

Principles of Polymer Synthesis
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Lecture - 27
Design of Chemical Reactors (Contd.)

Welcome back we have been continuing to talking about designing principle of chemical reactors. And so, today's topic is also going to be continuation of the same, and if you recall we discussed one problem of CSTR conversion in the previous class, we will continue and we will discuss some more problems. So, let us then define another problem here.

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$A + B \rightarrow C$
 $-r_A = k C_A C_B$

$\rightarrow 800 \text{ dm}^3 \text{ PFR @ } T = 300 \text{ K} ?$
 $\rightarrow 200 \text{ dm}^3 \text{ CSTR @ } T = 350 \text{ K} ?$

inlet stream: equal molar A and B.
 $U = 10 \text{ dm}^3 / \text{min}$

$k_{300} = 0.07 \text{ dm}^3 / \text{mol min}$
 $E = 85000 \text{ J/mol K}$

$C_{A0} (\text{before mixing}) = 2 \text{ mol/dm}^3$
 $C_{B0} (\text{before mixing}) = 2 \text{ mol/dm}^3$

$U_{A0} = 5 \text{ dm}^3 / \text{min}$
 $= U_{B0}$

Diagram of CSTR:
 Inlet: $F_{A0}, C_{A0} = 2 \text{ mol/dm}^3$
 Inlet: $F_{B0}, C_{B0} = 2 \text{ mol/dm}^3$
 Outlet: F_A, X
 Temperature: 350 K
 Volume: 200 dm^3

We are going to consider this particular reaction liquid phase reaction and this is following an elementary rate law which means minus r_A equals to k into C_A into C_B . So, both are first order now to do this reaction what we have is 2 reactors that are available, either you can do this reaction in a 800 decimetre cube plough flow reactor, which is operated at temperature of 300 kelvin so this is the volume of the plough flow reactor or you can do this reaction in a 200-decimetre cube CSTR which is operated at temperature of 350 kelvin.

Now for both this flow reactors either you do the reaction in this or you do the reaction in this basic basically the inlet us stream. The inlet stream is consisting of 2 separate

feeds of A and B they come together and they form one single inlet stream and, in this inlet, stream you have basically equal molar A and B.

And the total volumetric flow rate is 10 decimetre cube per minute and also what is given is you know that there are 2 separate streams that are coming for A and B they are coming together and forming one inlet stream that is entering your reactor. So, these 2 separate streams the concentration of A in one stream which is it is before mixing before mixing concentration of A is basically 2 moles per decimetre cube and concentration of B.

Before mixing is also 2 moles per decimetre cube and the volumetric flow rate of A is before mixing again is 5 decimetre cube per minute, the same as the volumetric flow rate of B and also since the reactors are operated at different temperatures you need to know the k value at these 2 different temperatures. So, what is given is the k value at 300 kelvin is 0.07 decimetre cube per mole per minute and the activation energy is 85000 joule per mole kelvin.

So, all these things are given now the question is which of the 2 reactors is going to give you a higher conversion. So, if you want to pictorially depict these thing at least for CSTR we will depict you can do this for PFR after, it is something like this. So, you have the CSTR this is the starrer and this is the reaction mixture where it is operating. So, one stream is coming for A separately another stream is coming for B separately and they are coming together, they are coming together and entering into the reactor.

And whatever is coming out has a separate molar flow rate out for A say and for B also and X is the conversion X is what we are going to find out. And so, this is CSTR we are talking about so CSTR is operated at 350 kelvin and the volume is 200 decimetre cube for the CSTR. And also, so this is a so separate stream of a is coming and separate stream of B is coming and then they are coming together and in this you have equal molar A and B and here also if your looking at C_{A0} am just putting small b.

So, C_{A0} before mixing is 2 moles per decimetre cube. So, from here and from here C_{B0} before mixing is 2 moles per decimetre cube and this is so the molar flow rate in F_{A0} here it is F_{A0} . So, when they mix up; obviously, the concentration for A becomes half and concentration of B becomes half and the total volumetric flow rate is basically 10 decimetre cube per minute. So, volumetric flow rate of A here is 5 decimetre cube per

minute and here it is they are coming at 5 decimetre cube per minutes. So, when they come together it is 10 decimetre cube per minute.

So, at least this is the definition of problem for CSTR the same thing you could do for PFR also, this is just to pictorially depict the meanings of this things because you might be confused what do you mean by before mixing what do you mean by before mixing and after mixing. So, that this is the situation so this is before mixing and then they mix and then they enter. Now let us try to solve this problem.

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The image shows handwritten mathematical derivations for CSTR and PFR design equations. The equations are as follows:

$$V_{CSTR} = \frac{F_{A0} X_A}{-r_A}$$

$$V_{PFR} = F_{A0} \int_0^{X_A} \frac{dX_A}{-r_A}$$

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

$$-r_A = k C_A^2 C_B$$

$$V_{CSTR} = \frac{F_{A0} X_A}{k C_{A0}^2 (1-X)^2}$$

$$V_{PFR} = F_{A0} \int_0^{X_A} \frac{dX_A}{(k C_{A0}^2 (1-X)^2)}$$

$$\frac{k_{250}}{k_{300}} = e^{\frac{E}{R} \left(\frac{1}{300} - \frac{1}{350} \right)}$$

$$k_{250} = 8.447 \text{ dm}^3 / \text{mol min}$$

$$(1-2X+X^2) = \frac{F_{A0} X_A}{k C_{A0}^2 V} \Rightarrow X^2 - \left(\frac{F_{A0}}{k C_{A0}^2 V} + 2 \right) X + 1 = 0$$

So, what is the mole balance of CSTR is F_{A0} into X_A divided by minus r_A and what is the mole balance? Actually, this is the design equation that we get from the mole balance. So, what is the design equation of V_{PFR} or PFR it is sorry you will get the V_{PFR} from there. So, that is F_{A0} into 0 to X_A to X_A dX_A divided by minus r_A . Rate law we already know this is the rate law.

So, stoichiometry now step by step let us proceed will go to the stoichiometry concentration of A is equals to F_{A0} into 1 minus X divided by small v and that is equal to so this is F_{A0} into 1 minus X by small v is equal to C_{A0} into 1 minus X this is appearing everywhere. So, am not going to explain again how these appears even before when we construct the stoichiometric table we had discussed about this. So, this is the expression so if you put this value this here in V_{CSTR} this expression in V_{CSTR} it will be equal to F_{A0} into X_A divided by remember minus r_A is equals to k into C_A into

C_B , and C_A and C_B are the same C_{A0} and C_{B0} are the same we have already talked about that. So, this would be F_{A0} and X_A divided by $k C_{A0}^2$ into $1 - X_A^2$.

So, C_A is this C_B is also this equal molar flow what about V_{PFR} it is F_{A0} into integral 0 to dX_A express write the expression of r_A minus r_A it will be a same expression as this into $1 - X_A^2$ whole square am just putting X it will be a X_A actually X subscript A . Now this case is 0 square is constant they come out so on and so forth. What is the value of small k at 350 ? Now remember the value of small k at 300 is given rate constant, at 300 it is given and the and the energy of activation is also given.

So, if you know the temperature at which we have to find out the rate constant. So, in this case 350 , then what you do your expression of k is nothing but A into e to the power minus E by RT . So, this is the value of k at that particular temperature now this value is given at 300 A we do not know we do not need to know also in this case T we know for 300 degrees it will be T_{300} and E .

We know activation energy that does not change with temperature. So, what we can do is that we can take a ratio of k_{350} to k_{300} , then this A will cancel out and we will get what you what you have has e to the power E by R into $1/300$ minus $1/350$, and these value is already known this value is 0.07 decimetre cube per mole per minute.

So, if you solve for these just take the ratio between the 2 this A is cancel it out you do not need to know the A you know the value of e . So, from here your k_{350} ; that means, rate constant 350 kelvin is 8.447 decimetre cube per mole per minute. Now let us solve these expression because we want to know V_{CSTR} is already known, we want to find the value of X , that is what we want to find. Now remember that this reaction is done at 350 kelvin 350 -degree kelvin at 350 -degree kelvin in the CSTR.

So, the value of k that you are going to use is that 350 . So, that is the value of k that you are going to use. So, if you now put those expressions here what you will get CSTR at 350 , this is $1 - X_A^2$ whole square these $1 - 2X_A + X_A^2$ these equals to this term is F_{A0} into X_A divided by $k C_{A0}^2$ this V comes here. These this into X just putting X here this is the term if you re arrange this what you will get this is a quadratic expression in terms of X F_{A0} divided by $k C_{A0}^2$ into V plus 2 into X plus 1 equal

to 0 this the quadratic expression that you will get. So, this you can easily solve remember this value is also known

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$$V_{CSTR} = \frac{F_{A0} X}{k_c C_{A0}^2 (1-X)^2}$$

$$V_{PFR} = F_{A0} \int_0^X \frac{dX}{k_c C_{A0}^2 (1-X)^2}$$

$$\frac{k_{350}}{k_{300}} = e^{\frac{E}{R} \left(\frac{1}{300} - \frac{1}{350} \right)}$$

$$k_{350} = 8.447 \text{ dm}^3 / \text{mol min}$$

$$1 - 2X + X^2 = \frac{F_{A0} X}{k_c C_{A0}^2 V} \Rightarrow X^2 - \left(\frac{F_{A0}}{k_c C_{A0}^2 V} + 2 \right) X + 1 = 0$$

$$ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$X = 0.926$$

What is this value? This value is nothing but F_{A0} divided by $k C_{A0}^2 V$, this value is nothing but F_{A0} is 10 mole per minute already it was defined in the in the problem that your inlet stream what is the volumetric flow rate in that is 10 decimetre cube per minute the total volumetric flow rate in, but if you look at

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$$-r_A = k_c C_A^2$$

$$\rightarrow 200 \text{ dm}^3 \text{ CSTR @ } T = 350 \text{ K}$$

$$\text{inlet stream: equal molar A and B}$$

$$v = 10 \text{ dm}^3 / \text{min}$$

$$k_{300} = 0.07 \text{ dm}^3 / \text{mol min}$$

$$E = 85000 \text{ J/mol K}$$

$$C_{A0} (\text{before mixing}) = 2 \text{ mol/dm}^3$$

$$C_{B0} (\text{before mixing}) = 2 \text{ mol/dm}^3$$

$$v_{A0} = 5 \text{ dm}^3 / \text{min} = v_{B0}$$

$$C_{A0} = 2 \text{ mol/dm}^3$$

$$v_{A0} = 5 \text{ dm}^3 / \text{min}$$

$$v_{B0} = 5 \text{ dm}^3 / \text{min}$$

$$C_{B0} = 2 \text{ mol/dm}^3$$

$$350 \text{ K}$$

$$200 \text{ dm}^3$$

$$F_{A0} X$$

The picture here, your C_{A0} which is the concentration before mixing these 2 moles per decimetre cube and what is the volume of volumetric flow rate in of A? It is 5 decimetre cube per minute. So, you have to multiply these 2 and if you multiply these 2 you get the value of F_{A0} which is 10 the value of F_{A0} is 10 moles per minute. So, here is 10 moles per minute small k is 8.447 we already determined the value of small k 350 kelvin.

So, 8.447 decimetre cube by mole minute. C_{A0} is basically 1 moles per decimetre cube that whole square 1 because ultimately the entering concentration has become halved it was 2 moles per decimetre cube here 2 moles per decimetre cube here for A and B. So, when they came together the C_{A0} at the entrance is basically 1 moles per decimetre cube. So, C_{A0} is 1 moles per decimetre cube and v is already known what is the volume 200 decimetre cube.

So, if you solved this thing and if you put here in this expression. So, remember this expression is you're a quadratic $ax^2 + bx + c = 0$. If you have quadratic equation like this $ax^2 + bx + c = 0$ then your X will have 2 solutions it will be $\frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ and both solutions may be visible or only one solution may be visible depending on if it is physically possible or not here only one solution is visible now work it out and the value of X from here that you will get because you know this value will be equal to 0.926; so 92.6 percent conversion. So, what will be the corresponding?

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$$V_{PFR} = \frac{F_{A0}}{k C_A^2} \int_0^{X_A} \frac{dX_A}{(1-X_A)^2} \Rightarrow \frac{k C_{A0}^2}{F_{A0}} V_{PFR} = \frac{X_A}{1-X_A}$$

$$\Rightarrow X_A = 0.84$$

* Pure styrene @ 60° with BPO initiator
 → 10% conversion

$f = 1, \frac{k_p^2}{k_t} = 0.95 \times 10^{-3} \text{ L/mole s}$
 $[I] = 4.0 \times 10^{-3} \text{ mol/L}$
 $k_d = 1.92 \times 10^{-6} \text{ s}^{-1}$

Solⁿ: $\ln \frac{[M]}{[M]_0} = -kt$
 $k = k_p \left(\frac{f k_d}{k_t} \right)^{1/2} [I]^{1/2}$

$k^2 = \frac{k_p^2}{k_t} f k_d [I]$

Value for PFR for PFR remember your expression was F_{A0} divided by $k C_{A0}^2$ into integral 0 to X_A dX_A by $1 - X_A$ square; I mean am using X or X_A interchangeably you can understand that both have the same. So, if you do the integration and do a rearrangement. Basically, what you will get is $k C_{A0}^2$ into F_{A0} .

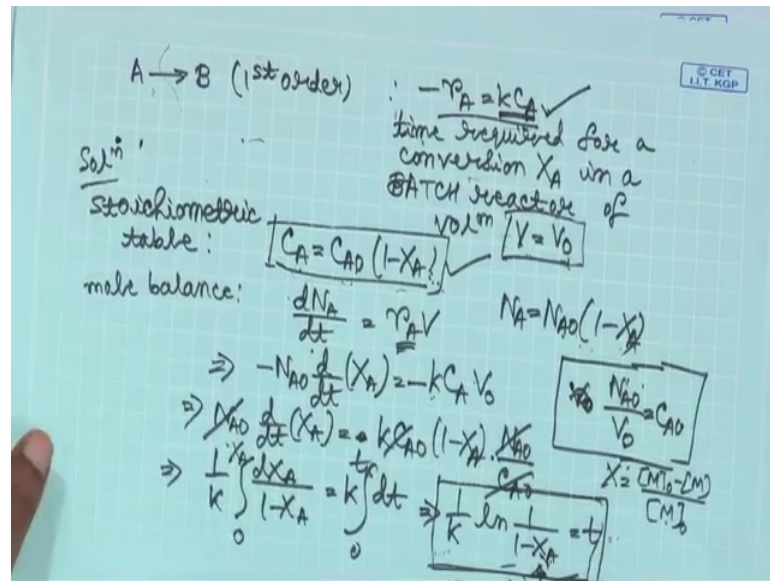
So, this goes here divided by F_{A0} into V which is a V PFR that becomes equal to if you do the integration here it will be X divided by $1 - X_A$ divided by $1 - X_A$. So, if you put all the values you know this values of C_A you know the value of F_A and you know the value of k . Now this value of k has to be the value of k at 300 because of PFR is the operated at 300 kelvin.

So, if you put all these things here your X becomes or X_A becomes 0.84. So, basically if your using a CSTR you will get higher yield around 93 percent yield and if your using a PFR you will get a lower yield. So, that is the solution of the problem. Now let us solve a problem a simple problem for polymerization. Let us say we are going to use a batch reactor and we are polymerising pure styrene at 60-degree celsius with benzoyl peroxide as the initiator.

And we are going to use a batch reactor and we are aiming for 10 percent conversion this is our aim and what is given is the initiator efficiency is one let us assume that the value of k_p square by k_t this is the propagation rate constant this is the timing rate constant this value is equal to 0.95×10^{-3} litre per mole per second and the concentration of the initiator is given as 4×10^{-3} moles per litre and dissociation constant is given as 1.92×10^{-6} per second.

So, the question is what is the time required to obtain 10 percent conversion in a batch reactor.

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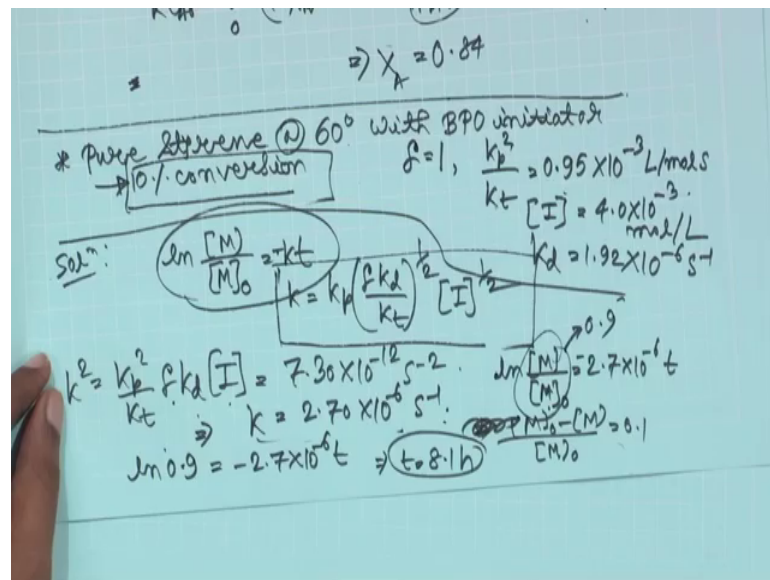


Now, remember that we had solved for a first order reaction previously we had solved this expression, this was the expression that we had got if the reaction is first order in order to get this kind of conversion we have this expression. Now if you replace this X the conversion remember conversion is nothing but initial concentration minus final concentration divided by initial concentration of the monomer, if you are looking at a polymerisation you replace that here.

Then let us just assume in this case it is a first order reaction for styling. So, if you put that value here what you will get is nothing but now we are solving the problem solution, we will get $\ln M$ by M_0 equals to minus kt . So, we are basically getting from here by replacing X_A with this value. Now this k is basically equal to k_p into fkd divided by kt to the power half into I to the power half, if you recall the expressions of the rate that we had. Then this is the value of k . So, if you recall what we discussed about in the during the classes on the analysis of kinetics for the rates of polymerisation so on and so forth.

So, then you can realise this k will be something like this. So, if you take the square of that will be k_p square divided by kt into fkd into I . Now you know all this values you know value of k_p square by kt put that value here k_p square by kt is this f is 1 I is already known kd is also known

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So, what you will get is 7.30 into 10 to the power minus 12 second square inverse so; that means, your value of k will be square root of that which will be 2.70 into 10 to the power minus 6 per second.

So, you now put this values here. Then what is the expression you will get from here if you put the value there you will get $\ln M$ by M_0 equal to 2.7 into 10 to the power minus 6 into t now there is a minus term here. So, if you do the calculation here what you will get you will get from here, let say you are going for 10 percent conversion then your M_0 minus M divided by M_0 is 0.1.

So, from there you can get this expression of M by M_0 . So, if you use this expression here in this term it will come out as 0.9. So, it will be basically \ln of 0.9 will be equal to minus 2.7 into 10 to the power minus 6 into t and if you solve that t is your 8.1 hour. So, that is how you get your final expression. In this case we assumed data styling polymerisation is first order and a low conversion of course, alright. So, we have done one simple problem for polymerisation here. Now what we are going to do is the following, let us try to probably workout one more problem let us try to work out one more problem.

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* Polyethylene (tubular reactor)
 dimension \rightarrow 2.5cm dia
 1m long
 @ 250°C and 2500 atm
 conversion per pass: 30%
 Flow rate = 40,000 kg/h

Diagram: A cylindrical reactor with mass flow M entering and $M+dM$ exiting.

Equations:
 $V = F_{A0} \int_0^{X_A} \frac{dX_A}{-r_A}$
 $F_{A0} \frac{dX_A}{dV} = -r_A$
 $X_A = \frac{M_0 - M}{M_0}$
 $dX_A = -\frac{dM}{M_0}$
 $U M_0 \frac{dX_A}{dV} = R_p$

Say let us say we are trying to appear polyethylene and you are using a tubular reactor it could be a plough flow reactor also and the dimension here is 2.5 centimetre diameter and 1 metre long tube and the reaction is done at 250 degree celsius and 2500 atmospheric ratio and conversion per pass is 30 percent, also what is given is the flow rate the flow rate is 40000kg per hour and also you assume that the polymerisation is the first order in ethylene concentration.

So, all these things are given then the question that is being asked is you should try to estimate the value of the rate constant for propagation. So, it is a polyethylene polymer ethylene polymerisation is being done. So, product is polyethylene ethylene polymerisation is being done at tubular reactor of these dimension this is diameter this is the length at 250-degree celsius and 2500 atmospheric ratio at high pressure under high pressure and the conversion per pass is 30 percent flow rate is this. So, what is the value of k_p this is the question.

So, remember that this was the plough flow reactor that we talked about and then if you have a small element small volume element here say mass M is going in and M plus dM that is going out. The molar flow rate in molar flow rate out so on and so forth and this dV is the volume of this. Now if you write down the design equation here if you remember it is $F_{A0} \int_0^{X_A} \frac{dX_A}{-r_A}$ this was design

equation. So, from here what you can actually write down is the following $F_A 0 \frac{dX_A}{dV}$ is equals to r_A . $F_A 0 \frac{dX_A}{dV}$ is equals to r_A .

And from these expression your $F_A 0$ which is the molar flow rate in this is the molar flow rate in right. So, this molar flow rate in is basically equal to volumetric flow rate in into the mass that is going in the concentration let us say concentration in this case the concentration of the ethylene, that is a go that is going in this $\frac{dX_A}{dV}$ equals to the rate of polymerisation basically this is the rate of polymerisation rate of propagation is a rate of polymerisation now if you do an integration here.

So, let us say you do an integration from volume 0 to V and you do the corresponding you know re arrangement it will be dV by v small v into M_0 equals to 0 to X_A $\frac{dX_A}{dV}$ divided by R_p . So, this is the expression that you will get here. So, this is dV by v M_0 and then this this side $\frac{dX_A}{dV}$ divided by R_p that will come. Now if you remember your value of X_A is nothing but M_0 minus M divided by M_0 this is the value of X_A . So, what is the value of $\frac{dX_A}{dV}$ the value of $\frac{dX_A}{dV}$ is nothing but minus dM by M_0 . So, you replace the value here and then what you will get is the following.

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$$\int_0^V \frac{dV}{v M_0} = \int_{M_0}^M \frac{-dM}{M_0 R_p} \quad R_p = k_p M$$

$$\Rightarrow \frac{V}{v M_0} = \int_{M_0}^M \frac{-dM}{R_p}$$

$$\Rightarrow \frac{V}{v M_0} = - \int_{M_0}^M \frac{dM}{k_p M} \Rightarrow k_p \frac{V}{v M_0} = - \int_{M_0}^M \frac{dM}{M}$$

$$\Rightarrow k_p \tau = - \int_{M_0}^M \frac{dM}{M}$$

$$\Rightarrow M = M_0 e^{-k_p \tau}$$

0 to V dV by small v into M_0 small v into M_0 equals to now you are replacing X_A by m . So, this integral will also change from initial value of M to final value of M .

So, if you put those values here that will be $M_0 - M$ divided by M_0 into R_p . So, finally, what you will get is this this small v comes out and when you integrate from M_0 to M the dM it becomes capital M by small v this equal to integral M_0 to M goes here. So, this is minus dM divided by R_p .

This is the final expression that you have now your R_p your R_p is nothing but k_p into M R_p is nothing but k_p into M . So, if your putting that expression here what you will get here is capital M by small v equals to minus integral M_0 to M into dM by M , because remember that the reaction is first order in ethylene that is what we talked about this k_p value here we are trying to find out. So, if you put that value here. So, R_p is replaced by R_p is replaced by k_p into M .

So, that will be k_p into M . So, if you put the k_p out of the equation that will be capital M by small v equals to minus integral M_0 to M dM by M , this is your residence time capital M by small v . So, it will be k_p into τ equals to minus integral M_0 to M dM by M and if you do integration ultimately what you will get is M equals to M_0 into e to the power minus $k_p \tau$ and also what you will get is the value of k_p which will be nothing but minus 1 by τ into $\ln M$ by M_0 .

You are trying to find out a value of k_p here now M by M_0 you already know it is 0.7 because you are look looking for 30 percent conversion so that is M by M_0 . So, if you put that value here then it will be minus 1 by τ $\ln 0.7$. Now what you have to find out the problem has been reduced to finding now the value of τ the residence time then you can find out value of the k_p or the propagation constant or the rate of polymerisation corresponding the rate constant.

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$$V = \pi R^2 L = \pi \left(\frac{2.5}{2} \times 10^{-2}\right)^2 \times 1 = 4.9 \times 10^{-4} \text{ m}^3$$

$$v = \frac{nRT}{p}$$

$$n = \frac{40,000}{28} \text{ mol/h} = 1.43 \times 10^3 \text{ mol/h}$$

$$v = \frac{(1.43 \times 10^3 \text{ mol/h}) (0.8206 \frac{\text{m}^3 \text{ atm}}{\text{mol K}}) (523 \text{ K})}{2500 \text{ atm}} = 24.55 \text{ m}^3/\text{h}$$

$$\tau = \frac{V}{v} = \frac{4.9 \times 10^{-4} \text{ m}^3}{24.55 \text{ m}^3/\text{h}} = 2.0 \times 10^{-5} \text{ h}$$

$$k = -\frac{1}{\tau} \ln 0.7 \Rightarrow k = 4.955^{-1}$$

So, tau is equals to capital V by small v, capital V is the reactor volume. So, the reactor volume is nothing but a cylindrical reactor pi r square into L, r is the radius, L is the length. So, if you put those values and because r is in centimetre.

So, you have to go to the metre into one metre is the length. So, ultimately what you will get is 4.9 into 10 to the power minus 4 metre cube then this capital V. Now what is the small v volumetric flow rate in what is a small v? Let us say ethylene is in if it is in gaseous state you can use this ideal gas equation v equals to nRT. So, here v equals to nRT divided by p, p being the pressure.

Now n is the number of moles right and the question actually mentioned the problem mentioned that the flow rate is 40000 kg per hour. So, correspondingly if you change that to number of moles what you will get? N equals to 40000 divided by number of molecular rules that will be this moles per hour this I have calculated as 1.43 this calculation is already done we are trying to explain the principle moles per hour. Now this R is known universal gas constant and your t is also known 250-degree celsius.

So, you just convert that to kelvin and you put all the values here then your small v is nothing but 1.43 into 10 to the power 3 moles per hour and the value of R is basically the 0.8206 metre cube atmosphere mole kelvin into your temperature is 523 kelvin you can convert to kelvin divided by p which is 2500 atmosphere.

If you can work this out it will come out as something like this 24.55 metre cube per hour. So, this is what you revised down to. So, what will be the residence time then because residence time is what you have to find out. So, that you can put into this expression. So, if you write down the residence time capital V by small v. Capital V is already known this is the capital V 4.9 into 10 to the power minus 4-meter cube divided by small v is 24.55 metre cube per hour.

So, if you work this out this 2 into 10 to the power minus 5 hour. Then the expression of k is nothing but minus 1 by tau into ln 0.7 if you put that value there the value of k will come out as 4.95 per second. So, that is how we solve this thing. So, what we will do is we will stop here today and tomorrow we are going to go to a different concept we are going to because we have talked about mole balance until now, we will now go in to a topic of what we call as energy balance and then we will talk about different kind of a steady state conditions for reactors especially for CSTR so until then.

Thank you and good bye.