Principles of Polymer Synthesis
Prof. Rajat K Das
Material Science Centre
Indian Institute of Technology, Kharagpur

Lecture – 28
Design of Chemical Reactors (Contd.)

Welcome, back. We have been talking about chemical reactors for last several classes now and today also we are going to continue the same trend. So, the topic is the same as before we continue with talking about design of chemical reactors and off late we had been working on several sets of problems and we are trying to elucidate the concepts that we have learnt as per as the design principles are concern we talked about CSTR we talked about PFR. We also talked about batch reactors and certain polymerisation reactions; we are also incorporated into the problem.

Now, let us for a while stop doing the problems and let us come to you know the main concept of this linking of polymerisation with this chemical reactors. Until now the main basic principles what we have discussed. We never mentioned polymerisation although we have off late done some problems where we have discussed certain polymerisation reactions with respect to chemical reactors.

So from now on, of course, when we discuss the when we continue to discuss the principles of chemical reactors those principles will also apply to polymers as well as to your small molecules I mean we will also specifically talk start talking about polymers from now on and then towards the next class probably towards the end of the next class or we will see how the things go we will also do some problem where we will directly correlate you know the design principles with pro with the complexity of defined chemical reactions or also the polymerisations.

So, speaking of polymerisation we have discussed the principle of radical polymerisation as well as if you remember the step polymerisation. So, the question is naturally arises let us say we have to do a radical polymerisation. So, chain growth polymerisation. So, whether we will do the reaction in a batch reactor or whether you will do the reaction in a continuous start tank reactor? This is a question. Now, remember that when you are doing a reaction in a batch reactor everything is put in together and then you wait for a certain amount of time and then you stop the reaction and then you take it out.

So, what is happening is that with time the concentration of different species is changing, you just allow the reaction to run its course. So, the conversion also is changing with time if you remember we did some problems where we related the conversion with time, if you are looking for a specific conversion what is the time required so on and so forth. So, this is something that you have to keep in mind in discussing this particular topic.

If you are looking at CSTR for example, what is happening is that you are fixing a specific conversion and then you are allowing this reactor to run at that particular condition, it is a steady state condition we are talking about. It is a steady state condition. So, the concentration of all the species whether reactant or product they do not change with time and you are always getting a particular conversion when it is in running condition CSTR in that in that steady state.

So, if you now discuss this difference with respect to whether we will do a free radical polymerisation in a CSTR or batch reactor what will be your conclusion? Remember, from our previous discussion on radical polymerisations that the radicals are normally very short lived unless you are doing a living radical chain in polymerisation, few seconds or less than a second.

So, what will happen is that the chains that are growing they will be dead in the matter of seconds, when you are talking about radical chain polymerisation then another chain is growing then another chain is growing and that is the reason why the molecular weight is quite you will get very high molecular species even at low percent conversion for radical polymerisation, because high molecular species is formed quite quickly unlike in step polymers.

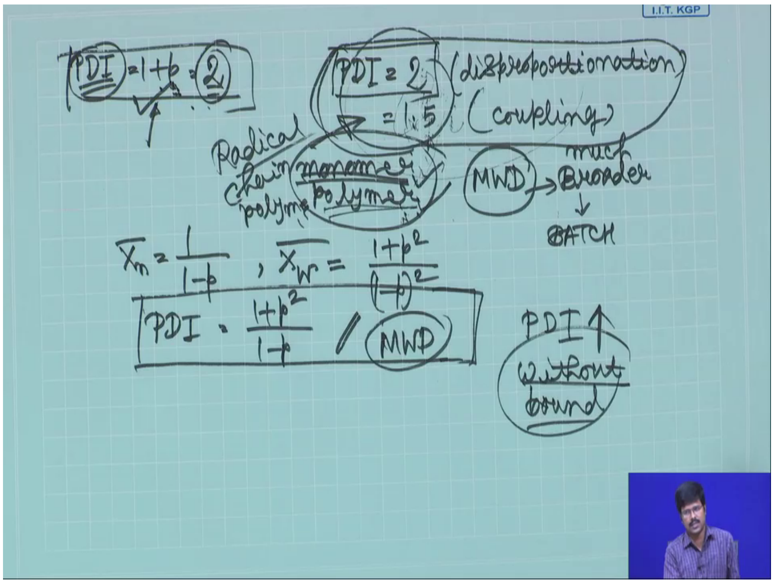
So, the thing is then the propagating species or the propagating the chains that are growing the lifetime of these chains is actually much lesser then the residence time of the batch reactor. If you are doing this reaction say in a batch reactor, say you are keeping for one hour the reaction, but each chain is growing within a matter of seconds and then they are dead. So, what is happening is that as the reaction is progressing as you are allowing more and more time to progress, what is happening your concentration is changing. So, the chains that are growing at the later time point they are seeing a different concentration of reactant and you know the rate is a function of concentrations. So, the rate also changes.

So, what will happen is that, all the chains that have grown at the end of the reaction when you see different chains that you have certain chains have grown at certain different time points and then they are dead. Once they are dead, they are not reacting any further. So, ultimately what is happening is that in the chain growth process, the radical chain growth process, what is happening is whatever chains you have ultimately the dead polymers they have experienced different conditions in this reactors, because simply they have found the different time points and the concentration has also changed at those time points.

So, ultimately the molecular weight distribution that you are going to get is going to be quite wide if you are doing a reaction in a batch reactor. Instead if you did the same reaction in a CSTR what would happen? If you did the same reaction in CSTR it is the steady state condition. So, whether you are looking at time 10 seconds or you are looking at time 1 hour your concentration is always the same.

So, whatever chains are growing whether the chains are growing at this time point or whether the chains are growing at that time point, at a separate time point all of them are basically seeing the same condition that is the same concentration. So, that is why the molecular distribution will be much narrower if you are doing the same free radical polymerisation in CSTR rather than in batch reactor.

(Refer Slide Time: 06:32)



So, if you are, let us elaborate on this particular thing something that I have not discussed before, but I will assume here. If you remember that the poly dispersity index we did not derive in a statistical approach, the polydisparcity index expression for radical polymerisation we did the thing for step polymerisation where this came as 1 plus p.

If you remember, if the conversion is 1, then your PDI is 2 and we told that even though we want an narrow distribution, but for a step polymer we cannot get less than 2 because the p has to be close to 1, fractional conversion of fractional extent of reaction it has to be close to 1. So, ultimately your step polymer of any reasonable molecular weight that is industrially important we will have a PDI at least 2. This we actually discussed it elaborately. But, what we did not discuss is the expression of PDI for radical polymerisation.

Here, I am going to assume this that if you have I mean the expressions I am going to assume, I am not going to derive this. So, you can have 2 limits of PDI. PDI will be 2, I mean attainable PDI will be 2 if the termination in happening through disproportionation and this will be 1.5, if the termination is happening through coupling. Now, these limits that we have that can be derived these are derived by considering that the monomer and polymer concentration are the same means they do not change with time and they do not change with the course of the reactions. So, whatever monomer concentration is there it remains same throughout the reaction, whatever polymer concentration is there it remains the same throughout the reaction.

By considering these aspects it can be derived that the PDI is to for disproportionation termination and PDI is 1.5 for termination through only coupling, but these kind of situation cannot be realised in a batch reactor because the monomer concentration and polymer concentration are not the same as a function of time, they are changing. So, these are unattainable limits for batch reactors, you will get in practice much higher PDI in a batch reactor, if you are doing a radical polymerisation.

So, this is limit for radical polymerisation; however, these limits are attainable quite attainable if you are doing the reaction in a CSTR. Because, in a CSTR that has been operating at a steady state the monomer concentration and the polymer concentration are not changing with time. So, there these things are attainable.

So, either your PDI will be higher than this or it will be this, the lower value, the lowest value that you will have. So, these values can be attained if you can control your concentrations carefully in CSTR, but this is something that cannot be attained. This only tell you the ideal limit for a batch reactor because for a batch reactor this concentration some changing. So, ultimately the molecular weight distribution that you will get the distribution will be much broader when you are doing a reaction in a batch reactor. And, here we are talking about radical free radical chain polymerisation and this limit of 2 and 1.5, they are attainable in a CSTR because here monomer and polymer concentration do not change with time. So, steady state condition.

What happens with a step growth polymer for a step growth polymer you know that the chains whatever chains that are forming here also I am telling chain polymer chain those chains they keep on forming then is not like there is nothing like termination if you have say 10 mark this 10 mark does not stay as 10 mark till the end, it can actually react with a monomer and form a 11 mark or at 10 mark can react with another 10 mark; this kind of reaction keeps going on and remember this PDI value is 1 plus p that that is something we derived for step polymerisation before the statistical approach.

So, this value 1 plus p this means that your conversion has to be the if you go to higher and higher conversion, of course, that is what you want for step polymers because the molecular it has to be higher. So, in a batch reactor what you can do, you just continue the reaction until close to 100 percent then PE is close to 1 and your PDI is close to 2 and also all the chains are basically growing as long as the reaction is progressing.

So, the residence time is very close to being equal to the lifetime of all the chains for step polymers. So, all the chains basically they are experiencing the same change in concentration, because for the batch reactor as the reaction progresses the concentration when is changing all the chains are experiencing the same similar conditions same change in concentration. So, that does not lead to broadening of molecular distribution for step polymers when the reaction is being done in batch reactor.

So, it is very simple then. You just do the reaction in a batch reactor, you allow the reaction to progress until close to a 100 percent conversion and then you have a your PDI value should be close to 2 because of a theoretical limit and you have a reasonably narrow molecular distribution as is allowed from this statistical approach, it cannot be less than 2, but it can be very close to 2 your problem is solved and you get a very high molecular weight what happens. So, stay for step polymers then you can do the reaction in a batch reactor; however, for a free radical polymerisation you better do in CSTR.

What if we do the step polymerisation in a CSTR? So, if you do the step polymerisation in a CSTR basically what will happen is that this X n if you remember the Carothers equation X n bar equals to 1 divided by 1 minus p and something that we are not going to derive, but we are going to assume this X w bar is the weight average degree of polymerisation. If you are doing the step polymerisation in a CSTR, Continuously Start Tank Reactor, then the expression of X w bar will be equal to 1 plus p square divided by 1 minus p whole square we are not going to derive this we are just going to assume this particular expression.

So, the PDI; you remember PDI was 1 plus p in a batch reactor actually whatever we derived before was like you know normal reaction that is going on in a batch reactor it can be going on, you are going to 99 percent conversion 100 percent conversion and then this will be the expression. But, for a CSTR the expression of PDI then will be X w bar by X n bar which will be equal to 1 plus p square divided by 1 minus p. So, in a CSTR if you are looking for a very high conversion what is happening if you go to higher and higher conversion your PDI goes up it goes towards very high value.

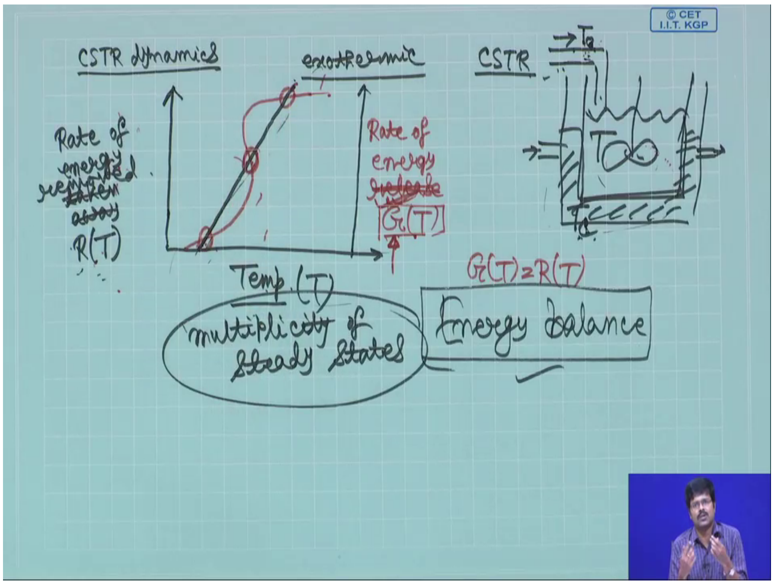
So, in a CSTR what will happen is that your molecular weight distribution will be much wider if you are targeting very high conversion as compared to your batch reactor when you are talking about a step polymerisation. So, that is also the reason why we will not do typically the step polymerisation reactions in a in a CSTR because the PDI will go up without bound, if you look at these particular expression. So, this is some general discussion that I wanted to do as per as in which kind of reactors you will do the reaction if you have a radical polymerisation free radical polymerisation or if you have a step growth polymerisation.

Now, something is we are going to talk about we are going to talk about steady state in little bit more detail. Remember, these mole balances that we have derived we talked about steady state equations, steady state for batch reactor, steady state for CSTR so on and so forth. Now, we are going to look at the steady state this steady states in little bit more detail especially for CSTR because it turns out that for CSTR there can be multiple steady states that are possible we will come into more detail of this a little while after. Before that, we are going to talk about what we call as energy balance you know for mole balance you know you have to balance the masses.

So, what is energy balance? When we are talking about say a steady state situation let us say you are doing a reaction which is exothermic it liberates heat say many of these find polymerisation reaction say ethylene polymerisation it will liberate heat exothermic reactions if you are doing the reaction in a CSTR, it liberates some heat so, the reaction temperature might go up, but in steady state it is not allowed because in steady state as a function of time all these properties have to be constant so that temperature should not go away.

So, we are talking about say an isothermal situation here. So, as the heat is released by the reaction mixture, that is, heat has to be taken away so you could put some coolant, a jacket around the CSTR that will take away the heat. So, in steady state then your rate of heat generation has to equal to the rate of heat that is taken away. So, let us first try to understand this situation in a little bit more detail way.

(Refer Slide Time: 16:37)



So, we will call these as CSTR dynamics. Let us say we are doing an irreversible first order reaction an exothermic reaction exothermic reaction in a continuously start tank reactor. Now, let us plot the reactor temperature on the x axis and rate of energy taken away. So, let us say this is R T. So, basically you have a CSTR, you are doing the reaction here and you may have a jacket around it where you have a coolant liquid. So, this liquid is going in and then it is also going out and it is at a particular temperature say T c.

And, so, this is say rate of energy or rate of heat removed you can say also. So, rate of energy removed. Now, depending on the temperature, so, this temperature T is basically the temperature inside the reactor. The rate of energy that is removed is basically a linear function of the temperature of the reactor. So, higher the temperature of the reactor the rate of energy removed will be higher in linear way. So, we will get something like this. So, rate of energy removed, R for the removal.

So, R T and this is as a function of temperature, this will vary like this now this particular curve that I have drawn this is for a specific condition. Specific condition means, it could be for a specific temperature at the inlet because you know the reaction mixture or the starting material that is entering it will be at the certain temperature, let us say that it is T 0, that you can change that you can increase or decrease. Same way, you can also increase or decrease this temperature.

So, let us say we will talk about this T 0. So, for different T 0 values you will get different lines like this, we will come to that after. So, let us say then the rate of energy removed by the coolant is basically equal to the, is basically linearly varying with respect to temperature. Now, if you are doing a reaction which is an exothermic irreversible reaction it is also using some energy to the resistant into the reaction mixture how does that vary. So, I mean let us label it like this, rate of energy release, I mean this is the rate of energy released by the by the reacting mixture because the reaction is going on temperature will rise if you do not take away the heat. So, this will be something like this.

So, let us say that curve is G T, this is G for let us say energy released or energy this is you know rate of generation. So, that is why it is G, rate of energy release. Now, you see that this particular curve which is for the rate of energy released by the reaction as a function of temperature of course, it is like this and the black curve is a straight line which is the rate of energy being removed as a function of temperature. Now, these two curves are intersecting at certain points.

The particular thing that I have drawn here it shows these two curves intersect at three points; first point here, second point here, the third point here. It may be as it changes the inlet temperature these this curve will shift, this linear arc which is the rate of energy released it will shift may be on this side if it shifts on this side or may be it shifts on this side. So, there may not be three intersections, there may be no intersections or there may be only one intersection also.

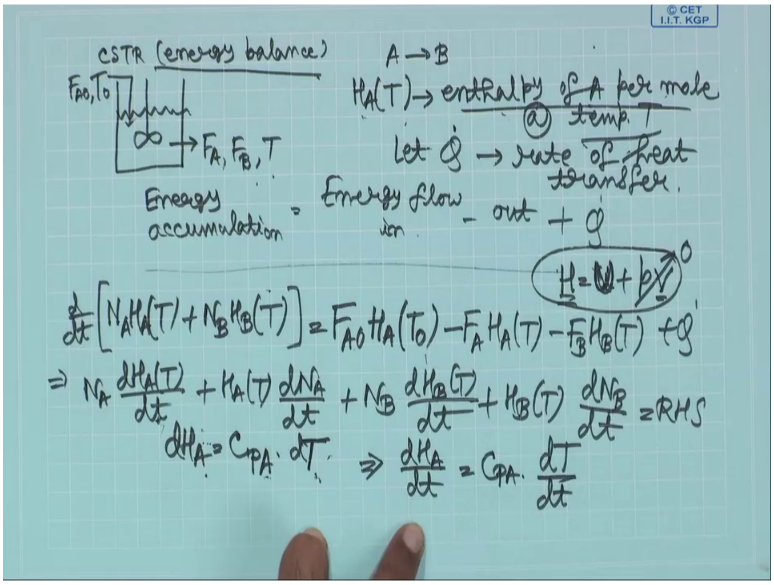
So, if it goes somewhere here then there will be only one intersection point. So, what happens at this intersection point? At each intersection you can see the rate of energy released or removed, sorry, rate of energy removed becomes equal to the rate of energy generated right; that is your steady state condition if that condition is fulfilled then the reactor temperature will not change.

So, in that situation your G T will be equal to R T. So, for CSTR what happens is that, if you are looking at this particular graph this black line indicates a specific operating condition that is being given by the specific value of T 0 specific value of T c, so on and so forth. Now, for this particular operating condition then you basically have three steady states that are possible. So, not one you can have, it turns out that in general, you can have a maximum of three steady states possible for a CSTR at a particular operating condition and you could have also one steady state that is possible for a CSTR.

So, the points of intersection are the points, which the steady state lies, that is, the steady state in it. So, under the condition that I have drawn here we have basically three steady state conditions that are realisable in this particular operating condition. So, basically this is rate of heat removal becomes equal to the rate of heat generated. So, this is something we are going to discuss in slightly more detail now because if you want to talk about this is called basically multiplicity of steady states.

So, this is multiplicity of steady states if you want to talk about these you have to also talk about what we call as energy balance, we will come to that in a little while otherwise we cannot talk about all these different steady states. Mass balance can only take you so far, because mass balance is actually applicable whatever I mean mass balance in applicable in whatever condition, but the particular design equations that we derived for steady state condition, considering the mass balance. So, those equations are only applicable the final forms whatever we had derived before they are only applicable in steady state condition and it turns out that you can have multiple steady states for a CSTR. So, this is the CSTR dynamics that we are going to talk about in more detail now.

(Refer Slide Time: 24:36)



CSTR (energy balance)

F_{A0}, T_0 → F_A, F_B, T

$A \rightarrow B$

$H_A(T) \rightarrow$ enthalpy of A per mole @ temp. T

Let $\dot{Q} \rightarrow$ rate of heat transfer.

Energy accumulation = Energy flow in − out + $\dot{Q}$

$$\boxed{\underline{H} = \underline{U} + \cancel{p\underline{V}}^{\,0}}$$

$$\frac{d}{dt}\left[N_A H_A(T) + N_B H_B(T)\right] = F_{A0} H_A(T_0) - F_A H_A(T) - F_B H_B(T) + \dot{Q}$$

$$\Rightarrow N_A \frac{dH_A(T)}{dt} + H_A(T)\frac{dN_A}{dt} + N_B \frac{dH_B(T)}{dt} + H_B(T)\frac{dN_B}{dt} = RHS$$

$$dH_A = C_{PA} \cdot dT \quad \Rightarrow \frac{dH_A}{dt} = C_{PA} \cdot \frac{dT}{dt}$$

So, we will do in same way as we did for the mass balance, we will do now energy balance for CSTR, let us say you are considering a liquid phase reaction where A goes to B and this is your CSTR the drawing the reaction mixture this is your input F A 0 and T 0 is the temperature of the inlet temperature of the reaction mixture at the inlet and this is what you have that outlet F A, F B and T.

Now, let us say you just put A and then B is also formed. So, A and B both are there because the conversion is not hundred percent. So, on and. So, forth let H A T be the enthalpy of a per mole at temperature T. The reactor is been operated at temperature T that is why am putting T in steady state situation. Actually, E H in general we will not talk about steady state situation at the moment we will come to that after just the reactor is being operated and this is the temperature here.

Now, also let Q dot be the rate of heat transfer. Rate of heat transfer we talked about this we have a jacket here, so, the rate of heat transfer that is Q dot. Now, we can write down the energy balance as something like this energy accumulation in the reactor is equal to energy flow in minus energy flow out plus heat transfer I mean heat could be transferred inside or heat could be transferred for outside, I mean heat could go inside or it could be taken away this is your expression.

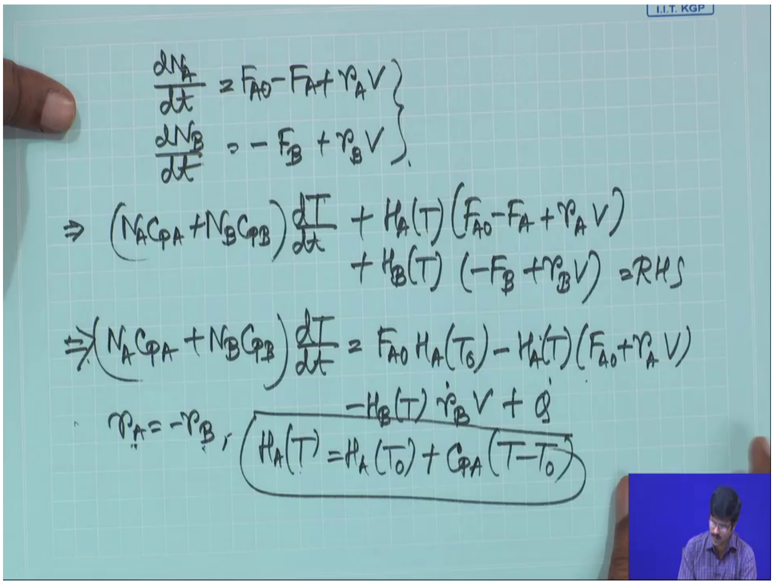
Now, since this is the liquid state reaction typically when you are talking about energy we talk about internal energy, but we are going to replace that with enthalpy here. How? Because, your H equals to u plus pV from thermodynamics and for a if you look at the molar volume in the liquid state that is quite small. So, this term is approximated to 0. So, your internal energy can be replaced by enthalpy term. So, what is the energy rate of accumulation? that is, d dt of, let us say N A number of moles for a that into H A at T because this is per mole. So, for N A number of moles this is this and for N B because for the species B this is NB is the number of moles. So, N B H B T.

So, as a function of time this is changing. So, this is the energy accumulation equal to energy flow in is basically F A 0 molar flow rate in into H A at T 0 because H A at T 0 is basically the enthalpy of a per mole at temperature T 0 energy. Flow out, two terms will be there; one term for A, and one term for B plus Q dot. So, if you apply the rules for differentiation here then what will what you will get it will be NA dH A T by dt plus H A T dN A dt plus N B dH B T dt plus H B T dN B dt equals to right hand side. Now, what is dH A? Change in enthalpy is nothing, but heat capacity multiplied by change in temperature. So, heat capacity is nothing, but dH dT.

So, dH A equals C PA; C P is the heat capacity for the species A and into dT. So, that means, dH A dT is nothing, but, remember here this t this small t is time as a function of time, energy accumulation here and here it is this T, capital T this is temperature. So, dH A, rate of change of enthalpy with temperature is basically your heat capacity. So, if you take derivative with respect to time on both sides then you have dH A d small t equals to C PA dT dt. This is rate of change of temperature with time.

Now, if you are considering. So, this is energy balance, we are not yet done with this we will go ahead with that. But, let us stop for a while and do the mass balance.

(Refer Slide Time: 30:17)



I.I.T. KGP

$$\left.\begin{aligned} \frac{dN_A}{dt} &= F_{A0} - F_A + r_A V \\ \frac{dN_B}{dt} &= -F_B + r_B V \end{aligned}\right\}.$$

$$\Rightarrow \left(N_A C_{pA} + N_B C_{pB}\right)\frac{dT}{dt} + H_A(T)\left(F_{A0} - F_A + r_A V\right) + H_B(T)\left(-F_B + r_B V\right) = RHS$$

$$\Rightarrow \left(N_A C_{pA} + N_B C_{pB}\right)\frac{dT}{dt} = F_{A0} H_A(T_0) - H_A(T)\left(F_{A0} + r_A V\right) - H_B(T)\, r_B V + \dot{Q}$$

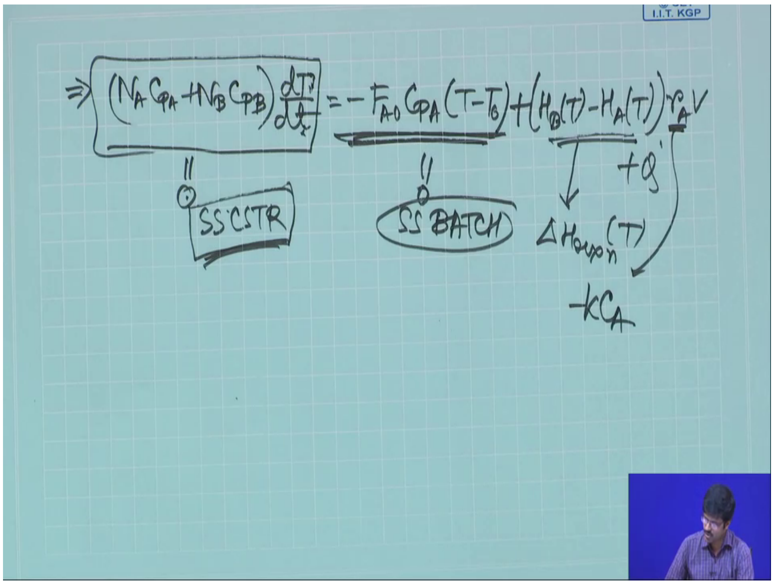
$$r_A = -r_B, \quad \boxed{H_A(T) = H_A(T_0) + C_{pA}(T - T_0)}$$

So, from mass balance d N A dt because d N A dt the term is there we are going to replace this. So, from mass balance this d N A dt is nothing, but in flow rate in flow in minus flow out plus r A V we talked about this and d N B dt flow rate in that is 0, because nothing is going in for compound for product b plus r B V. So, if we replace this terms and this term in this particular expression then what we get is the following we get this N A C PA plus N B C PB dT dt capital T small t here plus H A T into F A0 minus F A plus r A V plus H B T into minus F B plus r B V equals to the right hand side. You can actually replace these things there and you can see for yourself that is the expression that you will get.

So, ultimately, if you take this on the right side and remember, that the right side is this thing. So, you can work it out by yourself it will be coming as something like this N A C PA plus N B C PB dT dt that equal to F A0 H A T 0 minus H A T into F A 0 plus r A V minus H B T into r B V plus Q dot and remember in that r A is nothing, but minus r B rate of destruction of this, it is the rate of formation of this, this minus you can put on this side and replacing there and also you remember that enthalpy of a molar enthalpy of A at temperature T is nothing, but molar enthalpy of A at temperature T not plus heat capacity into T minus T naught.

If you remember this thing and if you replace that in this particular expression then the finally, what you get, is the following.

(Refer Slide Time: 32:54)



$$\Rightarrow \boxed{(N_A C_{PA} + N_B C_{PB})\frac{dT}{dt}} = \underline{-F_{A0} C_{PA}(T-T_0)} + \underline{(H_B(T)-H_A(T))}\,r_A V + \dot{Q}$$

N A C PA plus it is taking a while, but ultimately it is very useful expression you will see I hope this is the expression here it will be equal to minus F A0 C PA T minus T 0 plus H B T minus H A T into r A V plus Q dot. Now, this particular term here will become 0 for a steady state CSTR. For a steady state CSTR this particular term will become 0, there is no temp temperature change with number with respect to time that becomes 0 and for a steady state batch reactor you know this term will be 0, there is no flow rate in. So, for a steady state batch reactor this term will be 0.

So, this is the overall energy balance expression without considering steady state. If you are considering a steady state CSTR then this term becomes 0 and if you are considering a steady state batch reactor then this term becomes 0, what about this term? This is basically the enthalpy of reaction and what about this value of r A? r A is basically minus k into C a. So, actually we have run out of time today. So, what I will do is we have very close to deducing the final expression, you have to just work year your way through this maze of equations.

But, ultimately the concept is very simple it is the rate of energy, it is the energy accumulation equals to energy flow in minus out plus Q dot. So, from there we are just manipulating the different expressions replacing things and trying to make things easier and you see already here the delta each reaction appears that is the enthalpy of reaction.

So, this will be negative if the reaction is exothermic. So, we will stop here today and we will continue with this in the next class.

Thank you.