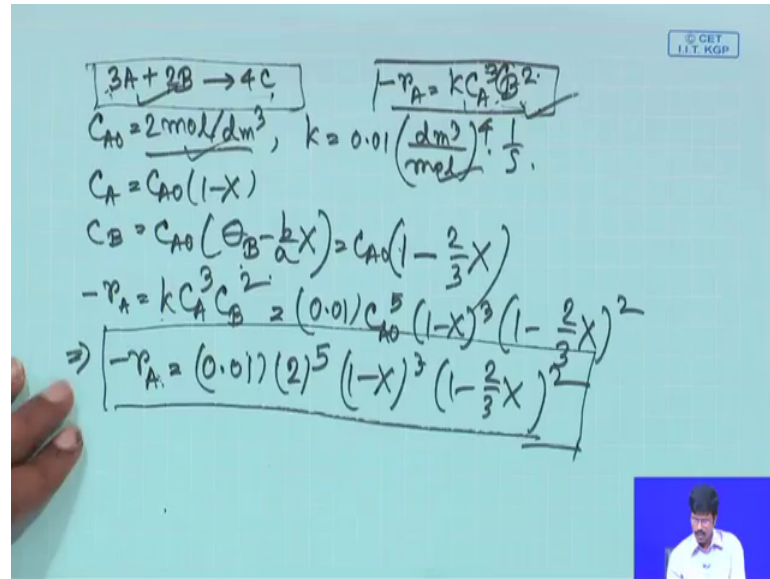
So, for a constant volume batch reactor what is the concentration of A , it is nothing but at that point of time what is the concentration of A at a time t , it is the amount of the species divided by the volume of the batch reactor. So, amount of the species from the stoichiometric table you can find out, it is N_{A0} into $1 - X$ divided by V . Now, N_{A0} by V is the initial concentration, so it is nothing but C_{A0} into $1 - X$.

Now, what is value of C_B ? It is basically N_B by V , which is equal to N_{A0} by V into θ_B minus b by a ; into X , because we know that is why you construct the stoichiometric table. Now, this is equal to N_{A0} by V is C_{A0} into θ_B minus b by a X . So, now, if you consider an elementary reaction or whatever, say you have a rate law let us assume the rate law is k into C_A square into B , A and B are reacting. So, in that case what will be the rate? So, k into C_A square, C_A is nothing but this and C_B , so this is basically C_A square into C_B .

So, C_B is nothing but this expression. So, basically this C_{A0} square into C_{A0} becomes C_{A0} cube into $1 - X$ whole square, because this square C_A square into C_B and the

CB is nothing but CA0 into theta B minus b by a; into X. Let us see, A0 comes here for C0 cube. So, for a reaction for which the rate law is like this, your rate can be expressed in terms of the conversion by this particular equation, when you are talking about a batch reactor of a constant volume V. So, let us then work out a problem with respect to this particular equation.

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Let us say we are talking about an elementary liquid phase reaction 3A plus 2B equals 4 C. So, when we are saying, so it is an elementary liquid phase reaction we are saying, so that means, the rate law is minus r A equals to k into CA cube into B square, because this alpha and beta will be equal to A and B, small a and small b, that is elementary reaction means the rate law is like this.

Now, the question is you have to write the rate law in terms of conversion, Write the rate law in terms of conversion, what is given is that for the batch reactor you have equal molar amount of A and B to start with and the concentration of A to start with is 2 moles per decimeter cube and the value of small k the rate constant is 0.01 decimeter cube by mole to the power 4 into 1 by S, that is a unit.

So, if you look at this particular reaction with all these things given, elementary reaction means the rate law is also known then. So, question is the rate of the reaction you have to now express in terms of the conversion. So, you can see that your CA is basically equal to CA0 into 1 minus X and CB equals to from the stiochiometric table you can you have

you can write the same thing here we have already derived in the previous page minus b by a ; into X , so it is CA_0 . Now θ_B is basically initial concentration of B divided by initial concentration of A , since the equimolar amounts, so this is 1.

So, that becomes $1 - b/a$, is basically $2/3$ into X . So, your rate is this, minus r_A because your starting material A is disappearing. So, that will be equal to k into CA^3 into CB^2 sorry, this is CB into CB^2 because this is elementary rate law. So, CA^3 into CB^2 this is not B^2 , CB^2 is the concentration, so CB^2 . So, k is 0.01. So, CA^3 is CA_0^3 and CB^2 is CA^2 here. So, this will be CA_0 to the power 5, so you just put the values here. So, this will become $1 - 2/3$ into X^2 .

So, ultimately your expression will become $-r_A = 0.01$ into CA_0^5 is 2. So, that will be 2 to the power 5 into $1 - X$ whole cube into $1 - 2/3 X$ whole square. So, if you are doing this particular reaction in a batch reactor, then how the rate is varying with conversion, you can actually find this particular thing out, so similarly then, so this stoichiometric table is important.

Similarly, like for batch reactor you can construct a stoichiometric table for your flow reactor also. So, in that case the stoichiometric in this stoichiometric table instead of N_A you will have F_A , instead of N_B you will have it AB all those other things will be the same. So, those things are not writing down again here.

So, it will be FA_0 , it will be FB_0 , FC_0 , FD_0 so on and so forth and your θ_i will be Fi_0 divided by FA_0 . So, molar flow rate in of the i th species divided by the molar flow rate in of species A you are considering conversion with respect to the species A all the time. So, the only thing that we need to consider is, I mean only thing extra that we need to consider here, is this thing.

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$$C_A = \frac{F_A}{V} = \frac{F_{A0}(1-X)}{V} = C_{A0}(1-X)$$

$$C_B = \frac{F_B}{V} = \frac{F_{A0}(\theta_B - \frac{b}{a}X)}{V} = C_{A0}(\theta_B - \frac{b}{a}X)$$

$$-r_A = k C_A^2 C_B = k C_{A0}^3 (1-X)^2 (\theta_B - \frac{b}{a}X)$$

* CSTRs series.

$$F_{A0} \rightarrow F_{A1} X_1 = 0.4 \rightarrow F_{A2} X_2 = 0.8$$

$$\text{in-out} + \text{gen} = 0$$

$$\Rightarrow F_{A0} - F_{A1} + r_{A1} V_1 = 0$$

$$\Rightarrow V_1 = \frac{F_{A0} - F_{A0} X_1}{-r_{A1}}$$

So, the concentration of A will be F_A divided by V ; this is the concentration of A in the flow reactor. So, let us say we are talking about a CSTR. So, the concentration of it does not change in the reactor it is the same as the flow as you have you can find out in the flow out, so that means, the species A has a concentration of C_A in the reactor as well as the concentration of C_A in the outward stream that is coming out that you are collecting.

So, that is equal to the flow rate out divided by the volumetric flow out. So, this is the molar flow rate, this is the volumetric flow and as I told you already that this molar flow rate equals to concentration into volumetric flow rate. So, this is $C_A F_A$ divided by V . So, that is nothing but F_{A0} into $1 - X$ divided by V , now F_{A0} by V is nothing but C_{A0} . So, C_{A0} into $1 - X$, so correspondingly your C_B is nothing but F_B divided by V .

So, this is F_B divided by V and F_B you can find out from the table of stoichiometry. So, it will be F_B equals to F_{A0} into this thing. So, this is for batch you replace N with F for the flow. So, that will be nothing but F_{A0} divided by V you can actually correlate to the particular table, $\theta_B - \frac{b}{a} X$, you should construct the stoichiometric table yourself that you can consider as a homework. It is exactly the same way that you construct for the batch reactor, minus b by a into X , again you assume let us say the rate of the reaction is second order in terms of A and first order in terms of B.

So, it is the same thing that we assumed for the batch reactor. So, let us assume that and then what you will get is if you put all the expressions here you will get $k C_{A0}^3$ into

$1 - X^2$ into $\theta B - b$ by aX . So, if you compare this particular expression with the expression that you got for the batch reactor both the expressions are actually the same.

So, whether you have a batch reactor or you have a flow reactor, your expression of the rate in terms of the conversion is basically the same, that is a very important thing that you should keep in mind. So, now, if you are looking at for example, the same problem let me allow myself to go back to this particular problem again.

So, if you are going for a batch reactor, if you are going for a sorry CSTR, the continuous stirred tank reactor and as we told that for say for example, for 0.4 conversion, you have this 2.05 is the value of FA_0 by minus r_A , this kind of thing you can actually construct because now, you know the r_A as a function of X and that is this, I mean this particular thing will be valid only for this rate law, if the rate law changes this will change.

So, the rate law you first determine, then you determine how the concentration is basically a function of X or the conversion, then you just collect them together then your rate law, so your rate will become a function of conversion and this is the expression that you can find out. So, from these things you can actually construct this particular table. Now, since we have already come back to this particular table let us do another small problem now. So, from this particular table we have already found out what is the volume of CSTR necessary for the conversion of 0.4, which is 0.8 to meter cube.

Then, what is the volume of CSTR necessary for a conversion of 0.8 or 80 percent that will be 0.8 into 8; 6.4 meter cube. So, this tells you although the inner expression itself it was immediately obvious, you need a higher volume in order to get a higher conversion. Of course, this is not the situation like you know when the if you are allowing the reaction to go on for a time t in CSTR the conversion will change that is not the case, your conversion is fixed that is fixed by the volume.

So, if you are using a volume of 0.82 meter cube for this particular reaction, that is given by that is characterized by this table, then you will always get only 40 percent conversion that does not change with time. Now, if you want to go to 80 percent conversion you have to change the reactor, you go to a higher volume; then you are always getting 80 percent conversion steady state, the reaction, so the reactor is operating all the time and

you are always getting 80 percent conversion and the conversion is the same whether you are looking at the reaction mixture inside or whether you are looking at the whatever outward flow is collected. So, you are ultimately getting 80 percent conversion.

Now, if you look at 80 percent conversion in order to get that you need higher volume. Basically, if your volume is higher, the time that particular species resides in that chamber is also higher because it has to take longer time to go out of the system. So, that is called a residence time. So, if you can increase the residence time then your yield also will be higher, that is the overall physical significance of that that; you need a higher volume in order to go to higher conversion on higher yield.

So, that is what we wanted to discuss as far as this is concerned. Now, the final thing that I want to discuss today is what happens if you have 2 CSTRs in series, let us say you have 2 CSTRs in series. So, how do you draw this particular graph, I mean not the graph the schematic excuse me, so you have the first CSTR, so this is CSTR1 and this is the second CSTR, the start tank reactor continuous start tank reactor CSTR 2. So, this is the molar flow rate in, in the first 1 F_{A0} , whatever is coming out from there.

So, the molar flow rate out is F_{A1} and the conversion at this point is X_1 , that is the inlet stream composition for the CSTR 2; that means, for the CSTR 2 the molar flow rate is now F_{A1} and the conversion you started with is X_1 . Here, the conversion is starting with was 0, there was no conversion here already X_1 conversion is there, that species we are putting here and then the output is F_{A2} , X_2 . So, for CSTR 1 write a mole balance equation in minus out plus accumulation equals to 0. So, ultimately the mole balance equation becomes your. So, F_{A0} minus F_{A1} plus sorry, plus generation equals to 0 because here is the accumulation sorry, plus generation is 0.

So, generation is r_A into V . So, let us say the rate of formation of or the reaction of A is r_A , we do not know if it is accumulating or I mean we do not know whether it is generating or destroyed there is no accumulation by the way because this is a steady state things going in, things going out, nothing is reading accumulated, that is why the concentration is not changing, that is why the rate is not changing as far as a particular CSTR is concerned, so this is equals to 0. Now, F_{A1} is nothing but F_{A0} minus F_{A0} into X_1 , we have already talked about that, from the stoichiometric table we can find out F_{A1} is F_{A0} minus $F_{A0} X_1$.

So, this is the molar rate of consumption of FA0 sorry, molar rate of consumption of A and this is the molar rate of molar rate in A. So, this difference is basically the molar rate out for A. So, if you just put that value here, so your V 1 becomes equal to FA0 divided by minus r A 1 into X1, what about V 2? So, if you are now considering the second CSTR let us consider now the second CSTR for the CSTR 2, this will be the mole balance equation F A 1 is in, F A 2 is out plus r A 2 into V 2 equals to 0.

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$$F_{A1} - F_{A2} + r_{A2} V_2 = 0$$

$$\Rightarrow V_2 = \frac{F_{A1} - F_{A2}}{-r_{A2}}$$

$$= \frac{F_{A0}}{-r_{A2}} (X_2 - X_1)$$

$X = X_2$

$$\left. \begin{aligned} F_{A1} &= F_{A0} - F_{A0} X_1 \\ F_{A2} &= F_{A0} - F_{A0} X_2 \end{aligned} \right\}$$

So, F A 1 is in, F A 2 is out and r A 2 let us say is the rate of the formation or destruction of A. So, correspondingly or I mean consumption of A. So, correspondingly let us say r A 2. So, this is the equation. So, from here your expression of V 2 becomes equal to FA1 minus FA2 divided by minus r A 2. So, if you now, remember that your FA1 is equals to FA0 minus FA0 X 1, we have already talked about that.

F A 2 will be equal to FA0 minus FA0 X 2 by the same analogy here, if you put those values here then your V 2 becomes equal to FA0 by minus r A 2 at X equals to X 2 into X 2 minus X1. So, that is what it turns out to be. So, you have to actually take the value of this FA0 by minus r A 2 at X equals to X 2 and the base of the rectangle has to be X 2 minus X 1.

So, if you now consider the example that I talked about, let us say you are talking about 80 percent yield of the reaction, if you are talking about 80 percent yield of the reaction if you are using only 1 CSTR, then you are having 6.4 meter cube is the volume. Now,

let us say you are what you are doing is, you are using 2 CSTRs in order to get 80 percent conversion. So, first CSTR you design such that your X_1 is basically 0.4. So, you get 40 percent conversion to start with, then this is the inlet for the other CSTR and ultimately you will get 80 percent conversion, then what are the volumes for these 2 that is the problem.

So, if you are looking at that particular problem, then what are the volumes of these 2 CSTRs? So, volume of the first CSTR then because it is 0.4 is the X_A or the conversion, that is already determined, we have already determined this before 0.82 meter cube, 40 percent conversion. Now, this is the inlet for the; this is the inlet composition for the second CSTR and this is the outlet composition for the second CSTR.

So, then the volume of the second CSTR, I will do it here. So, volume of the second CSTR will be nothing but equal to if you look at this expression here and use that particular expression, then that will be the FA_0 by minus r_A at 0.8, which is nothing but 8 into X_2 minus X_1 0.8 minus 0.4. So, that becomes 3.2 meter cube. So, if you add these 2 up that becomes 4.02 meter cube. So, if you are affecting same 80 percent conversion with 1 CSTR only, then you require 6.4 meter cube volume of the CSTR.

If you are affecting this 80 percent conversion with 2 CSTRs provided that in the first CSTR you have 40 percent conversion and then that is the inlet for the second CSTR in that composition for the second CSTR. Finally, you get 80 percent conversion; then you see the total volume required is 4.02 meter cube.

So, in general actually it can be said that for the same amount of conversion if you are using multiple CSTRs the total volume necessary will be lower than if you are using only 1 CSTR. So, we will continue to talk about different problems and continue to develop these principle more and use the stoichiometric table for different reactors in the next class. So, we will stop here and until then.

Thank you and goodbye.