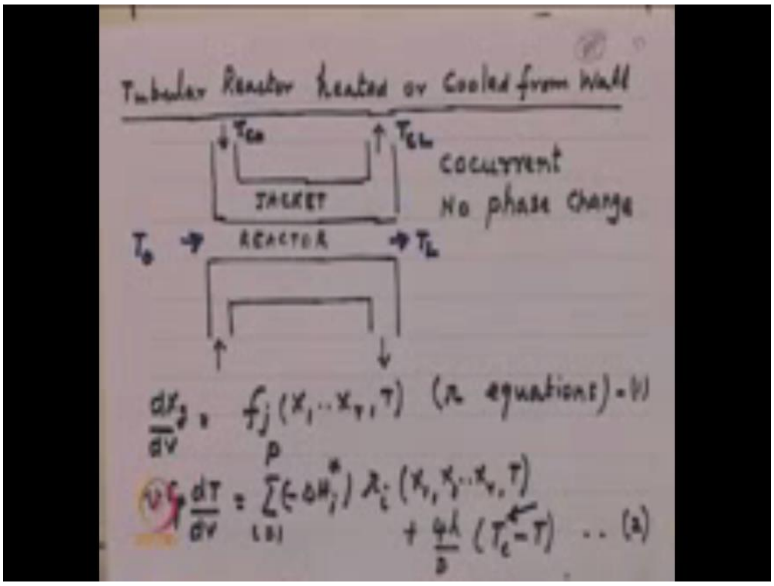
Advanced Chemical Reaction Engineering
Prof. H. S. Shankar
Department of Chemical Engineering
Indian Institute of Technology, Bombay

Lecture - 22
Energy Balance VI: 1) Tubular Reactor Heated/Cooled from Wall 2) Transient Behavior of CSTR

Today, we look at tubular reactors heated and cooled from wall.

(Refer Slide Time: 00:26)



Tubular Reactor heated or Cooled from Wall

cocurrent
No phase change

$$\frac{dx_j}{dV} = f_j(x_1 .. x_r, T) \quad (r \text{ equations}) \quad .. (1)$$

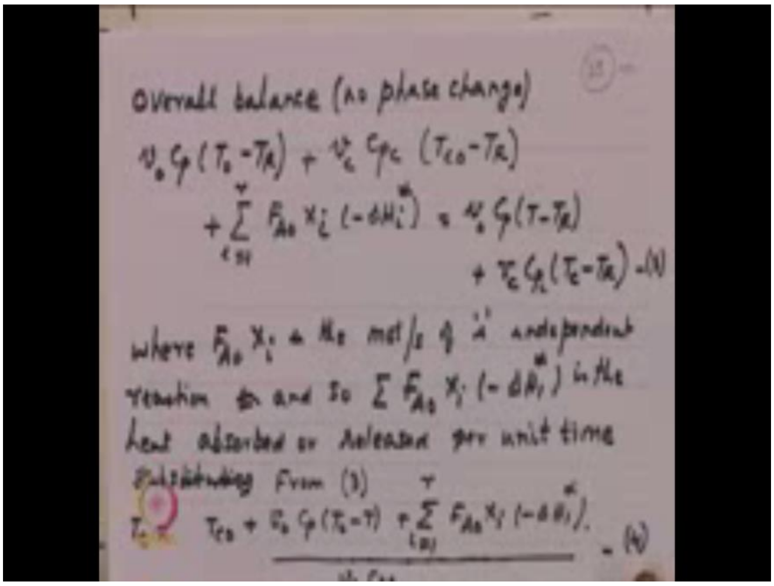
$$v\rho \frac{dT}{dV} = \sum_{i=1}^{P} (-\Delta H_i^*)\, r_i (x_1, x_2 .. x_r, T) + \frac{4U}{D}(T_c - T) \quad .. (2)$$

Now, we know our tubular reactor equation looks like this so, Q is heater mole for unit volume. And we represent this in this form r i this goes from i equal to 1 to P there are P rate processes. So, delta H s star is the enthalpy change for reactions for a pipe our equation looks like this where T c is the temperature of the cooling fluid. This is the reactor this is the jacket, jacket is a T c the reactor is T. Therefore, this heat transfer is this is the heat transfer and if it is cooling it will be negative so, T will greater than T c. So, if you have to integrate this we need to replace this T c appropriately so that we can integrate this equation. So, how do we do this?

So, this is the case we want to consider in this lecture. So, let us look at the situation in some detail. So, we have here a representation of a tubular reactor cooled form the jacket. And you have a cooling fluid entering at T c 0 and going at T c shall we say T c l. And then you have the reactor in which fluids are entering at t naught and living at T l the flow is co-current as you can see both are co-current. And there is no face change is the, we are assuming the situation why the face change is a not they so, how does our equation look like? Now, we have this methyl balance equation which you have written number of times in the fast it looks like d by d B of x J where J is the extent of reaction in the different independent reaction. There are r such reactions such you have to consider so, the right hand side becomes f J which is the function determines variation of x s which respect to temperature in the equipment. This we know how to get? We have done this before.

Now, the energy balance equation for the case of no phase change it looks like v C p d T d v this C p is volumetric specific heat and v is the volumetric equipment and sigma i equal to 1 to P. There are P rate processes r i is the intensive rate of the different reaction 1 to P and 4 H by d times t minus T c. This is the equation which want to handle if you want to integrate this r plus 1 equations. We must handle know how to manage replace T c in terms of capital T and x 1 x 2 to x r so, that is what we would like to do know. Now, to do this what we recognize is that since there is no phase change.

(Refer Slide Time: 04:03)



Overall balance (no phase change)

$$v_0 C_p (T_0 - T_R) + v_c C_{pc} (T_{c0} - T_R) + \sum_{i=1}^{r} F_{A0} x_i (-\Delta H_i^*) = v_0 C_p (T - T_R) + v_c C_{pc} (T_c - T_R) \quad -(1)$$

where $F_{A0} x_i$ = the mol/s of 'i' independent reaction and so $\sum F_{A0} x_i (-\Delta H_i^*)$ is the heat absorbed or released per unit time

Substituting from (1)

$$T_c = \frac{T_{c0} + v_0 C_p (T_0 - T) + \sum_{i=1}^{r} F_{A0} x_i (-\Delta H_i^*)}{} \quad -(2)$$

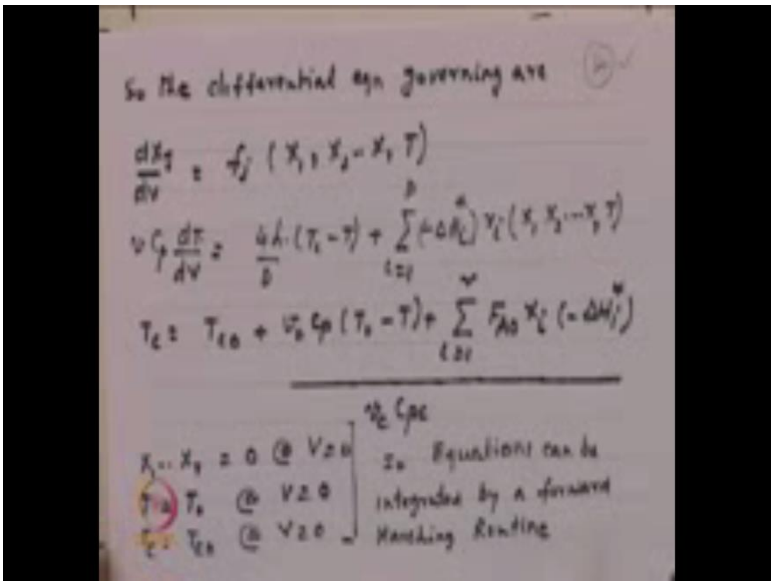
We can write what is called as an overall balance which says this is t naught is the entry with the, this is the energy that is coming to the fluids that is entering so, this is v naught all right. So, we call this as v c this is volumetric flow at the inlet v naught in v c. So, we have v naught times C p multiplied by t naught minus of T r. So, this is the energy that is coming in with the reagence and v naught v c times C p c multiplied by T c naught minus of t this is the energy that is coming with the cooling fluid. So, at any position suppose we take any position here any position here and then we can write the balance up to that position. So, what is the energy that is released by the chemical reaction i equal 1 to r F A naught x i multiplied by delta H i star. So, what is this? What we are doing is that we are looking at between position 0 and position. Any position say how much is the energy there is coming in with the reacting regence? How much is the energy there is coming in with the cooling fluid? And how much is the energy there is release by the chemical reaction in this equipment?

So, that is what this is term F A 0 x i minus delta H i. So, is this plus this is a total amount of energy this is coming in so, how much of energy is going out? The going out stream as you can see here the going out stream both the streams are going out here this is the going out stream going out stream. So, the temperature here is T c temperature here is t. Therefore, the going out stream goes out with v naught C p t minus of T r assuming the C p is the same for the inlet fluid in the, at any position. So, this is the energy that is that is taken by the re agence and v c C p c multiplied by T c minus of T r. This is the energy that is taken up by the cooling fluid or heating fluid. So, this is the energy out so, we have energy in and energy out so, statement of energy balance is that is energy conservation therefore, what comes in what go out?

Now, what is being said here is that F A naught x i is in the terms of mole per second in the i-th independent reaction. And there are r independent reaction there are looking at i equal to 1 to r Now, you also recognize that as for the first law conversion, we are looking at first law convention which me the energy is going from the cooling fluid in to the heating fluid. That is the first law convention so if T c is less than t this becomes negative. So, it does not change the form of the equations all these equations will stand whether delta H i is negative or positive it does not matter appropriately the temperature will adjust themselves. Now, having said this if you look at this is equation 3 from equation 3 you can easily find out what is temperature T c at any position simply by rearranging all these equations.

You can find temperature T c at any position which is simply T c 0 plus these term v naught C p t naught minus of t sigma. What is the heat generation or release divided by this C p c? In other words what we are saying now is that by writing the overall balance we have been able to find out what is T c in terms of variables which is in our differential equation. Our differential equation involves x 1 to x J x 1 to x r and temperature t there r plus 1 variable here and this T c what you have done by this overall balance. We have replace in terms of quantity is we know and quantity is we do not know which is t and x i going from 1 to r. And other words, we are now able to replace T c in equation 2 in equation 2 in terms of capital t and capital x 1 to x r. And therefore, all the equations 1 2 r equations and so r plus 1 equations the left hand side which involves derivative involves x 1 x 2 to x r and t. And the right hand side involves functions with dependents on x 1 to x r and temperature that T c has now been removed, because of this relationship. So, these makes it possible for us to do what is called as forward integration. Now, we have virtue of this relationship of this relationship.

(Refer Slide Time: 08:17)



So the differential eqn governing are

$$\frac{dX_j}{dV} = f_j(X_1, X_2 \ldots X_r, T)$$

$$v C_p \frac{dT}{dV} = \frac{4h}{D}(T_c - T) + \sum_{i=1}^{r} (-\Delta H_i) r_i(X_1, X_2 \ldots X_r, T)$$

$$T_c = T_{c0} + \frac{v_0 C_p (T_0 - T) + \sum_{i=1}^{r} F_{A0} X_i (-\Delta H_i)}{v_c C_{pc}}$$

$X_1 \ldots X_r = 0$ @ $V = 0$

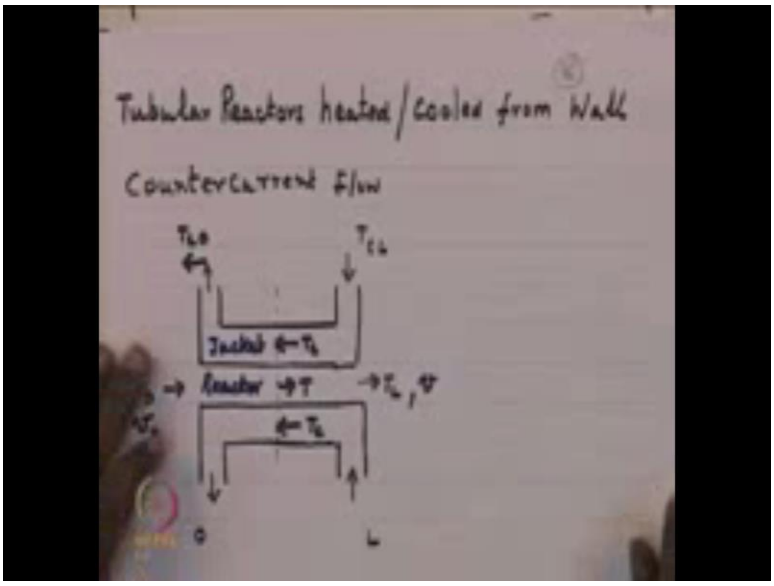
$T = T_0$ @ $V = 0$

$T_c = T_{c0}$ @ $V = 0$

So Equations can be integrated by a forward Marching Routine

T c equal to what we have written down just now we are now able to integrate this forward, because x 1 to x r is 0 at v equal to 0. That means at the entrance to the reactor all the x’s are 0 and then t equal to T c that means v have fully specified the initial state of x 1 to x r and t. And therefore, the right hand side that means we can calculate the right hand side at t at the entrance. Therefore, we can do forward marsh and then so all these equations using well known techniques of integration of these equations. So, this is this general procedure that is adopted to take care of the effect of the jacket fluid on the reactor performance. Let us look at the second case, the second case of tubular reactor heated and cool from the wall is.

(Refer Slide Time: 09:09)

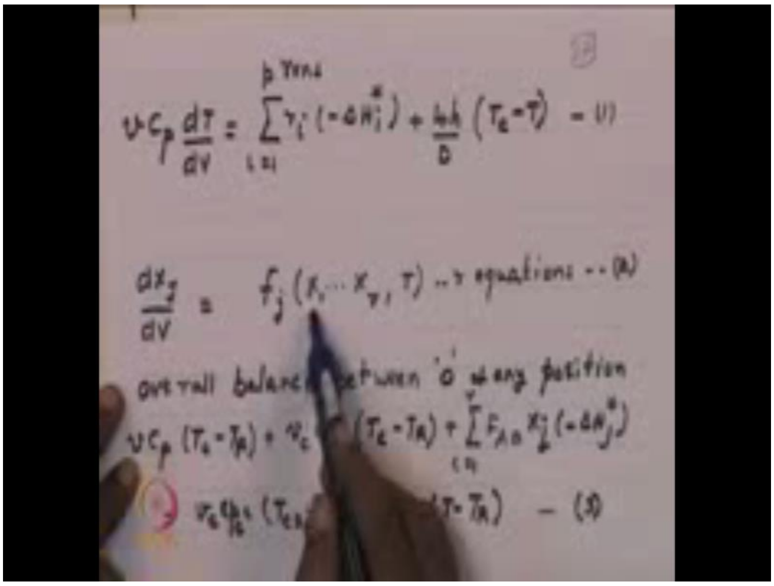


Tubular Reactors heated/cooled from Wall

Countercurrent flow

You have feed entering the reactor this is the reactor so this is the jacket as you can see here fluid enters at T 0 and v naught goes out at v and T l and fluid is entering at T c l and leaving at T c 0. So, this is the familiar counter current k which we must now learn to deal with. Once again let us recognize let us recognize that our equations are that.

(Refer Slide Time: 09:45)



$$v C_p \frac{dT}{dV} = \sum_{i=1}^{p\ \text{rxns}} r_i(-\Delta H_i^*) + \frac{4h}{D}(T_c - T) \quad - (1)$$

$$\frac{dx_j}{dV} = f_j(x_1 \cdots x_r, T) \quad .. r \text{ equations} \; -- (2)$$

overall balance between '0' & any position

$$v C_p (T_0 - T_R) + v_c \ldots (T_c - T_R) + \sum_{i=1}^{r} F_{A0} x_j (-\Delta H_j^*)$$

$$= v_c C_{pc} (T_{c0} \ldots (T - T_R) \quad - (3)$$

You have r d x d x J by d v equal to f J x 1 to x r there r such equations. And then you have the energy balance v C p d T d v equal to sigma i equal to 1 to P r i minus delta H i. This is the reaction term and 4 H by d T c minus of t; this is the heat transfer from the cooling fluid or heating fluid in to the reactor equipment; this is by first law convention heating of the control volume is taken as a positive. So, if that means T c minus of T if T c is less than t this will be appropriately negative sign showing that the heat flows from the reactor into the cooling fluid. So, depending upon the direction of transfer the signs take care themselves. Therefore, there is no problem here now how do we solve the equation 1 and 2? Now, that T c is T c is coming from this counter current relationships which we have to appropriately account for this what we do is once again the same procedure we will write the energy balance.

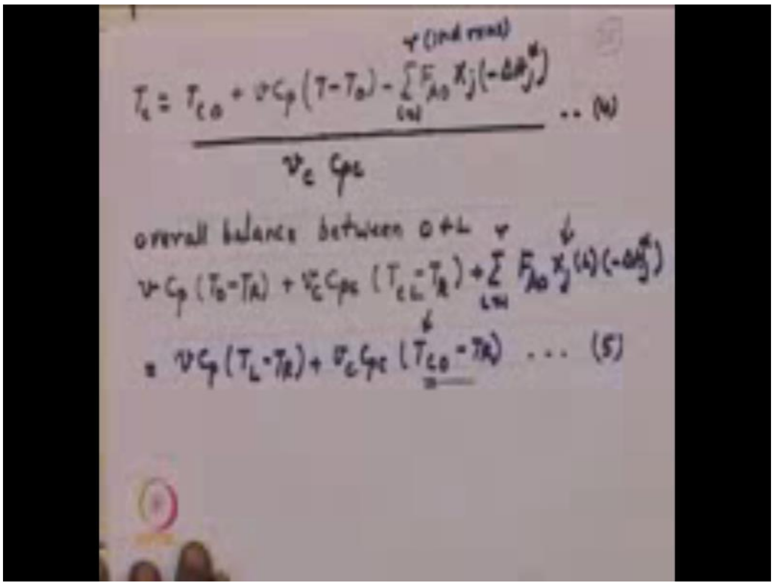
So, we done here overall balance between 0 and any position so you have position 0 this is position 0 and any position here. So, what are inputs? What are the outputs? We can see here the inputs are coming from the regence and coming from cooling fluid or heating fluid. So, you have 2 inputs coming here that 2 outputs regence here and regence here this is what we have to appropriately count for that is what I have done. So, v C p so, we can show v C p t naught minus of t we should be put naught here v naught C p so v naught C p t naught minus of T is a regence entry. Once again no phase changes assume similarly, we have what is the energy that is coming in? Because of the cooling fluid or heating fluid at position any position.

So, that is that is written as v c c P c T c minus of T r. So, you have this input coming from the regence you have the input coming from the energy input coming from the heating or cooling fluid and now between i equal to 1 to r we can see going from 0 to position any position. So, in that position we would had reaction 1 to r independent reactions this taken as. Therefore, we some over i equal to 1 to r F A 0 x J multiplied by delta x J this shows the heat released are absorb depending upon whether delta x positive or negative. So, the left hand side represents 3 terms; term 1 is what happens to the reagents the energy picked up by the reagents; term 2 is energy picked up by the heating or cooling fluid.

Third is the energy release by the chemical reaction there was this much v equal to the leaving stream what are the living streams living streams are T c 0. So, v c C p c multiplied by T c 0 minus of T r so, this is the energy there is in the living stream and then we have the other living stream is the reagents which is v C p multiplied by t minus of T r. So, we have energy in equal to energy out same statement of energy balance. Now, let see what this gives us so by appropriately re arranging we can get what is T c.

After all we need to replace this T c in the whole idea is here that get rate of this T c. So that we can integrate so that is what we are trying to do here also we replacing this T c from equation 3. So, by rearranging this you can get T c in terms of others which is what I have done here.

(Refer Slide Time: 13:05)



$$T_c = \frac{T_{c0} + v C_p (T - T_0) - \sum_{i=1}^{r\,(\text{ind rxns})} F_{A0} X_j (-\Delta H_j^{*})}{v_c C_{pc}} \quad \ldots (4)$$

overall balance between 0 + L

$$v C_p (T_0 - T_R) + v_c C_{pc} (T_{cL} - T_R) + \sum_{i=1}^{r} F_{A0} X_j(L) (-\Delta H_j^{*})$$

$$= v C_p (T_L - T_R) + v_c C_{pc} (\underline{T_{c0}} - T_R) \quad \ldots (5)$$

You can see what I have done here is that I have put T c in terms of others T c 0 I mean you can look at this perhaps understand what I have done see can see here. So, from this equation I get T c replace and rearrange this and find T c what I have done here? We need do that manipulation you get T c in terms of others T c 0 T 0 temperature at any position and F A 0 i equal to 1 to r independently. Actually this r is independent reaction all right now that we know T c. So, it is now possible for us to replace in this equation 1 this relationship; this relationship can be replace in to equation 1 and once we do that.

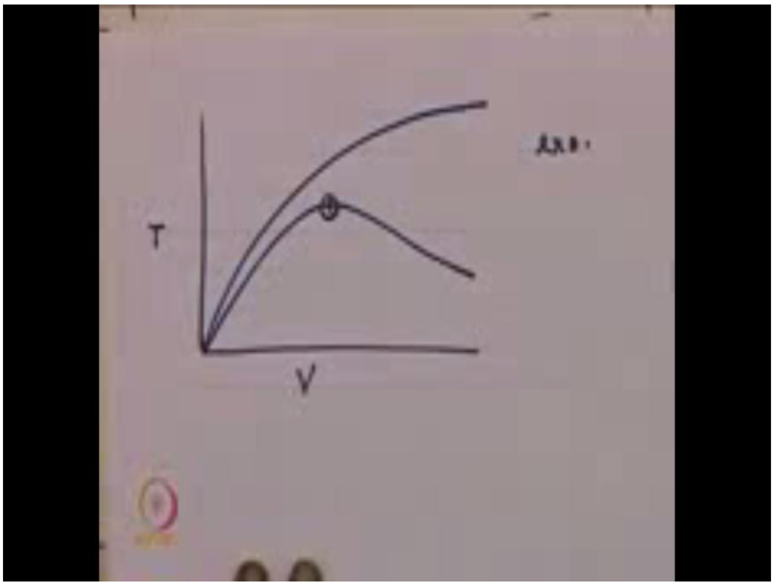
So, we find that you have this r plus 1 differential equation the right hand side involves terms that you know all the terms that you know x 1 to x r x 1 is 0 x r is 0 at t equal to 0 at the inlet. Now, only thing that you do not know in this integration is T c 0 or in other words when we want to integrate this r plus 1 equations by replacing T c from equation 4 into equation 1. The integration now becomes possible, because you know what is x 1 to x r initially they are all 0 you also know what is t equal to t 0 at the inlet. Therefore, the right hand side involves terms that you know fully excepting T c 0, because out T c now involves T c 0. So, in other words what we are now saying is that to be able to integrate this equations 1 to r r plus 1 equations.

We have to assume a value of T c 0 once you assume T c 0 now you can integrate and then complete the exercise. Now, the question is how do you know, how whether this assumption that you have made is right or wrong? Not to be able to take care of that what we do is that we do what is called as a overall balance. That means we look at overall balance between position 0 and position l we do a overall between position 0 and position l. Once again overall balance is what is the energy coming in what is the energy going out, but it is between position 0 and position l. Now, that means see v C p t naught this is what the energy coming in v C p c T c l. This is the energy coming in i equal to 1 to r F A 0 x J is a energy coming in notice here this x J refers x J at l. And then the output streams are v C p the the reagents stream output and then you have the coolant stream, but the going out stream the temperature is T c naught.

So, what have done now? We have now by assuming T c 0 we have integrated equations 1 and 2. Then at the end of the integration what we get we will get the value of x 1 to x r at every position including at position l. Similarly, you will get temperature at every position including at position l. Or in other words u from this in this equation you know all the numbers T c l you know from your integration x l x 1 to x r at position l you know from your integration. Therefore, everything that is here in known from your integrations therefore, if the assumption of T c 0 was correct equation 5 would be satisfied. Therefore, what we do is that we perform the integration determine the numbers x 1 to x r and t at every position including the n point. Then we come back to equation 5 to check whether our assumption of T c 0 is right or wrong if it turns out then it is incorrect. Then this equality will not hold then we know that we have a bad assumption. And therefore, we have to reset our assumptions.

Now, the question is how do you reset you assumptions correctly every time you make? So, this is something that comes by experience and you will have to move the assumption assume value of T c 0 in the right direction so that you answers converge. So, experience will tell you how to move that T c 0 assumptions iteration to iteration. So, what we are try to do in this exercise of tubular reactor heated or cooled from the wall is that we have been able to determine the positions and the temperatures the compositions. The extent of reaction for all the independent reactions at every position including the end points whether it is co current whether it is counter current it does not matter. Because the procedure tells you how to handle this having said this there are few points that we might like to recognize that is why are we heating or cooling a fluid. We are heating or cooling, because the reactor the catalyst perhaps which is inside the reactor requires that the temperature must be appropriately regulated or the temperatures must be appropriate to the reaction that you are carrying out. Now, frequently what may be of concerned to all of us is that the temperature let me just make a small plot.

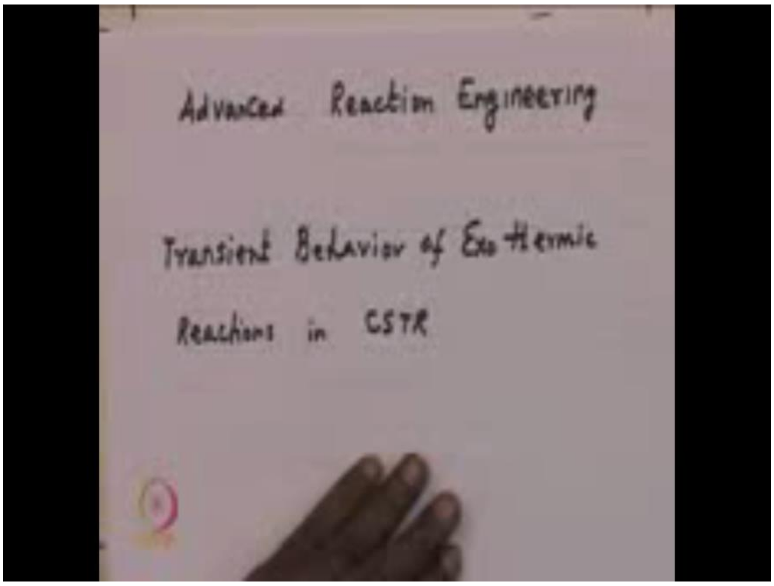
(Refer Slide Time: 18:05)



If this is volume versus temperature so, if you had an adiabatic reactor the temperature keeps on increasing this is exothermic reaction. If it is cooled from the wall you will find there is a cooling that means there is a point of maxima in reaction rate m maxima in temperature in the reaction equipment frequently. This hotspot it is called hotspot temperature is a specification on the catalyst that we will engage. Now, is the specification of the temperature maximum temperature is the catalyst is able to perform is given to you our design of the system must ensure the, this temperature is never exceeded. And it is that interest that we lined try and look at all the simulations to see how best we can adjust this term.

So, that the maxima in this temperature is well within what is specified. So, our simulations by an large are towards ensuring that our system performs as expected. And towards to do that we adjust our process to ensure that this T c is so chosen that our temperature are maximum temperature are well within what is specified. So, trying to understand how to manage the hotspot temperature is one of the important issues that try to do in our design. And more importantly we ensure that this temperature is not exceeded in our process computation. So, I am said this you will go on to the next item of our interest which is. So, our next topic of interest is we want to look at we want to look at we want to look at.

(Refer Slide Time: 20:05)

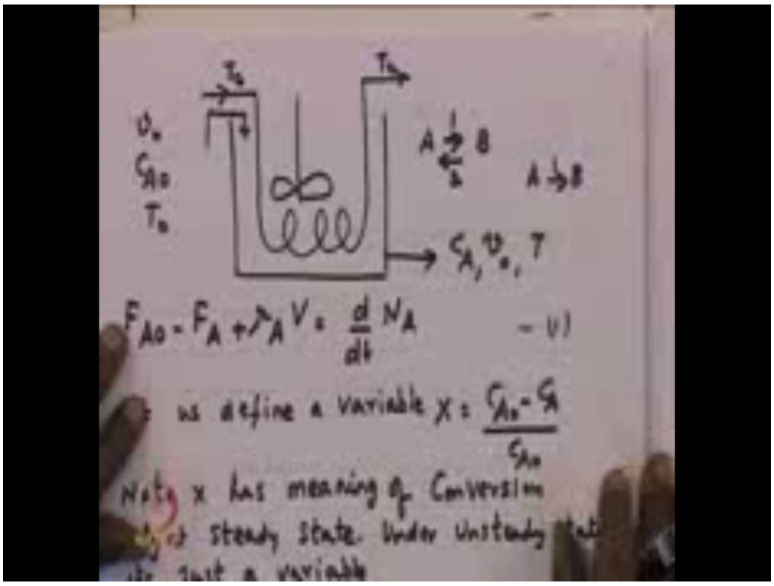


Advanced Reaction Engineering

Transient Behavior of Exothermic Reactions in CSTR

This whole issue of transient behavior of exothermic stirred tank. Now, stirred tanks are very common devices particularly in small scales and but the interested thing about stirred tanks. That it brings out very interesting features of the reaction which were able to use effectively in our design of even other types of reactors. So, that is the object of trying to look at exothermic stirred tanks.

(Refer Slide Time: 20:30)



$$F_{A0} - F_A + r_A V = \frac{d}{dt} N_A \qquad -(1)$$

us define a variable $x = \frac{C_{A0} - C_A}{C_{A0}}$

Note x has meaning of Conversion at steady state. Under unsteady state it is just a variable

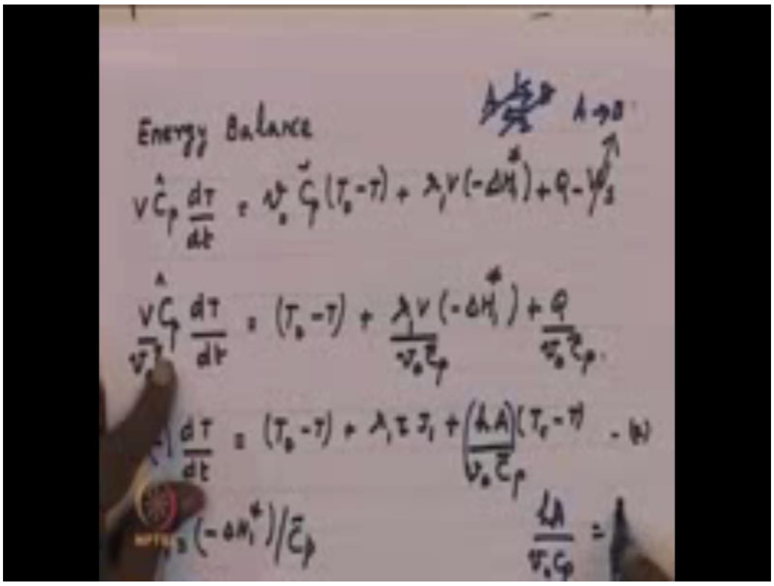
Now, what is our system? Here we want to look at this system in a very simple systems of that in all the issues are fairly understood. So, we have a tank which is well stirred there is cooling coil through which a coolant circulates and the, this is circulation of this coolant let us say is very large. So, that the temperature of the coolant coming in and the temperature of the coolant going out is not very different. So, that T c inlet could be T c at the exit. This need not be, but it is in assumption that we may exist to may cover mathematic is little simple to handle.

So, you have a reaction a going B we are only looking at case of single independent reactions when there are more reactions. Of course, there are more features which we are not going to consider. Now, there is a single independent reaction which means that even if there is reaction which is reversible like this. This analysis is quite satisfactory by we will by a large be looking at 1 reaction a going to B a going to B single independent in we just look at a simple situation. So, our statement of material balance is what, what is coming in F A 0? What is going out? What is the rate of generation equal to the accumulation?

So, this statement of energy material balance we can write in various ways, but for this case of trying to understand unsteady behavior of a stirred tank. We have written this in the form of variable x which is defined as C A 0 minus of C A divided by C A 0. Now, this definition of x commonly done and it is has a meaning of conversion whenever you operate the process at steady state. When the process is not at steady state then the x does not take the meaning of conversion. Therefore, it should be treated as a variable whose definition given by x equal to C A 0 minus of C A by C A 0 we on that. No other meaning can be attached in the unsteady state so, we have a variable x which is define this way.

And therefore, we can replace this equation 1 appropriately in terms of x this is what I have done. So, replacing F A 0 as v 0 C A 0 F A as v 0 c v v equal to v 0 is assumed assuming that there is no volume in volume change do the reaction this is a to B there is no volume change anyway. So, this is satisfactory representation now the right hand side right hand side d by d T of N A what N A is simply v times C A. Therefore, since there is no volume change since our reactor volume does not change therefore, v can be taken out of the derivative.

(Refer Slide Time: 23:06)



Energy Balance

A → B

$$v\hat{C}_p \frac{dT}{dt} = v_0 \hat{C}_p (T_0 - T) + r_1 v(-\Delta H_1^*) + Q - W_s$$

$$\frac{v\hat{C}_p}{v_0 \hat{C}_p} \frac{dT}{dt} = (T_0 - T) + \frac{r_1 v(-\Delta H_1^*)}{v_0 \hat{C}_p} + \frac{Q}{v_0 \hat{C}_p}$$

$$\tau \frac{dT}{dt} = (T_0 - T) + r_1 \tau J_1 + \left(\frac{hA}{v_0 \hat{C}_p}\right)(T_c - T) \quad - (4)$$

$$J_1 = (-\Delta H_1^*)/\hat{C}_p \qquad \frac{hA}{v_0 \hat{C}_p} =$$

Therefore, we write the equation this is 4. Now, we notice that the term r A the term r A is replaced with r 1 with a minus sign. That is because our rate of formation a this is the reaction a going to B our rate of formational a rate of is a equal to minus 1 times r 1 where r 1 is intensive velocity of the reaction minus sign is put, because a is reactor. So, we have r A is minus of r 1 volume of system is constant v equal to v 0 is assumed. With all these assumptions this equation becomes something like this we can very easy to notice this.

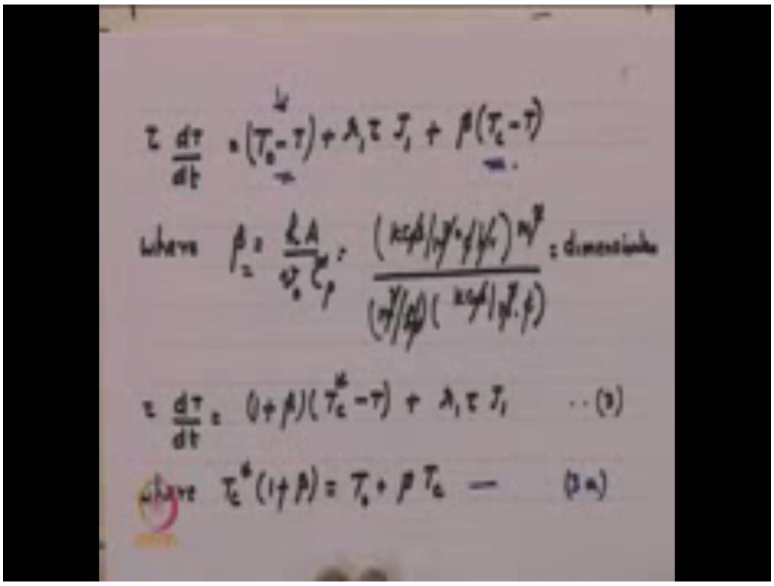
So, it divide throw out by v 0 it divide throughout by v 0 v equal to v 0. Therefore, this goes away and becomes v by v 0 equal to tau v by v 0 which is equal to tau. So, this is equation becomes minus of tau d x d T is x minus of r 1 tau by c 0 or equation 1. This is final representation of the material balance equation for a stirred tank it says d by d T of x multiplied by tau is minus of x plus r 1 by C A 0 times tau. And this something that we know this is not mu to us you have been doing this for a long time, but in this form there are certain advantages. So, we want to retain it this form now what is our energy balance our energy balance we have written many times. So, I am writing it again which says this is single reaction.

So, the left hand side is v C p d T d t and the right hand side is first term is v naught C p t naught minus of t and. Then the reaction heat generation term in this cases r 1 v minus delta H 1 star and Q is the heat inputs and w is heat work out put which is taken as 0. Each of this terms I have not explain it again because you have done it so many times. So, this is the accumulation of energy and this is the energy that is coming in from the fluids and it is getting heated from T naught to T. So, that is the energy picked by the fluids there is a entering in the system and this is energy that is release. Because of chemical reaction this term is the, is the intensive velocity it is only reaction we are taken. Therefore, it is only r 1 v minus of delta H 1 star Q is the heat added to the system as per first law convention.

Now, if there is if you had one independent reaction, but in other hand 2 rate process apposing in this case instead of r 1. It will become r 1 minus of r 2 something we have done in a earlier classes so, this is not something new. But in this case you are only looking at a single reaction A going to B n naught not this. Now, if we divide throughout by v naught C p c P is volumetric specific heat something that we know. So, if we divide throughout by v naught C p what we get v by v naught C p and then this is disappears here r 1 v v naught C p Q by v naught C p. Now, what I am done here v by v naught I have taken it as tau residence time. So, the left hand side is simply tau time d T d T. So, first term is t naught minus of t as can we seen here is the second term is r 1 tau and I did not this J delta H 1 star by C p as J 1 this is the convention that I mean using in the literature.

So, I am retaining that minus delta H 1 C p is J 1 there was this whole term become r 1 tau J 1. This term Q by v naught C p what is Q is the heat transfer. So, I have written it as a k H times k the heat transfer surface T c minus of t. So, this is the amount of heat that is transfer by the cooling or heating fluid to the reaction mixture h A by v naught C p multiplied by T c minus of t. So, it is sort of simply did appropriately so that it is convenient for us to deal with it in a certain way. So, equation 2 let me write equation 2, once again, but only here what I have done is that I have replace this whole term h A by h A by v naught C p v naught C p equal to beta I have just called it as beta.

(Refer Slide Time: 27:16)



$$\tau \frac{dT}{dt} = (T_0 - T) + \lambda_1 \tau T_1 + \beta (T_c - T)$$

where $\beta = \frac{hA}{v_0 C_p} =$ [illegible] : dimensionless

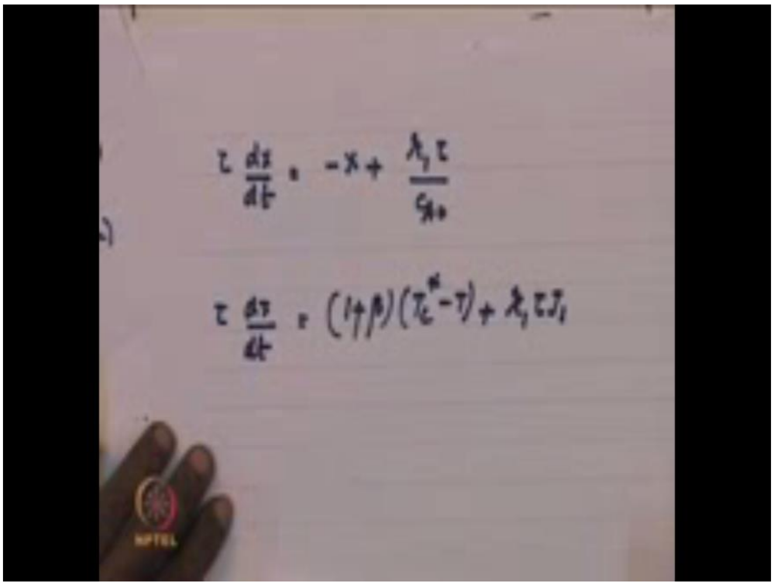
$$\tau \frac{dT}{dt} = (1+\beta)(T_c^* - T) + \lambda_1 \tau T_1 \quad \cdots (3)$$

where $T_c^*(1+\beta) = T_0 + \beta T_c$ — (3a)

So, this equation looks like this. In the literature the term beta which is H a by v naught C p put all the units you notice that it is dimension less so it is a dimension less parameter beta. So, I have replace it as beta here and now this is also a form of in our energy picked up or moved out and this is the energy there is. So, it is convenient to combine the first term and the second third term and literature does this in this form put this in the form of 1 plus beta T c star minus of t. That means T c star minus of t equal to t naught plus beta T c that is how it is written. So, that it looks like you know the whole term first on the third term looks in a more simple form 1 plus beta times T c star minus of t where T c star is define by this equation 3 there is a 3 a.

So, if you are given t naught beta and T c you can find out T c star, because you know all this. On other words t star is some kind of fictitious temperature which sort of enables us to combine equation the terms 1 and 3 in forms that is makes it convenient to to handle mathematically. So, what are we having our equation now is tau d T d t is 1 plus beta T c star minus of t plus r 1 tau J 1. So, this is the heat generation and in a sense this is the amount of heat that is removed. So, you can say that heat generation this is heat it is not heat it is reverse of heat removal. This is minus of heat removal there is just recall what we have done, what we have done is that we had our material balance equation which look like this we have the energy balance equation which looks like this. So, there are 2 equations describe our unsteady state which is tau d x d T is minus of x r 1 tau by C A 0 this is important to write this term, because it is. So, let me just write this term.

(Refer Slide Time: 29:22)

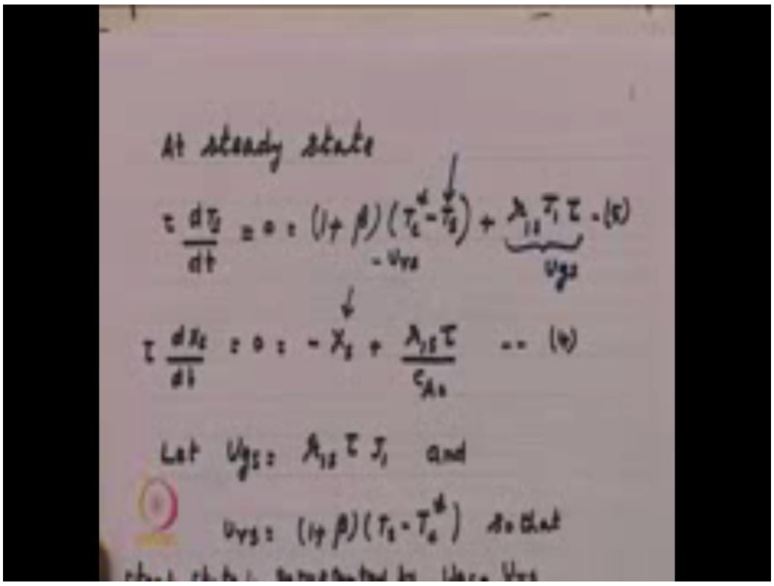


$$\tau \frac{dx}{dt} = -x + \frac{r_1 \tau}{C_{A0}}$$

$$\tau \frac{dT}{dt} = (1+\beta)(T_c^* - T) + r_1 \tau J_1$$

Our differential equations are tau d x d t equal to minus of x plus r 1 tau by C A 0. This is the material balance equation energy balance equation looks like this tau d t d t equal to 1 plus beta T c star minus of t plus r 1 tau J 1. So, there are two equations which will the govern, what happens to our process? Now, if I ask you what happens to this process at steady state? Now, clearly steady state means what the left hand side is 0; left hand side 0 means what?

(Refer Slide Time: 30:08)



At steady state

$$\tau \frac{dT_s}{dt} = 0 = \underbrace{(1+\beta)(T_c^{*} - T_s)}_{-U_{rs}} + \underbrace{A_{1s} T_1 \tau}_{U_{gs}} \quad \text{..(5)}$$

$$\tau \frac{dx_s}{dt} = 0 = -x_s + \frac{A_{1s}\tau}{C_{A0}} \quad \text{.. (4)}$$

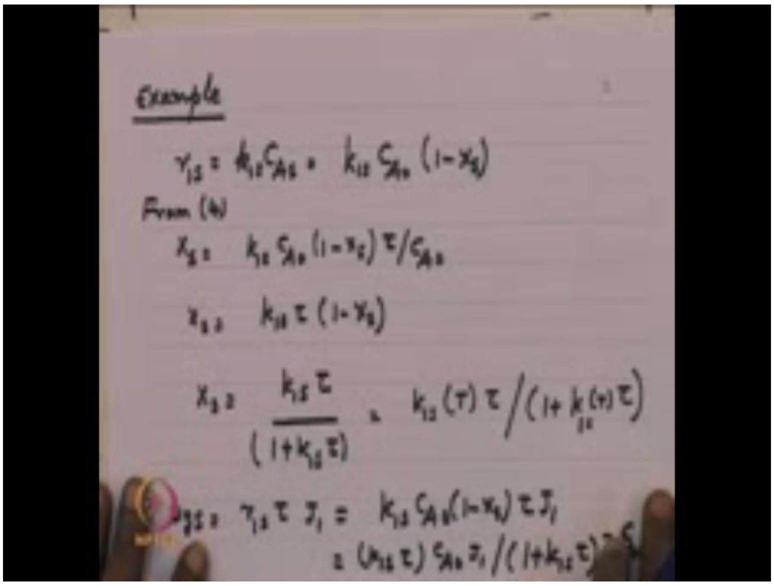
Let $U_{gs} = A_{1s} \tau T_1$ and

$U_{rs} = (1+\beta)(T_s - T_c^{*})$ so that

Left hand side 0 means that 1 plus beta T c star now, that is at steady state therefore, the temperature becomes t becomes T s r becomes r s. So that at steady state our equations these 2 equations can be written as 1 plus beta T c minus of T c star minus of T s which is steady state temperature. And similarly, tau d x s d T equal to 0 because steady state means 0 x becomes x s. Now, in this form it has a meaning of conversion now r 1 s is the rate of generation of rate of consumptions component a our rate of generation of component B whatever is r 1 s. Now, what meaning can be attached to this? The meaning we can attach to this is that it is rate of generation of heat so r 1 s A 1 tau.

We can call it as rate of generation of and then what is what is this term T c star minus of T s it is in a sense 1 plus beta if I put a put it as a reverse other words I call this as minus U r s I call this as U g s. Then this becomes rate of heat removal or in other words what we are trying to say is that what we are trying say is that this equation 5. Can we thought of this steady state can we thought of as 2 terms U g s equal to minus of U r s equal to 0 this is how we can look up on equation 5. U g s minus of U r s equal to 0 or steady state is describe as U g s equal to U r s. So, this is how we can understand steady state now, let us take a small example to understand how we can deal with all these things.

(Refer Slide Time: 31:53)



Example

$r_{1s} = k_{1s} C_{As} = k_{1s} C_{A0} (1 - x_s)$

From (4)

$x_s = k_{1s} C_{A0} (1 - x_s) \tau / C_{A0}$

$x_s = k_{1s} \tau (1 - x_s)$

$x_s = \frac{k_{1s}\tau}{(1 + k_{1s}\tau)} = k_{1s}(T) \tau / (1 + k_{1s}(T) \tau)$

$U_{gs} = r_{1s} \tau J_1 = k_{1s} C_{A0} (1 - x_s) \tau J_1$

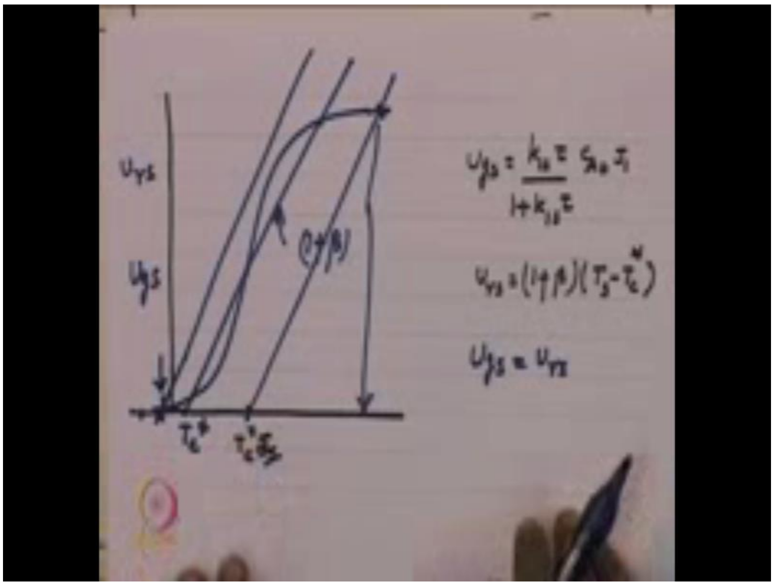
$= (k_{1s}\tau) C_{A0} J_1 / (1 + k_{1s}\tau)$

Say we have let us say we have a first order reaction the first order reaction r 1 the rate of generation I mean component of r 1 is given as k 1 s C A s. We know this r 1 s means k 1 s C A s what is k 1 s C A s C A s by our definition is C A 0 times 1 minus of x s. We know this now, we know we also know from our material balance say for example, we have done this just now this come back to a minute. From this equation x s given by this we can substitute for r 1 s and we refined that x s is actually given by k 1 s tau divided by x s is given by this expression. So, we can solve our material balance equation and find that our excess can be given simply by k 1 s which is a function of temperature tau times 1 plus k 1 s tau. On other words the steady state conversion in the equipment is k 1 s tau divided by 1 pus k 1 s tau this comes from our material balance.

Therefore, the rate of generation of heat or rate of generation of energy which is r 1 s tau J 1 which is once again we have said this. We have said all these things this is U g s that is U r s what is U g s for a first order reaction. We can now calculate this by substituting for r 1 s r 1 s comes from here this is r 1 s. So, you can substitute all these and find that the rate at which U g s is actually C A 0 x s J 1 or U g s is given by this expression which is k 1 s tau divided by 1 plus k 1 s tau multiplied by C A 0 J 1 we know all these things. So, what we have done? We are now able to express our rate of heat generation U g s in terms of k 1 s tau divided by 1 plus k 1 s tau. And this k 1 s depending only on temperature or in other words by our manipulations you are able to express the rate of heat generation in terms of 1 variable which is temperature.

Now, if you look at the other term which is the other term the rate of heat generation. So, this is the rate of heat removal which is 1 plus beta times T c star minus of T s heat removal is minus of U r s. So, U r s is 1 plus beta T s minus of T c star or in other words if I ask you what is the dependence of u r and temperature depends on u r. And temperature it is simply multiplied by T s minus of T c star T c star is known it only depends on T s. In other words what we have done now is that u g which is the rate of heat generation, rate of heat generation is got as a functional temperature. Similarly, you have rate of heat removal which is U r s which is also as function of temperature. So, once you have both U g s and U r s as a function of temperature now you can.

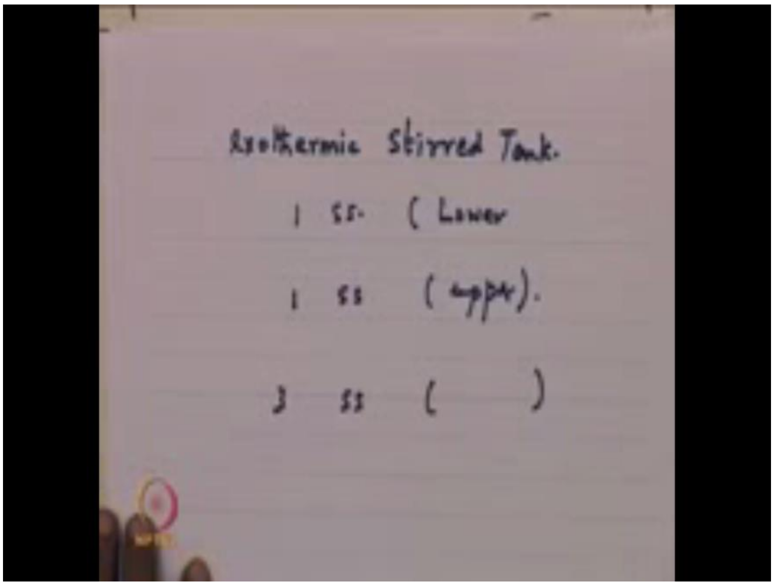
(Refer Slide Time: 34:34)



Plot U g s so, this let us say this function looks like this see U r, s u r s is what? 1 plus beta. So, it has a let us say what is a slope of this? The slope of this is 1 plus beta. So, what have we done? So, this is started a t 0 T c star. So, this is it is start a T c star and it seems to intersect at A 3 point suppose our T c star here. So, it intersects at this point suppose your T c star is here so this is equation is like this. So, it intersects at only 1 point so what we are trying to say is that depending on choice of T c star. You can have the intersection or you can have the U g s equal to U r s.

This equality is satisfied when it is satisfied at only 1 point when you have choice of T c star at a very high temperature or it is at 1 point. That is choice of T c star at a very low temperature or at 3 points when you make choice of 3 star appropriately. So, you can have a steady state whose temperature is this is this or a steady state temperature is this. So, you can have case of steady state temperature which is very high or a steady state temperature is very low or a steady state temperature which is intersecting at 3 points. So, what we want to conclude is that if you have an exothermic stirred tank.

(Refer Slide Time: 36:30)



Exothermic Stirred Tank.

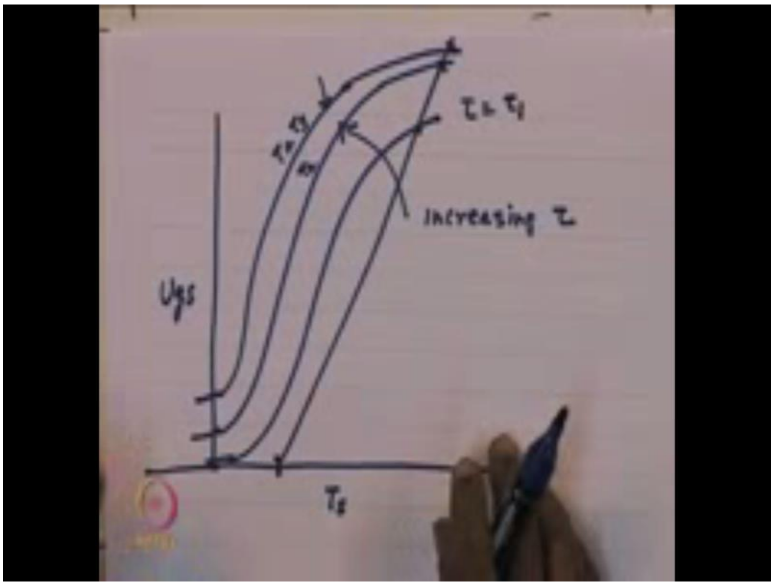
1 ss. (Lower

1 ss (upper).

3 ss ( )

This is the point we would like to get across to you if you have an exothermic stirred tank you can have what is called as one steady state. We can called it lower stead state we can have one steady state which is called as upper steady state. Or we can have a 3 steady states which is intermediate we have upper lower and intermediate. That is what we have try to show here you have it is an upper steady state is a lower steady state. Or it can be 3 upper lower and intermediate now, let us try to understand this in another way.

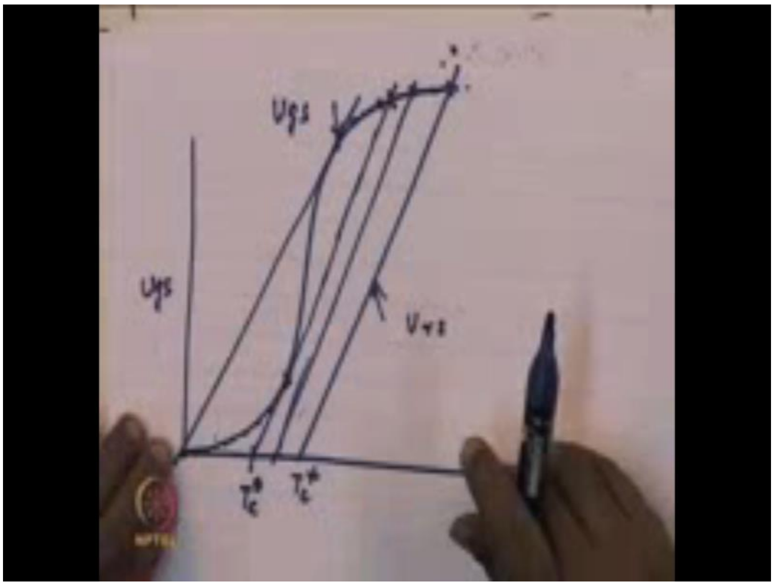
(Refer Slide Time: 37:13)



Now, let us say i want to plot U g s versus T s so, let us say you have this is one such curve. Now, if we change this is for let us say tau equal to tau someone suppose you increase tau. So, you will get curves like this if you is the this is increasing tau it stands to reason why it is increasing tau if you increase tau you will get curves like this. On other words you can you can generate curves of rate of heat generation versus reactor steady temperature for different values of tau at which you will operate the process. Now, your heat removal see suppose your heat removal curve is here let us say this is heat removal curve now you will find that if you are operating here.

So, you will all will gets only once if you are operating the reactor at this tau equal to tau 3 You will only get the upper steady state our tau equal to tau 2; you will get this state upper steady state tau equal to tau 1 upper steady state when will you get the lower steady state. You will get only when you choose this T c star sufficiently low other then only you will get over steady state. On other words the steady state that you will get in a process is something that you have to think deeply. And find out which steady state is what you will reach in your process and that will come from an understanding of the transient which will do shortly.

(Refer Slide Time: 38:49)



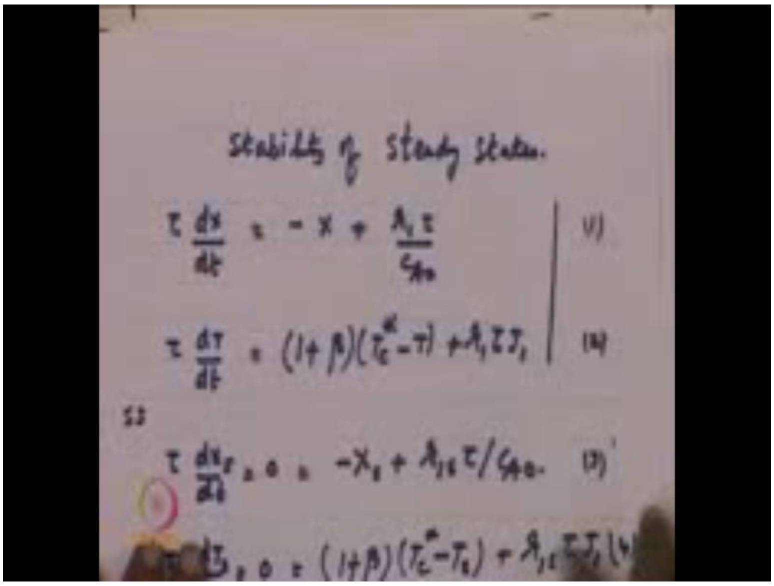
Let us look at one more exercise let us say you are operating at the steady state on other words this is u g and this is U r and this is U g. Now, as suppose you want to travel down to a lower steady state that means by changing T c star you can change T c star keep on changing T c star. And depending on the choice of T c star if you choose here you will get a steady state here if you choose a lower steady state. You can come to lower point lower point, lower point that means depending upon the choice of T c star. You will start moving down from your upper steady state to lower and lower temperature.

You will come to a point at which you will find that the next intersection is only here. What are we saying now is that if you have an a exothermic stirred tank then as your changing your T c star form point, point, point. And you will finally, come to a particular value of T c star after which you are further small decrease in T c star. You will intersect at much lower point which mean this change from a temperature high temperature to a very lower temperature is in instants of what is called as sudden cooling there is sudden cooling. So, in the same way if you are changing temperature from here; from here; from here; from here; from here; from here and then changing T c star a point will come suddenly it is get heated up.

So, this is what is called as ignition what we are saying that means what we are saying is that let us say this is T c star there is a particular value of T c as your operating form lower steady state in keeping on increasing T c star. There is a particular value of T c star when you reach suddenly the reactor heats up and then goes to the upper steady state you understand. That this behavior of exothermic stirred tank sudden drop in react temperature and sudden increase in reactor temperature. These are all issues associated with in interplay heat between heat generation and heat removal. And this these are crucial issues which can which can lead to accidents etcetera if you are not care full, but these issues are well understood now days.

And then we can take care of by an appropriate design these are the kinds of issues which you must take care when you try to understand what is called as a transient behavior of a stirred tank. And not only that we want to understand transient behavior stirred tank, you want to see how best we can ensure that the process operates in a stable ways. So, that there is a disturbance if they disturbance does not grow it sort of a you know it starts to decrease rapidly. So, that the steady state that you want to operate on you are able to reach in that point without too much of difficulty. In other words the whole issue of stability of steady states stability of steady state is a matter that is of great interest to us stability of steady states.

(Refer Slide Time: 41:59)



Stability of steady states.

$$\tau \frac{dx}{dt} = -x + \frac{\mathcal{R}_1 \tau}{C_{A0}} \quad (1)$$

$$\tau \frac{dT}{dt} = (1+\beta)(T_c^* - T) + \mathcal{R}_1 \tau J_1 \quad (2)$$

SS

$$\tau \frac{dx_s}{dt} = 0 = -x_s + \mathcal{R}_{1s} \tau / C_{A0} \quad (3)$$

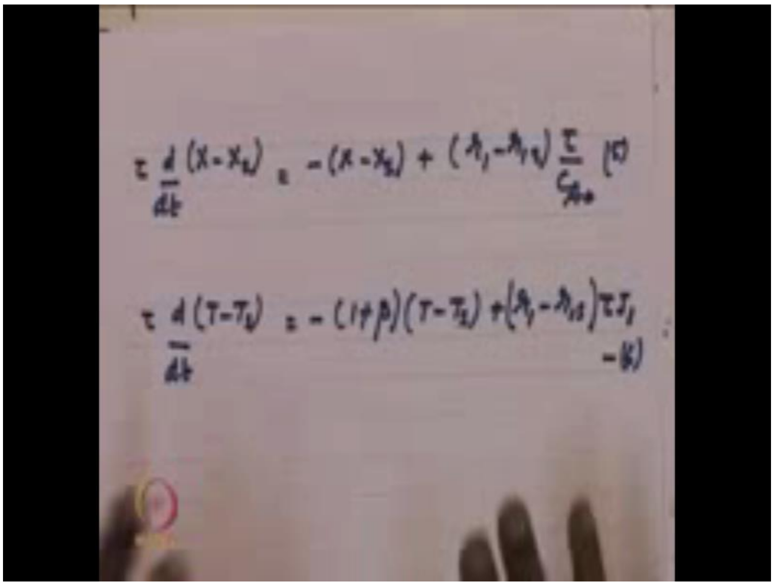
$$\tau \frac{dT_s}{dt} = 0 = (1+\beta)(T_c^* - T_s) + \mathcal{R}_{1s} \tau J_1 \quad (4$$

This is something that we want to understand and then take appropriate measures. Now, how do we understand stability? To understand stability what is done is that we should look at the steady state behavior. We should look at the unsteady state behavior, we should look at the difference between stead state and unsteady state behavior. And find out how best differences can be kept a smallest possible in a process. So, to do that let me write the steady state equation unsteady so, our steady state equation. Let me write d x d t minus of x plus r 1 tau C A 0 which is our material balance tau d T d t equal to 1 plus beta T c star minus of T plus r 1 tau J 1 this is our energy balance.

So, this is values of x and t in the unsteady state now, at steady state at steady state we said tau d x d t this is d x s d t equal to 0 is equal to minus of x s plus r 1 s tau by C A 0. And then tau d t by d t s equal to 0 equal to 1 plus beta T c star minus of T s plus r 1 s tau J 1. So, you have this is the unsteady state equations unsteady states these are the steady states. So, our interest now is to actually find out what is the deviation between x and x s t and T s why are we interested in this deviation? We interested in this deviation, because our interest is to operate the process at steady state, but due to variety of reasons the steady state gets disturb.

Therefore, we are away from steady state that means we are at x and not at x s. Therefore, our interest is always what is x minus of x s what is t minus of T s and indeed how we can operate the process. So, that x s minus x minus of x s t minus of T s as smallest possible or within the limits that U and I will specified. So, let us try an understand deviation from steady state so to do this what I do is that I subtract 1 minus 2. So, I call this is 1; I call this is 2 call this is 3 and call this is 4. So, I do 1 minus 3 and 2 minus of 4 so, I will do 1 minus 3 and 2 minus of 4. So, let me see how it looks like.

(Refer Slide Time: 45:06)



$$\tau \frac{d}{dt}(x - x_s) = -(x - x_s) + (r_1 - r_{1s})\frac{\tau}{C_{A0}} \quad (5)$$

$$\tau \frac{d}{dt}(T - T_s) = -(1+\beta)(T - T_s) + (r_1 - r_{1s})\tau J_1 \quad -(6)$$

So, it becomes tau d by d t of x minus of x s equal to minus of x minus of x s plus r 1 minus of r 1 s tau by C A 0. The other one is tau d T minus of T s by d t equal to minus 1 plus beta t minus of T s plus r 1 r 1 s multiplied by tau and J 1. So, what we have done? What we have done is that we are now looking at the deviations from the 2 steady states looking at deviations. So, the various things we can do with this right now. So, x minus of x s and t minus of T s. We like to see there are x minus of x s and t minus of T s are within limits that u and I will be specified. So, we want to know understand the solution to 5 and 6 and how these solutions can be understood as stable within our way of understanding the process. So, this is what we will do when we meet next.

Thank you.