Principles of Polymer Synthesis
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Lecture - 26
Design of Chemical Reactors (Contd.)

Welcome back everyone. In the last week, if you recall, we had been talking about chemical reactors the design principle of that and this week we are going to continue with the same topic and in the same way; so, a little bit of recollection of where you were left in the; at the end of the week.

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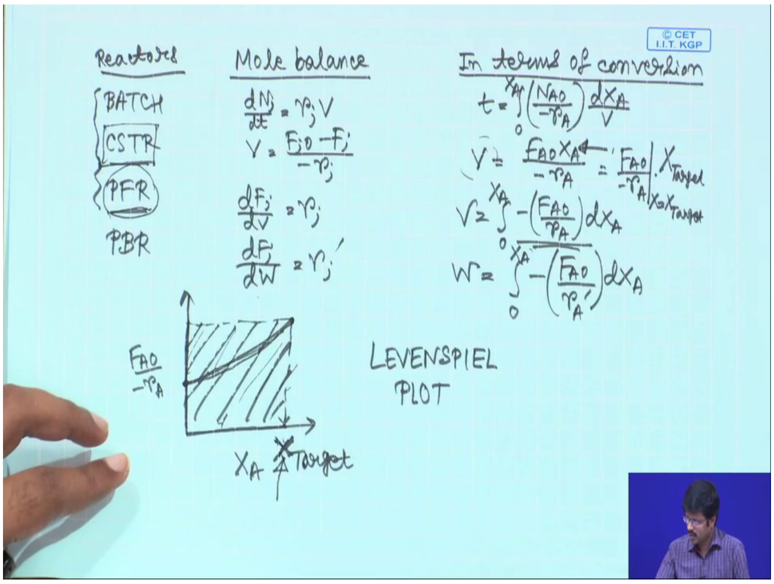

Reactors

- BATCH
- CSTR
- PFR
- PBR

Mole balance

$$\frac{dN_j}{dt} = r_j V$$

$$V = \frac{F_{j0} - F_j}{-r_j}$$

$$\frac{dF_j}{dV} = r_j$$

$$\frac{dF_j}{dW} = r_j'$$

In terms of conversion

$$t = \int_0^{X_A} \left(\frac{N_{A0}}{-r_A}\right) \frac{dX_A}{V}$$

$$V = \frac{F_{A0} X_A}{-r_A} = \left.\frac{F_{A0}}{-r_A}\right|_{X = X_{Target}} \cdot X_{Target}$$

$$V = \int_0^{X_A} -\left(\frac{F_{A0}}{r_A}\right) dX_A$$

$$W = \int_0^{X_A} -\left(\frac{F_{A0}}{r_A'}\right) dX_A$$

LEVENSPIEL PLOT

So, we had talked about different kinds of reactors say you have batch reactor or CSTR continuous start tank reactor or plough flow reactor or for example, PBR; packed baked reactor. Now if you are looking at for example, the mole balance of these reactors. So, correspondingly, I am going to write down again d Nj dt equal to r j V, then for CSTR, it is V equals to Fj 0 minus Fj divided by minus rj. So, this is molar flow rate in molar flow out this is the rate of the reaction for the particular species j th species for PFR. It was d Fj dv equals rj and for PBR it was d Fj dw equals to rj prime; the w being the catalyst weight and then also we expressed this mole balance in terms of conversion in terms of conversion.

We had expressed this, it was required rate because when we are trying to target a particular conversion for a reaction, what we need to know is with respect to that targeted conversion; how the different parameters have to be adjusted for that particular reactor and the design equation gives us the handle. Once, we are able to incorporate the conversion into this design equation and what we had obtained then was something like this for batch reactor.

It was t equals you integrate from 0 to XA where XA is the targeted conversion na, 0 divided by minus r A into d XA by V for CSTR. It was volume equal to FA 0; FA 0 being a molar flow rate in for the component a FA 0 into XA divided by minus r A for PFR, it was V equals to integral 0 to XA minus FA 0 by r A into d XA and for PBR. So, weight of the catalyst is related to conversion 0 to XA minus FA 0 by r A prime into d XA and when we derived this expressions we started from the expression of rate.

So, the rate as a function of the concentration of different species and then we expressed the concentrations of different species in terms of the conversion that is so called stoichiometric table and then you combine these 2; the rate it law and stoichiometric table; in order to get a final expression of the rate in terms of conversion for the reaction and since the rate appears in all the design equation, then you replace the rate we that particular expression and you will getting final expressions. We discussed this since in detail in the in the last week.

Now if you can recall also, we specifically talked about this say batch CSTR reactors PFR reactors some problems, we are going to also discuss this week, but say for example, if you are looking for CSTR design equation here. So, if you target a particular conversion what is the volume that is required we told that we have to do what we call as Levenspiel plot; Levenspiel plot where you plot FA 0 minus r A; this term is a function of XA and then you are targeting a particular conversion that is a x target.

So, the volume of CST on this is a necessary is the area of the corresponding parallelogram. So, this length into this length so, basically then the volume necessary will be FA 0 by minus r A at x equal to x target x equal to x target into x target these things we discussed we also told that when we go to the PFR we have actually solved this integral and for that we have numerical approach to approximate the expressions of this integrals like siu sounds three eight through siu sounds one third 2 rule trapezoid rule we did some problems and also we told that basically if you are targeting the same conversion in CSTR as well as PFR then the CSTR following necessary is these volume of this parallelogram and the volume of the PFR necessary is basically the area under this curve.

So, the volume of PFR necessary will be less also we talked about a targeted conversion if we are trying to achieve by using 2 CSTR in this series in total volumes necessary will be lower than the volume necessary if you are using only one CSTR to achieve this particular conversion; however, if you are using PFRs or if you are using several PFRs in the series or if you are using only 1 PFR and targeting a particular conversion the total volume necessary will be the same it is always the area under the curve this things we discussed and we also worked out some problems. So, today we are going to start with the topic of selectivity.

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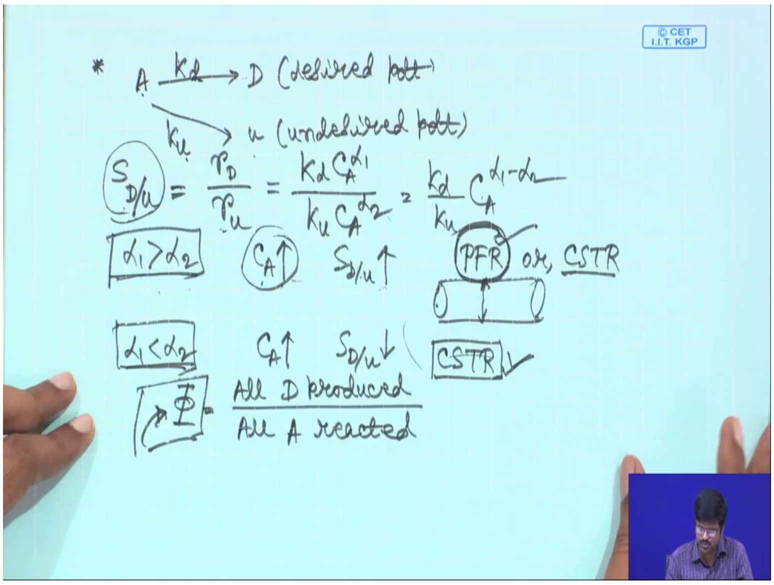

* $A \xrightarrow{k_d} D$ (desired pdt)

$A \xrightarrow{k_u} u$ (undesired pdt)

$$S_{D/u} = \frac{r_D}{r_u} = \frac{k_d C_A^{\alpha_1}}{k_u C_A^{\alpha_2}} = \frac{k_d}{k_u} C_A^{\alpha_1 - \alpha_2}$$

$\boxed{\alpha_1 > \alpha_2}$ $C_A \uparrow$ $S_{D/u} \uparrow$ PFR or, CSTR

$\boxed{\alpha_1 < \alpha_2}$ $C_A \uparrow$ $S_{D/u} \downarrow$ $\boxed{\text{CSTR}}$ ✓

$$\Phi = \frac{\text{All D produced}}{\text{All A reacted}}$$

So, very quickly we are going to discuss how the selectivity go on selectivity of chemical reactions go on; so with that we use one kind of reactor another kind of reactor say for example, if your comparing between CSTR and PFR the continuous start tank reactor and a plough flow reactor which one to use and why.

So, let us say you have a reaction generically, this is a starting material and a can give rise to a desired product. This is the desired product or a can give rise to an undesired product undesired product. Let us say the rate constant for them is correspondingly very small Kd and here small Ku giving the suffix to tell you that this is rate constant for desired product this is the rate constant for undesired product.

So, what is the selectivity let us just say selectivity is selectivity of the product D over u is equal to rate of the formation of D divided by rate of the formation of u and that will be equal to Kd into CA to the power alpha 1 divided by Ku into CA to the power alpha 2, I mean let us say this follows a rate law where the rate is having an order alpha 1 with respect to a, then it will be rate constant into concentration of a to the power to the term. So, correspondingly for the undesired product let the rate expression be this. So, the order of the reaction is alpha 2.

So, this will be then equal to Kd divided by Ku into CA to the power alpha 1 minus alpha 2 now there are 2 situations that you can increase such here alpha 1 is greater than alpha 2 this is possible if alpha 1 is greater than alpha 2, then from these expression as concentration of a goes up the selectivity also goes up this is what you want. So, the question is in this situation whether you are going to use a plough flow reactor or CSTR which one is going to give you better selectivity intuitively you can understand this that this expression tells you if the concentration goes up and the selectivity goes up assuming this alpha 1 is greater than alpha 2 then this is valid.

So, if you are looking at a PFR then the concentration progressively changes as you go along the length of the tube we talked about it is the cylindrical tube where the concentration radiant all though radially; radially means along these direction the concentration does not change, but the concentration progressively changes along this direction you start with higher concentration and you go to a lower concentration say you are talking about a reactants say A.

So, there is a concentration gradient. So, situations where higher concentration are there are also encountered here in this reactor because it starts from a higher concentration and goes to a lower concentration on the other hand if you are looking at a CSTR basically you are putting say a higher concentration of the reactant you are putting in the feed stream in the inlet stream when it goes in the reaction mixture it immediately goes to the diluted condition because the reaction mixture is operating at a steady state at a particular conversion.

So, if it is operating at particular conversion then the concentration of all the species present including reactant as well as the product all of them are constant whatever it is in that reaction mixture say you are actually opting for eighty percent or ninety percent conversion then generally or naturally your concentration of starting material is quite low in that reaction mixture because it is always operating at that particular conversion.

So, whatever higher concentration you start within the feed stream when it goes in it immediately get diluted that the steady state concentration of a starting material which is lower and then that concentration does not change with time. So, you do not encounter this kind of thing where you can go from higher concentration to lower concentration that higher concentration regime we do not access in CSTR.

So, the selectivity will be lower for CSTR; this is what you can understand intuitively we will come to it graphically after; now let us say we are talking about alpha 1 less than alpha 2 another case. So, if this is the situation say alpha 1 is less than alpha 2 then as the concentration of a goes up selectivity goes down in that situation you will basically use CSTR where your reactant is in dilute condition you are doing the reaction at a lower concentration of a starting material because the reaction is already in progress and in steady state.

So, conversion does not change the targeted conversion whatever you are looking for and concentration of the reactant whatever that diluted species because that has been diluted into that dilution mixture after coming through the feed stream at a higher concentration. So, that is the concentration at steady state that does not change.

So, this is a lower concentration then the concentrations that are encountered in PFR at least in the regime in the region where the entry point is there it enters with a higher concentration and slowly gradually it goes down as you go along the length of the tube. So, if alpha 1 is less than alpha 2 you will get a better selectivity CSTR then PFR and if alpha 1 is greater than alpha 2 then you will choose PFR. So, in this case you will choose PFR and in this case you will choose CSTR.

Now I mean we are talking about is selectivity it is also important to talk about overall fractional yield. So, we will stick to this selectivity. So, overall fractional yield let us say this capital 5 is will be equal to all of the d produced divided by all of a reactant that will be the that will tell you the selectivity. Now if you are considering this case alpha 1 greater than alpha 2.

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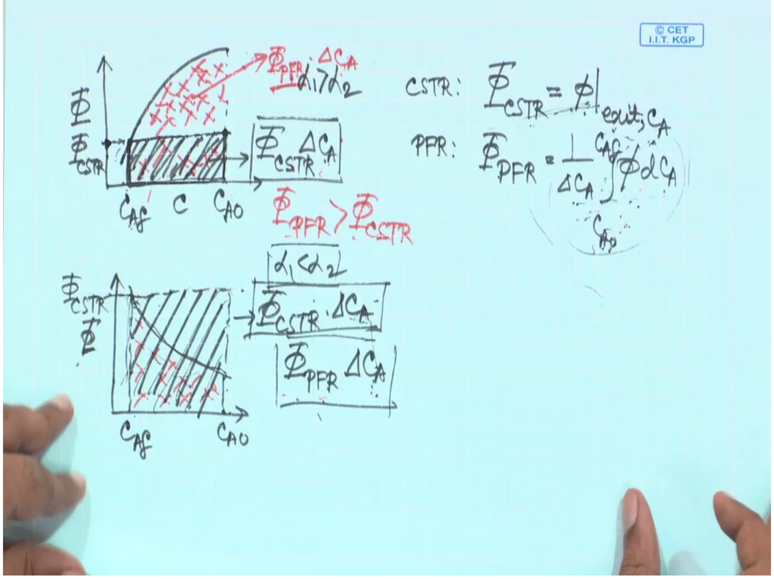

Let us now plot a graph and see the situation. So, you are plotting your yield with respect to concentration now remember what if you are trying to get an expression for this yield of the desired product of the selectivity correspondingly you have expressions like this say if you are going for a CSTR, then this overall yield of this product the selectivity for the product this yield is basically equal to the yield at the exit and the constant at a corresponding concentration of CA, I mean this is it is because whatever is the composition of the reaction mixture that is the same composition that you are getting a in the whatever is the output.

So, whatever yield is there for d or the selectivity yield is there for d the desired product it is the same everywhere to the reaction mixture as well as at the exit and this CA is the concentration of steady state concentration of the reactant in the reaction mixture. So, that is why this CSTR is this what about PFR for PFR the fi PFR is basically equal to 1 by delta CA integral CA 0 to CA f 5 d CA, this is because the concentration there is a concentration radiant out PFR. So, you start from a initial concentration you go to final concentration. So, you integrate your yield over this whole concentration and then you divide by this change in concentration that is something that is not a that mean in CSTR the concentration is always same in this if always the same here the yield is changing with respect to the length of the PFR.

So, the overall selective yield for d is this now let us go to the graph and let us consider the situation where alpha 1 is greater than alpha 2 remember when alpha 1 was greater than alpha 2 intuitively we told that we should use PFR then will get a better selectivity and we do not use CSTR. So, let us say if alpha 1 is alpha greater than alpha 2 then the curve will be something like this it will be having a positive slope you look at this your alpha 1 is greater than alpha two. So, your yield with respect to your concentration then that will have a positive slope. So, if your yield with respect to concentration having a positive slope, it will give this kind of graph now let us say this is CA 0 initial concentration and this is final concentration now what is the yield at final concentration that is this value now as far as CSTR is concern this yield does not change throughout the system.

So, whether you are looking at this point or this point your yield will be given by this particular graph here. So, you see here this area under the curve will be equal to your fi CSTR into delta CA. Now if you are looking at this particular graph. So, the yield that is get in this way concentration yield here is like this with concentration now when you are looking for CSTR for CSTR this is the yield and if you are drawing a parallelogram like this the length of this side is basically a delta CA the change in concentration and the height is basically the yield in CSTR.

So, the area of this parallelogram will avenue delta CA into fi CSTR, this is the area of parallelogram now what happens if you are looking at say PFR the same graph if you are considering of for PFR then what is the situation in PFR. So, you look at this particular integral here if you look at this particular integral your delta CA into PFR is basically this integral overall integral.

So; that means, let me take a different marker if you look at these overall area under the curve is full area under the curve what is this area this area is nothing, but phi PFR into delta CA that is the area because phi PFR into delta CA; CA is the integral from CA 0 to CA f phi d CA this is nothing, but the area under this curve this area is basically bigger than the area that we had for CSTR and for both the area one term is common this delta CA. So, from these graph also we can see that the phi PFR is basically phi CSTR a phi

PFR is basically greater than phi CSTR excuse me. So, phi PFR is greater than phi CSTR when alpha 1 is greater than alpha 2.

So, graphically we can show that this is the case also intuitivity, we understood now what happens if alpha 1 is less than alpha 2 then as a function of concentration your selective yield will be something like this say here you have CA 0 and here you have CA f now if you are looking for this particular time which is phi PFR into delta CA because this is the term that gives you this integral for PFR and let us apply this situation for PFR then what is this term this is again the same this is the integral under this particular graph this curve; this is the whole area under the curve this area phi PFR into delta CA and what is the situation for CSTR for CSTR the area under this parallelogram is equal to phi CSTR into delta ca. So, remember when you are looking for the phi for PFR it is basically an integration because over the length of the PFR the concentration is changing. So, it is an integration.

So, you see the integration here whereas, for CSTR these have only one phi and that is this phi this is the phi CSTR here this is the phi CSTR and that is why the area under the graph basically is your phi CSTR into delta CA so; that means, this length into this length that is the area under the graph and for PFR your phi PFR into delta CA is basically the area under this curve again you see that the area that we are considering for CSTR is greater than the area that we are considering for PFR and in both the cases one term is common delta CA which is the same. So, basically here a phi CSTR is greater than phi PFR.

So, when alpha 1 is less than alpha 2 your phi CSTR is greater than phi pr. So, PFR. So, we showed both graphically as well as through intuition and through the mathematical expression here that when here alpha 1 is greater than alpha 2 you will get better selectivity when you are using a PFR and when here alpha 1 is less than alpha 2 you will get a better selectivity when you are using a CSTR. Now as we have completed our discussion on CSTR; let us go ahead and solve some simple problem again related to our chemical reactor design principles.

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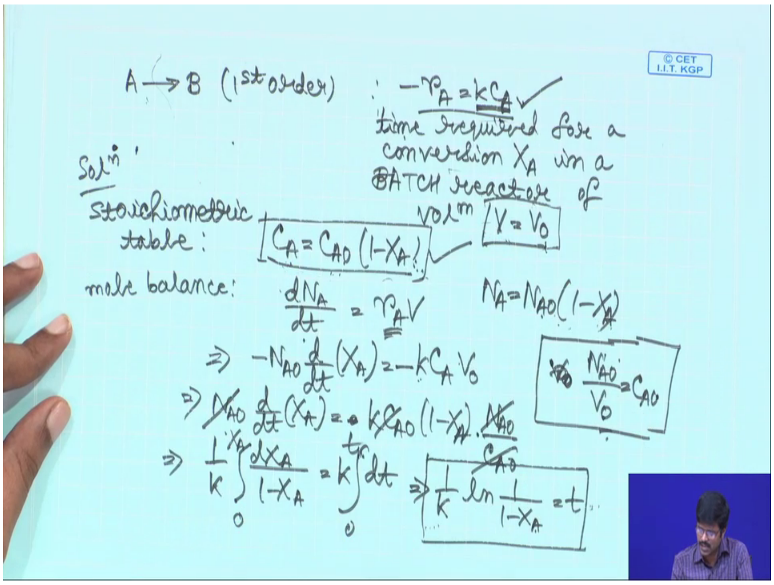

A → B (1st order) : $-r_A = kC_A$ ✓

time required for a conversion X_A in a BATCH reactor of vol^m $\boxed{V = V_0}$

Sol^n:

stoichiometric table: $\boxed{C_A = C_{A0}(1-X_A)}$

mole balance: $\frac{dN_A}{dt} = r_A V$ $\quad N_A = N_{A0}(1-X_A)$

$$\Rightarrow -N_{A0}\frac{d}{dt}(X_A) = -kC_A V_0$$

$$\Rightarrow \cancel{N_{A0}}\frac{d}{dt}(X_A) = k\cancel{C_{A0}}(1-X_A)\cdot\frac{\cancel{N_{A0}}}{\cancel{C_{A0}}}$$

$$\boxed{\frac{N_{A0}}{V_0} = C_{A0}}$$

$$\Rightarrow \frac{1}{k}\int_0^{X_A}\frac{dX_A}{1-X_A} = k\int_0^{t}dt \Rightarrow \boxed{\frac{1}{k}\ln\frac{1}{1-X_A} = t}$$

So, let us define the problem like this say we are considering this particular reaction and this reaction is first order in a which means your rate law is this minus r A equals to constant into CA. Now the question is you have to calculate the time you have to calculate the time required for a conversion, let us say we targeting a particular conversion which is XA in a batch reactor in a in a batch reactor of constant volume V equal to V not this is the problem.

So, you we have been given this reaction this is the rate law. So, the question is what is the time required for a specific conversion in this batch reactor of volume V equals to V naught. So, when you are serving all these problems you should go step by step as we have discussed previously you start by having the rate law expression here the rate law expression is given now you start by writing down the rate law expression then you go to stoichiometry; that means, the concentration as a function of conversion and then you put them together in the design equation you replace this rA.

So, we will do that step by step. So, this is the rate law. So, the solution, rate law is already given now what is the stoichiometric table that that tells you. So, what is the stoichiometry remember we cons constructed this stoichiometric table for batch reactor before in a previous class. So, that tells you your concentration of a, at a particular time t is equals to initial concentration of a into one minus XA where XA is the conversion that has been attained by the reaction at that time. So, this is CA equals to CA 0 into one minus XA then once you have initiated the rate law and then once you have constructed the stoichiometric table or expression then you directly go to the mole balance or the design equation. So, the mole balance is basically nothing, but dna dt equals to r AV; if we can recall from previous class this is the mole balance now remember that NA that is the number of moles of a at a time particular time t is equals to initial number of moles into 1 minus x.

So, if you replace that here then what do you get ddt of NA 0 minus ddt of NA 0 into x or XA now ddt of NA 0 is 0 because NA 0 is constant and ddt of NA 0 into minus XA will be equal to. So, minus term will come out minus NA 0 ddt of XA and rate you are putting this expression k into CA that you can put here minus k into CA into V minus goes. So, that will be any 0 into ddt of XA equals to minus k. So, minus is not there anymore. So, k into CA; CA you can get the expression of CA in terms of conversion and the initial concentration. So, just put that expression here k into CA 0 into one minus x V is V 0 here V 0 is basically the volume of the batch reactor that we already defined the problem before and this is basically XA. Now V 0 what is V 0 what is V 0 V 0 is basically nothing, but. So, like this NA 0 divided by V 0 is equals to CA 0.

So, concentration is equals to number of moles divided by total volume. So, V 0 is nothing, but NA 0 divided by CA 0, right. So, V 0 will be NA 0 divided by CA 0 this CA 0 goes and NA 0 also gets cancelled out. So, ultimately will left with solving a simple integral. So, d XA divided by one minus XA equals to k dt. So, you integrate from time 0 to t this time t that is the t is what the time is that we are trying to find out with respect to the particular targeted conversion and then this is also integrated from 0 conversion to the final conversion. So, if you do this you will get the final expression as one by k into ln 1 by 1 minus XA equals to t. So, this is the final expression this expression tells you that if your targeting conversion which is XA or a reaction that is where the reaction is first order in a then this is the time that is required and k is rate constant for this reaction.

So, like these you can solve different problems here I did not give you any particular values for the different species the amounts of different species I just give you a general term now if the rate is second order in a then accordingly this integration will change like that. So, this is the general thing. Now if the r A rate is second order you can you can change the CA accordingly CA square then this will be CA 0 square into one minus XA square and then the integral will change then ultimately expression will also change, but overall is the principle . So, now, before closing this class we will do one more problem this time let us do a problem for CSTR ok.

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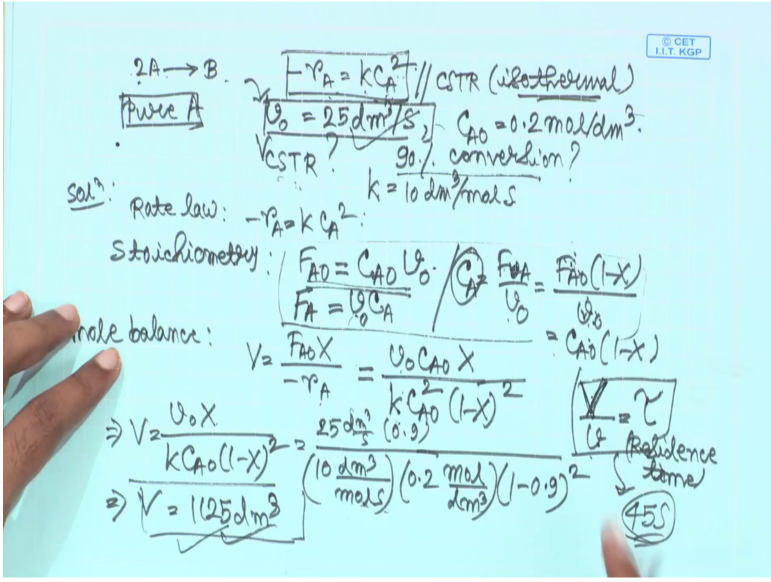

$2A \rightarrow B$. $\boxed{-r_A = kC_A^2}$ // CSTR (isothermal)

$\boxed{\text{Pure } A}$ $\boxed{\upsilon_0 = 25\,dm^3/s}$, $C_{A0} = 0.2\,mol/dm^3$.

V_{CSTR}? 90% conversion?

$k = 10\,dm^3/mol\,s$

Soln: Rate law: $-r_A = kC_A^2$.

Stoichiometry: $F_{A0} = C_{A0}\upsilon_0$. $F_A = \upsilon_0 C_A$ / $C_A = \frac{F_A}{\upsilon_0} = \frac{F_{A0}(1-X)}{\upsilon_0} = C_{A0}(1-X)$

mole balance: $V = \frac{F_{A0}X}{-r_A} = \frac{\upsilon_0 C_{A0} X}{kC_{A0}^2(1-X)^2}$

$\Rightarrow V = \frac{\upsilon_0 X}{kC_{A0}(1-X)^2} = \frac{25\frac{dm^3}{s}(0.9)}{\left(10\frac{dm^3}{mol\,s}\right)\left(0.2\frac{mol}{dm^3}\right)(1-0.9)^2}$

$\Rightarrow \boxed{V = 1125\,dm^3}$

$\boxed{\frac{V}{\upsilon} = \tau}$ Residence time

$45\,s$

So, let us say this is the reaction we are considering this is the liquid phase reaction which is having an elementary rate law and as you know elemental rate law means it will be k into CA square because this is the coefficient and that will be exactly equal to the concentration to the power whatever is the order of the reaction with respect to that species that will be equal to the coefficient which appears with that species in the reaction.

So, this is the elementary rate law it could be CA to the power q or it could be CA to the power 0 or it could be CA to the power one then it will not be elementary rate law or CA to the power point 5. So, elementary rate law now you are doing this reaction in a CSTR under isothermal condition; that means, the temperature is not changing you can take away the heat if it is exothermic reaction on its. So, fourth same temperature throughout now pure a is entering the reactor at a volumetric flow rate. So, small V is the volumetric flow rate and volumetric flow rate in at a volumetric flow rate of 25 decimetre cube per second and the concentration of a that is entering; that means, CA 0 is equal to 0.2 moles per decimetre cube question is what is the volume of CSTR necessary in order to achieve a conversion of ninety percent.

So, we know the volumetric flow rate the flow rate at which it is entering we also want to know the initial concentration at which it is entering that is feed we also know this is the rate expression. So, question is can we find out the volume of we can achieve ninety percent conversion something is missing here we need also a value of k rate constant it is also given ten decimetre cube per mole second. So, that defines the whole problem. So, again your rate law is there. So, start by writing down the different expressions. So, you start with your rate law your rate law is minus r A equals to k into CA square then you go to stoichiometry.

So, rate law stoichiometry mole balance the same sequence we are following all true then you go to stoichiometry for stoichiometry your FA 0 that is the molar flow rate in is equal to your concentration of the entering a into the volumetric flow rate in that is the thing and your molar flow rate out is equals to volumetric flow rate out into exit concentration of a or the concentration of a in the reactor now this volumetric flow rate out is equal to volumetric flow rate in when you are doing a liquid phase reaction an EFTA; CSRT is available in steady state condition. So, V equals to V is replaced by V not. So, this is the situation then also your CA concentration of a is nothing, but FA by V or V not same here thing, I just put it here like this sorry this is FA and FA is nothing, but FA 0 into 1 minus x.

So, this is this divided by V 0 now you can write down the mole balance. So, if you write down the mole balance what do you get V equals to FA 0 into x divided by minus r A this is the expression for V. Now from these relationships what you can write here it you can write V 0 into CA 0 because FA 0 is basically V 0 into CA 0 into x divided by minus r A minus r A is k into CA square. So, that will k into CA square now what is CA square this CA has this expression. Now FA 0 is divided by V 0 molar flow rate in divided by volumetric flow rate in is nothing, but the concentration at which it is entering the ca. So, this ratio from this expression this comes out to be CA 0 into one minus x for stoichiometric table already we had illustrated this before.

So, minus r A equals to k into CA square. So, that will be CA 0 square into one minus x whole square right. So, from here what you get is this V equals to small V 0 into x divided by small k into CA 0 into one minus x. So, targeted conversion you know volumetric flow rate in everything you know. So, volumetric flow rate in is 25 decimetre cube for second x has no unit 90 percent conversion into 0.9. So, you put it in fractional terms now small k is 10 decimetre cube per mole second now entering concentration of a is 0.2 mole per decimetre cube into 1 minus 0.9 square.

So, always write down the units. So, that ultimately you will see that you will get the unit of decimetre cube the most mole seconds these things will go. So, the ultimate expression of V here as I have calculated already is 1125 decimetre cube volume you require to get the particular conversion further mode I can ask you what is the residence time; what is the residence time for this problem. So, if you have ninety percent conversion you find out the volume then what is the residence time that you get. So, what is residence time residence time is how long the reactants or whatever species is there stay in the reaction itself. So, the residence time is nothing, but capital V divided by small V capital is the reactor volume divided by small V which is the volumetric flow rate in this ratio is your residence time ok.

So, this is your residence time. So, in this case the expression; so, this what does it tell you what is the rate what is the residence time capital T is already known and 25 decimetre cube per second. So, if you take the ratio it will be 45 seconds. Now this residence time is very very important you can change the residence time by changing the volumetric flow rate in when the capital V is constant you are not changing the reactor value, but change the residence time if you change the residence time you may change the extent of conversion.

So, we will stop here today and we will continue to discuss different problems and progress in terms of also understanding some other remaining concepts for the chemical reactors till, then good bye and see you in the next class.