Principles of Polymer Synthesis

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Lecture – 29
Design of Chemical Reactors (Contd.)

Welcome, back. We have been talking about the energy balance expression for a general chemical reactor and we were right midway through it and, so, the topic of the day will continue to be a design of chemical reactors as it has been for several classes prior. So, will directly go back to where we left you in the previous class in the middle of the derivation.

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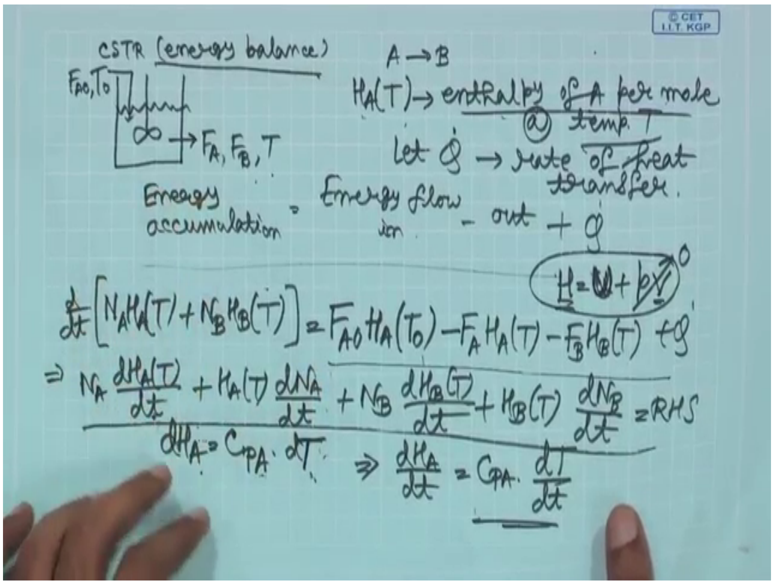

CSTR (energy balance)

$A \rightarrow B$

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

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

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

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

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

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

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

So, if you look at that, we started with an energy balance expression and I mean it is quite general although we started with CSTR, I mean for a batch reactor these terms will become 0 so on and so forth ultimately. So, we started with this assumption I mean this particular concept that energy accumulation is equals to energy flow in minus out plus heat transfer rate of heat transfer from the reactor, it could be positive, it could be negative and since this is a liquid reaction. So, this pV goes to 0.

So, internal energy you can replace by enthalpy and then you have energy accumulation is nothing, but this, rate of change of the difference with time. The different species amount might change, correspondingly their enthalpies will also change, because these enthalpies are per mole to N A moles. So, it will be total enthalpy into N A into H A. Again we are not talking about total internal energy which is U, we are talking about H because H equals U approximately, this pV tends to 0, this molar volume is very small when you are talking about the liquid state reactions.

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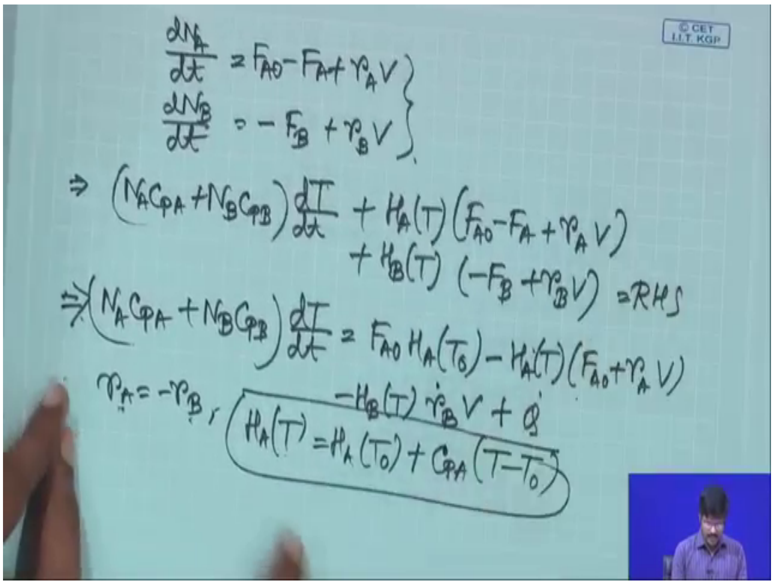

$$\left.\begin{aligned}\frac{dN_A}{dt} &= F_{A0} - F_A + r_A V\\ \frac{dN_B}{dt} &= -F_B + r_B V\end{aligned}\right\}$$

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

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

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

And, then we had you know certain expressions that we replaced into this particular equation and I mean we used to replace the terms here in the particular equation.

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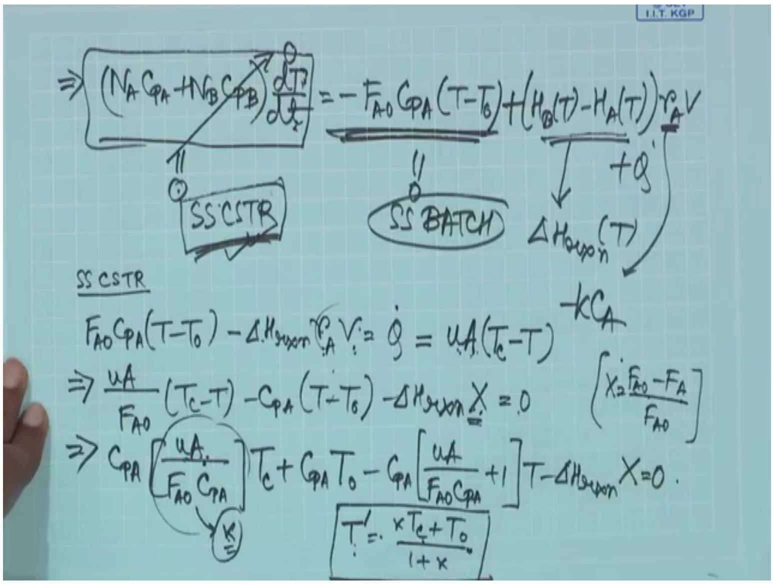

$$\Rightarrow \underbrace{\boxed{\cancel{(N_A C_{pA} + N_B C_{pB})\frac{dT}{dt}}}}_{\substack{\| \\ 0 \\ \boxed{\text{SS CSTR}}}} = \underbrace{-F_{A0} C_{pA}(T - T_0)}_{\substack{\| \\ 0 \\ \text{SS BATCH}}} + \underbrace{(H_B(T) - H_A(T))}_{\Delta H_{rxn}(T)} \underbrace{r_A}_{-kC_A} V + \dot{Q}$$

SS CSTR

$$F_{A0} C_{pA}(T - T_0) - \Delta H_{rxn} r_A V = \dot{Q} = UA(T_c - T)$$

$$\Rightarrow \frac{UA}{F_{A0}}(T_c - T) - C_{pA}(T - T_0) - \Delta H_{rxn} X = 0 \qquad \left[X = \frac{F_{A0} - F_A}{F_{A0}}\right]$$

$$\Rightarrow C_{pA}\underbrace{\left[\frac{UA}{F_{A0} C_{pA}}\right]}_{\kappa} T_c + C_{pA} T_0 - C_{pA}\left[\frac{UA}{F_{A0} C_{pA}} + 1\right] T - \Delta H_{rxn} X = 0.$$

$$\boxed{T' = \frac{\kappa T_c + T_0}{1 + \kappa}}$$

And, ultimately we arrived at these expression for the energy balance and this is a quite general expression in the sense that if you have a steady state CSTR, then this term goes to 0, your temperature does not change with time, your steady state batch reactor this term goes to 0 because molar flow rate in is 0 and T 0 is the temperature of inlet and this difference is the enthalpy of the reaction and r A you can replace by the concentration of A.

Now, going ahead if you now talk about a steady state CSTR, now we are going to go the energy balance equation for steady state CSTR. We are more interested in CSTR because we observe steady state multiplicity here, which we do not observe in the batch reactors. So, if we derive this equation this will be 0, then just these expression here for steady state CSTR what you will get, it will be F A0 C PA T minus T 0.

So, this term is 0 minus delta H of reaction delta H of reaction into r A V equals to Q dot. Now, this Q dot rate of heat transfer from the reactor is nothing, but small u, which is heat transfer coefficient of the reactor material means the material which is used to prepare the to construct the reactor. So, this is the heat transfer coefficient of that material into the area of heat transfer multiplied by the difference in temperature between the coolant liquid and the reactor. So, that will be T c minus T; T is the temperature of the reactor and small u is the heat transfer coefficient A is the area of heat transfer.

So, now if you do a little bit of re-arrangement and this, let me not skip any step. So, uA by F A0, T c minus T minus C PA into T minus T 0 minus delta H reaction into X equals to 0, this X is basically r A into V. You remember that X is nothing, but F A0 minus F A divided by F A0. So, if you on both sides if you divide by F A0 then your r A into V divided by F A0, it is nothing, but because r A into V is F A0 minus FA. So, it will be F A0 minus F A divided by F A0 which is your conversion. So, the conversion now makes an appearance here.

So, this can be re arranged at as like this C PA into uA divided by F A0 C PA into T c plus C PA into T 0 minus C PA into uA by F A0, C PA plus 1 into T minus delta H reaction into X equals to 0. Now, let us assume that this term is kappa just replace this term with something else, kappa and let us define another term T prime it should be equal to kappa T c plus T 0 divided by 1 plus kappa. This is just to simplify this expression. So, we are replacing this term with kappa. Now, this kappa basically it is what it is going to tell this is heat transfer coefficient and this is the area of heat transfer. So, basically and what is this C PA; C PA is the heat capacity of A. So, this these term tells you influence of heat exchange on reactor temperature. So, if you it tells you influence of heat exchange on the reactant temperature to that of the heat transfer fluid that ratio because, you have a heat exchange during that process.

Now, this heat exchange will basically influence the ratio of the reactor temperature to that of the heat transfer fluid. So, that is what is being given by these, because you know this uA this is directly related to your reactor temperature also. Because, ultimately how much heat is being transferred that is directly related to temperature difference between the reactors and the coolant and not only that, so that directly relates to also the heat transfer fluid.

Because heat transfer fluid is the fluid to which the heat is being transferred. So, those information is contained here, also if you are defining another term which is T prime your see here this T prime is basically some kind of an average kind of thing between T c and T 0. So, this T prime will be something like an intermediate temperature between this feed temperature and the temperature of the heat transfer fluid. So, we are defining these 2 terms here.

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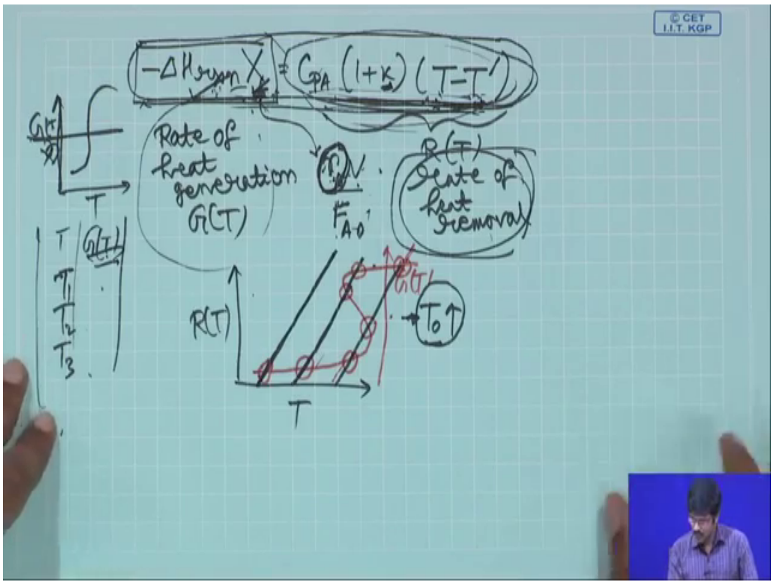

So, if we define these 2 terms and if we re-arrange you can actually work it out then what will happen is you will get finally very simplified expression which is minus delta H reaction into conversion equals to C PA into 1 plus kappa into T minus T prime. Now, so, this is the energy balance equation for a steady state CSTR. The left hand side you see here this is conversion, here this is delta H of reaction that is enthalpy of reaction. So, the left hand side basically tells you this left hand side is a rate of heat generation which is nothing, but G T, remember that we had in the previous class we had talked about.

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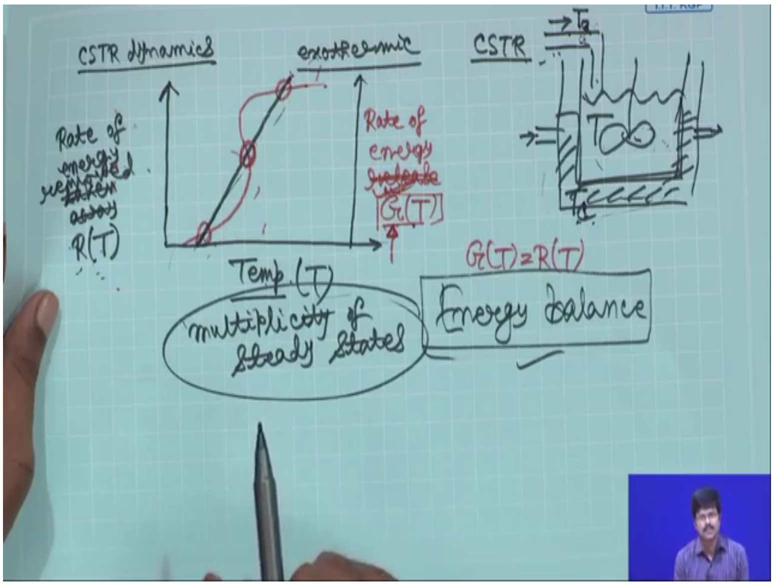

This particular graph, so, this is G T. This is G T, the red one rate of energy released or rate of heat generation whatever. So, rate of heat generation for the reaction from the reaction mixture, that is this. So, this G T is this G T that is the rate of heat generation because ultimately how do you get this kind of graph? You have to plot the G T as a function of T. So, you have to you need to know the expression, because when your operating a CSTR you need to know what are the steady state conditions under that operating systems or operating situation.

So, you need to have this kind of graph. So, need to generate that in order to generate that you have to have an expression of G T; that means, the rate of heat generation as a function of T, this particular thing will give you that that expression. So, here basically this is the rate of heat generation G T, the left hand side because you know this X basically contains this information. This X is nothing, but r A V divided by F A0 because you know r A V is nothing, but F A0 minus F A. So, that is F A0 minus F A divided by F A0 into X equals to X and this r A this contains the temperature term because the rate constant that is there rate constant is equals to erroneous factor into in exponential minus activation energy divided by r T that temperature term comes there. So, that is the dependence of temperature that you get. So, that is dependence of temperature.

So, what you can do? You have this term, you just find out this term as a function of temperature. So, on the excel sheet what you can do is that you can actually plot your X. So, your x axis and your y axis; y axis is your G T and the x axis is your temperature. So, you have an expression of this as a function of temperature and then you keep changing the temperature you keep feeding the different values you get different values of this the corresponding values of y. So, let us say you change temperature for 290, 291, 292 like that you go to say 500 Kelvin.

So, correspondingly in the excel sheet you can write down the formula of this G T and then you can directly correlate with that particular box for the column of T. So, you have a column of T temperature and then you have a column of G T and you know the G T has function of T. So, all these corresponding to each T value you get the value of G T and then you can construct this particular plot which is like this. So, that is how you will construct this particular red plot.

What is on the right side, whatever is on the right side this is basically your rate of heat removal, that is, the heat transfer fluid removing the heat, because if you are looking at this particular term here what is this kappa? This kappa basically contains all these information this u is the heat transfer coefficient; A is the area available for the heat transfer.

So, those things are contained in this kappa here and this T prime also contains kappa and it also contains T c. So, this heating characteristics or the cooling characteristics of the reactor those things are basically contained here as far as the heat removal is concerned with respect to the heat transfer fluid. So, this term on the right hand side is basically your rate of heat removal and both are equal from the general expression of the energy balance we assumed this equal to 0 because, it is steady state condition CSTR we assumed that and then we derived.

Once we have assumed steady state CSTR ultimately what we will get the temperature change with respect to time is 0 and that can happen if you arrive ultimately at this equation, that is rate of heat generation is basically equal to rate of heat removal, that is what we have been always talking about here and if you see this particular term this particular expression is linear in T. So, if your plotting this thing as a function of T the reactor temperature you will get a straight line like this and if you see the left hand side the expression of X which is r A V by F A0 this expression is basically derived from mole balance equation.

So, in deriving the left hand side the final expression in terms of the temperature you basically make use of mole balance equation, although one of this is your energy balance equation these thing are important to keep in mind. So, ultimately you can use this particular term get an expression of X in as a function of T and you can plot this as a function of T reactor temperature and you get this curve and this expression you plot as a function of T.

And get this curve and as you can see as the T prime changes the position of this graph also will change and T prime is of course, related to both T c and T 0. So, this will define different operating conditions. So, this line also will shift when you change this T 0 and T c, because T 0 and T c are contained both and in this T prime both of them are contain this prime. So, these are some certain things that we have to keep in mind.

So, this is the rate of heat generation this is rate of heat removal. So, if you plot rate of heat removal as a function of temperature of the reactor, you will get a line like this, we have already talked about that this line using a heat transfer fluid. As you keep increasing the temperature of the inlet what happens is that if you put those values here you will see this line will keep shifting to the right. So, this line this rate of heat removal that line shifts to the right as the temperature of the inlet goes up, temperature at the inlet that is here.

And, correspondingly, if you are also plotting in the same graph let us plot also the G T which is this side this what you are getting on this side let us say it is something like this it could be something like this. Here, we have drawn several lines as per as the rate of heat removal is concern because we are considering several operating conditions here we only consider one operating condition, but this rate of heat generation it has only one line, you are doing only one reaction. So, that is only one line you can see that depending on a operating condition your rate of heat removal will follow either this line, this line or this line. If it follows this line there is only one point of intersection.

So, if you are operating under this condition here, then you have only one steady state because both of them have to intersect. If you are operating under this condition that is given by this line you have actually three steady states again if you are operating at this line you have again three steady states like this. Now, let us go into some more detail of this situation.

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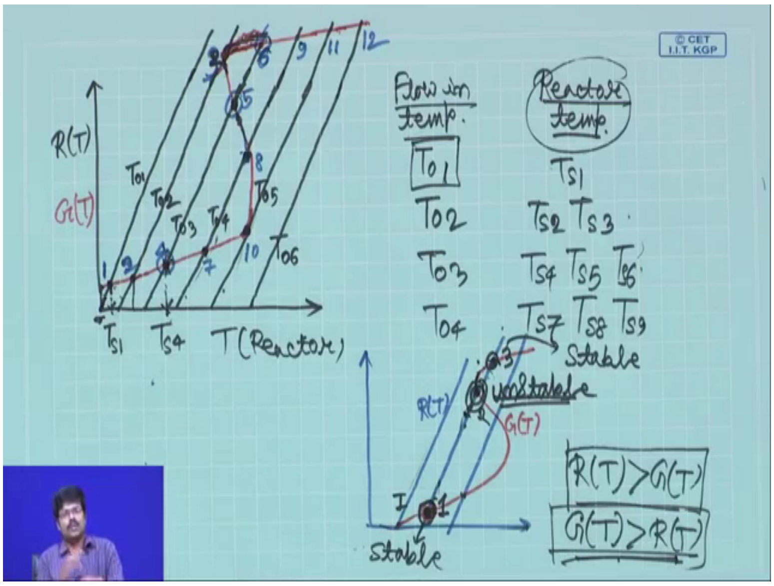

Flow in temp.	Reactor temp.
T_{01}	T_{S1}
T_{02}	T_{S2} T_{S3}
T_{03}	T_{S4} T_{S5} T_{S6}
T_{04}	T_{S7} T_{S8} T_{S9}

$R(T) > G(T)$

$G(T) > R(T)$

Let us now draw very carefully a graph where I will plot R T in the black and G T in the red. So, your R T is something like this. So, several values of R T are possible I mean several lines like this because as you keep changing the temperature you can get this kind of lines this is with increasing T 0.

Now, let us draw the curve of G T a very specific way am trying to draw this, I will draw this first and then I will explain to you, let it go like this. So, because this is not to scale, so, I just want to do it like this, now this curve. So, you know this is the G T curve that crosses this R T lines these are at different inlet temperatures now if you see the first line it is crossed at only point.

So, let us say it is point 1. So, there is only one steady state for the first line for the second line, I am again taking the wrong pen excuse me. So, for the second line it crosses the second line this is the second line it crosses the second line at point 2. In fact, it is better that we tell this point as point 2 because it crosses first and this point as point 3. So, basically for the second R T line your G T will cross it 2 times so; that means, for the second R T line you have 2 steady state points which is point 2 and point 3. So, for the third R T line this is R T line for the third R T line. So, this is point 3, now this is point 4 all right and this is point 5. Let us draw this graph like this because let us draw the graph like this I will come to that after.

So, this is point 5. 4, 5 and then you have a point which is point 6. So, basically this R T this R T line and the G T line they intersect at 3 points 4, 5, 6. What about the fourth R T line? It is intersect at point 7 at point 8 somewhere here let us say at point 8 this is point 6 at point 8 and at point 9 and as per as 1, 2, 3, 4, 5, let us go to the fifth line the fifth line there is an intersection point with the red line which is G T for fifth line let us say this is tenth point and again it intersects at eleventh point and then for sixth line there is only one intersection point, it is 12.

So, you see that depending on where this line of R T is which is also being determined by the value of T c and T 0, coolant your heat transfer fluid temperature and the temperature of your inlet, your line will change and then either you make it only one steady state you might also get 2 state steady state or you might get 3 steady state typically you would not get more than 3 steady states. So, then I can also draw a table like this. So, these are at different flow in temperatures. So, this is temperature; reactor temperature and let us say these particular graph is at a flow in temperature of T 01 this particular graph is at a flow in temperature of T 02 this is the T 03 this is T 04, T 05 and T 06.

So, we can have a table like this. So, you have a flow in temperature; that means, the temperature T inlet whatever feed is there what is the temperature of that feed. So, this is a flow in temperature and corresponding to that flow in temperature there will be a steady state condition given by the temperature of the reactor, which means let us say you talk about this particular operating condition. So, where the flow in temperature is T 01 you see this line this line is generated when the flow rate in temperature is T 01 and this line is being cut by this red line which is for the heat rate of heat generation at point 1.

So, what is the temperature of this corresponding to point 1 for the reactor temperature? So, this is the reactor temperature, at what temperature does this point correspond to as per as reactor temperature is concern let us say that is T S 1 because that is steady state you know this point is a steady state point. So, what is the temperature corresponding to that steady state point of the reactor? This is the temperature of the reactor. So, that is T S1, S designates steady state. So, for the flow in temperature T 01 the corresponding reactor temperature that has to be attained for the attaining the steady states is T S1.

So, for T 02, it is this line. So, you have basically for T 02 you have basically two temperatures at which the reactor can attain steady state. So, those are T S2 and T S3 and correspondingly for T 03 this is T 03, there are three temperatures corresponding temperatures on the x axis at which the steady state can be attained. So, that will be T S4, T S5, T S6 that is why I have drawn the you know I have marked the points like that 4, 5, 6 and for correspondingly for T 04, the flow in temperature will generate this value of R T this curve of R T. So, for that there are basically again three steady states point 7, point 8 and point 9 and the corresponding temperatures of reactor let us say T S7, T S8 and T S9. So, like these you can go on.

So, if you have constructed this particular graph, both the sides because you know this is steady state equation and if your plotting this as a function of temperature then you get your plotting this part then you are getting this red line your plotting this point then you are getting this line depending on where the temperature is this T prime if you change this T prime which is basically a combination it has both T c and T 0; T c is the temperature of the heat transfer fluid, T 0 is the temperature of at inlet if you change that then you can get basically your heat transfer lines different heat transfer for lines.

So, at what point you will operate at what temperature the reactor you will operate that will also then depend on the temperature of the inlet as well as the temperature of the coolant or the heat transfer fluid and corresponding that will be designated by say for example, if you are trying to operate at 4, this is a steady state situation you will trying to operate at point 4, so, in that case you should be on these line.

So, you have to take the value of T 0 that is the inlet temperature as well as the heat transfer fluid those temperature values you have to take corresponding to this line, firstly and, secondly, if you have to operate at this point, your reactor temperature should be this temperature and that temperature is T S4, S indicating your steady state. So, that is why these are.

So, if your operating at flow in temperature of T 03 you have basically three different temperatures at which you can operate the reactor. At all these three temperature the system will be in steady state that is the idea of this particular graph. Now, if you look at it in some more detail; for example, if you are looking at say I will draw the graph in a slightly more elaborate way. I will use the blue pen for these. So, let us look at this graph let us say this is your R T and let us say this is your G T. Now, this is one particular line for the R T which corresponds to a particular T 0 values and T c value you can have another line like this you can have different lines like this.

So, you can have a line like this, so on and so forth. Now, let us say we consider this particular line. So, we have basically three steady states if you are considering this particular line you have three steady states corresponding to that let me use the black pen for this. So, corresponding to this value of this line of R T you have three steady states. So, point 1, point 2 and point 3. Now, let us look at the steady state of one when you are at this particular point your rate of heat transfer rate of heat removal is equal to the rate of heat generation.

Now, let us destabilize the system little bit let us increase the temperature of the reactors very slightly. So, if the temperature of the reactor increases this x axis is the reactor temperature. So, then the then you will move somewhere on this direction the moment you move in this direction, what will happen? Your rate curve is basically below the blue curve. So, once you have come to this equation here basically your at that point your R T is greater than G T rate of heat removal is higher than the rate of heat generation.

So, that would mean the reactor when immediately cool off. So, if you have heated slightly the reactor will immediately cool off and it will go back to this steady state, because once you have com come to this situation your R T is basically higher than your G T if you come to this sight you will see your R T is greater than G T. Now, what happens if you are at point one and if you cool down slightly if you come slightly on this side? Now, your red curve is at a higher position then your blue curve that means, if you have come slightly to the left your G T is higher than R T that means, rate of heat generation is higher than that of heat removal.

So, that means, the reactor will heat off, heat up. So, under this condition when the reactor will heat up and you will come back to this point one, that means, this is a stable steady state you slightly disturb on this side or that side it will come back to it is position this is a stable steady state. So, what happens at steady state three? You will have a same conclusion you heat up little bit now the heating curve now heat generation curve is at a lower position then the heat removal curve which is blue curve; so, that means, now reactor will cool out and it will come back to this point.

If you cool down little bit then from this point you come to this side little bit once you have come to this is little bit your rate curve is basically higher at a higher position than a blue club blue curve; that means, your rate of heat generation is higher than rate of heat removal. So, your reactor will heat up and it will come back to this position. So, this position this point is also a stable steady state. What about this point? If you are at this particular point and if you are say if you heat up the system little bit, then what will happen? You will come to this position little bit here.

So, if you are coming to this position say you are you have this particular curve here and let me elaborate further. So, this point is a stable steady state point this point is also a stable steady state point. So, what will happen? If you have this particular point here if you are little bit off from this point, say, you heat the system up a little bit it has to go to a stable steady state ultimately right. If you heat the system up a little bit what you will what you get here if you heat the system up a little bit you are going. So, if from these point to this side, if you go from this point to this side your heating curve is basically at a higher point than your cooling curve.

So, if you heat up slightly what will happen the reactor will spontaneously heat up further and it will go to this point because once you have come to this position little bit your blue curve is basically lower than the red curve. So, if you heat up the reactor will heat up further because the rate of heat generation is higher G T is higher than RT.

So, if you spontaneously heat up, it will come to this particular point. Now, what happens if you cool down this system a little bit if you cool down this system a little bit, say you come to this position somewhere here you cool down the system little bit you come to this position somewhere here, what will happen? Your blue curve is now at a higher position then your red curve.

So, basically your rate of cooling or rate of heat removal is higher than the rate of heat generation. So, it will then spontaneously cool off further and it will go to this particular point. So, ultimately, that means, this particular steady state that you have is an unstable steady state. It is an unstable steady state. So, if you heat up little bit it goes to the higher steady state, if you cool down little bit then it goes to the lower steady state. So, when you have these kind of three steady states typically, what you will get is the higher steady state and the lower steady state will be stable and the middle steady state will be unstable and very frequently at lower state your conversion is very small at the higher steady state your conversion is quite high in the middle range you will typically have to work sometimes, because although this curve is accelerated many time the temperature of the higher steady state is much at a higher value much higher value.

So, it is difficult to control. So, maybe you want to work in the middle steady state, but you have to be very careful. So, have not to disturb it otherwise it will go away from this unstable steady state. So, what we will do is we will stop here and we will continue to discuss this situation little bit further in the next class till then

Thank you and good bye.