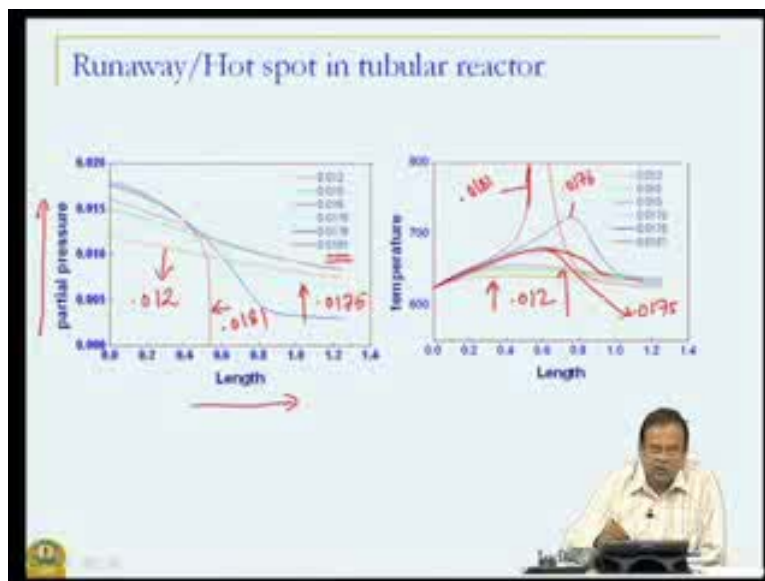# Chemical Reaction Engineering
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## Lecture No. # 35
## CSTR - Multiple Steady States


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Friends, let us continue our discussion on run away reactions and hotspots in the <mark>in the</mark> tubular reactor, and just to refresh ourselves. Let us look at this simulation of xylin oxidation, and what we are seeing here is the oxidation by carrying out this reaction at different partial pressure of oxygen. So, we have on our x axis the length of the reactor, and on y axis the partial pressure of the <mark>of the</mark> reactant. And these different colored line that you are seeing are essentially different partial pressure such as 0.012, 14, 16, 175, 178, 181, and so on.

The point I want would like to make here is that if for example, if our partial pressure that is initial partial pressure is 0.12, then we have a slow decrease in the <mark>in the</mark> partial pressure as the reaction takes place. And corresponding temperature results are shown over here, where temperature is maintained at a <mark>at a</mark> fairly low value. But as we are increasing the partial pressure, we notice that the reaction is progressing now rapidly for

the reason that not only the partial pressure is high, because reaction is progressing rapidly there is more heat generated. So, temperature are also high, and because temperatures are high once again reaction rate are high.

So it is a feedback kind of kind of loop and these are all these case that we that we see. For a partial pressure such as 0.175 I notice the small difference that we are making. We are actual changing partial pressures now in the second digit or third digit so which imply the sensitivity of the process. We see that the temperature for example, if you look at this result at 0.1075 temperature has arisen and given rise to what we can say small hotspot in the reactor this is that line in case you are not able to see it at 0.0176. So we have now changed it in only third decimal place the temperature has gone up in the reactor by the order of almost hundred degree Kelvin.

But what happens when our when our partial pressure is 0.0181 the reactant comes down to a zero value in a very short span of time but what is what is worrisome look at the temperature when the partial pressure is 0.181. These are the temperatures which is actually now over shooting this cane that means very high temperature in excess of three hundred to four hundred k increase and what happens then is that you have a hotspot and this is phenomena I was referring to the slope of this curve is almost infinity at this particular location.

Now what happens when the temperatures go very high reaction rates go very high? So we have a rapid decrease in the in the partial pressure or the reactant is consumed and once the reactant is consumed the heat generation term has been disappeared. Because reaction has come to a halt and therefore temperatures rapidly go down also. But we are not so much interested in this part of the curve because we do not know what will happen if temperature go out significantly high and we were trying to analyze these behavior by looking at how we can analyze this in terms of in terms of the heat behavior and for that we our wrote our mass and energy balances, which we could we could represent in terms of heat generation term and heat removal term.

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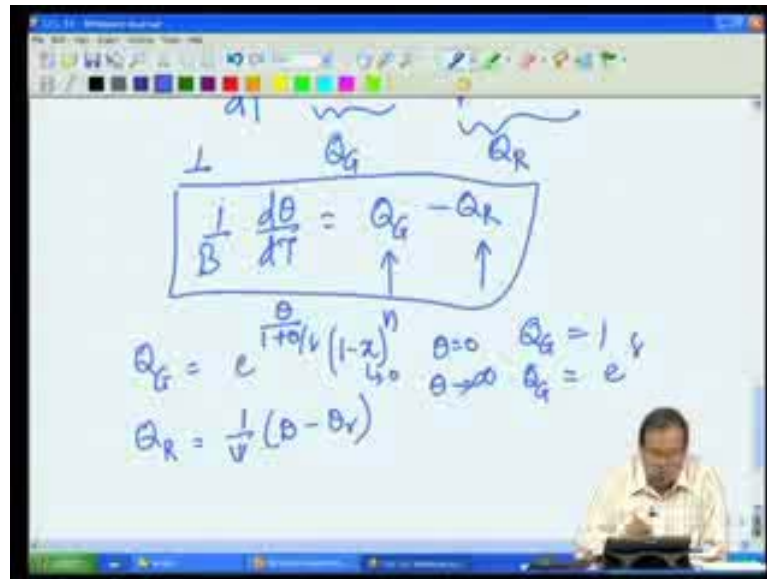


We simplified this generation term because in actual practice this would have a term conversion. But we said that we will set this to close to zero because we would like to analyze and what we saw in the last session was this kind of kind of behavior namely if we look at look at our Q G curve Q G curve was of this nature.

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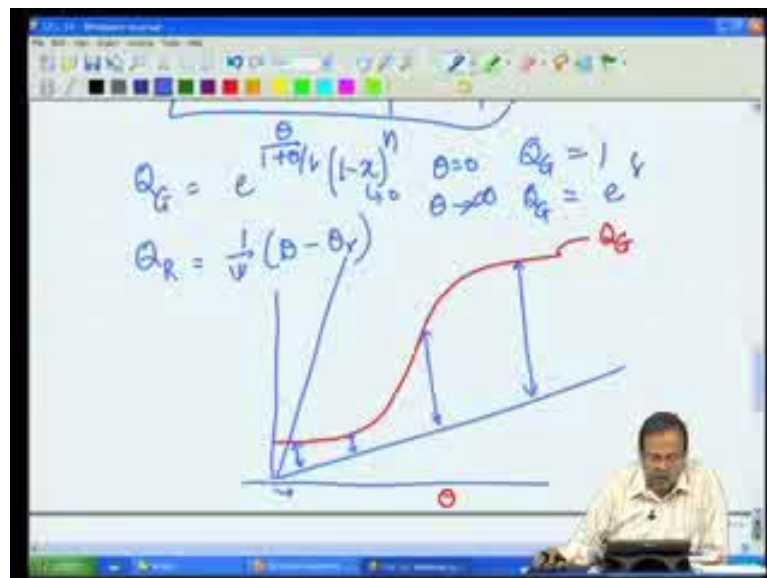


So what we are plotting here is temperature versus this is Q G and Q R curve can take different values depending upon this parameter side which is a Semenov parameter as we had we had define over here, which is combination of all heat removal term and heat

generation term. So in fact it is the ratio of these two potentials. So what happens is when psi value is very high that means heat generation term is much higher compare to heat removal we have the operating line which let us show it by different color of this nature and on the other hand if psi is a low value then we have a operating line of this nature.

So we last time saw that what happens when your operating line is with high value low value of a psi then the slope is very high and as temperature is temperature is increasing the difference between the generation and the heat removal is progressively decreasing. And so we will have an operation where temperature is more or less constant this is what is seen in this particular behavior when partial pressures were low that is temperatures are fairly rapid. But let us consider another situation where psi value is very high. So this is the slope so notice what is happening as temperature is increasing the driving force it appears that it will go down but then it goes on increasing. Or in other words generation term is in far excess of heat removal term and that is where we will get our hotspot.

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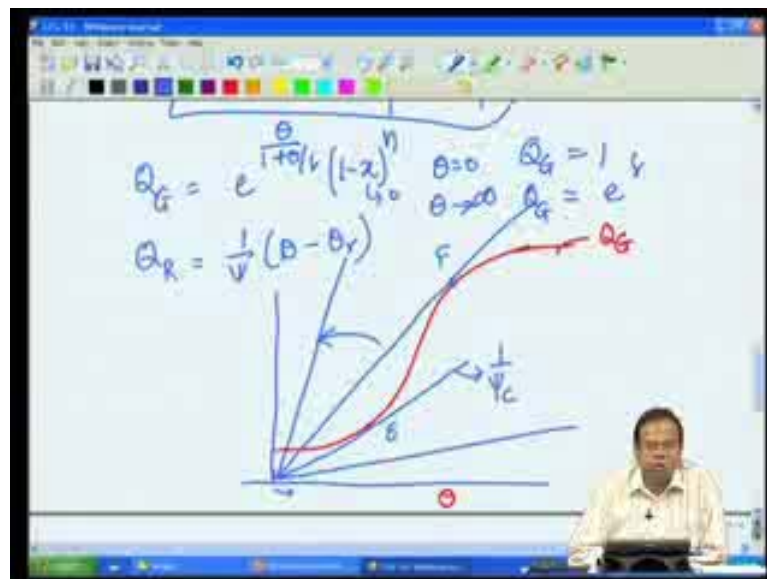


Now this is was the case when we neglected the reaction. So even for this particular case let us try to see how we can how we can how we can get those get those conditions. So let us let us try to try to look at this behavior once again so this was our generation term and now we know that if you have if you have actually an operating line, which is just tangent to this curve at this point let us call this point as E. So this slope as let us say one

over psi c some critical point. Then any value any line which is below this is a sure shot for sure shot for runaway reaction.

So this gives me one bound on what is the limit of my safety operation that is if this heat remover line is a tangent to heat generation line at point E. Similarly I could have another tangent at point F I know if my cause are on this side and I have a safe operation. So in short we can therefore find out the range of operations for which my operation will be a runaway reaction or a safe operation or may be runaway may be a safe operation.

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So how do we how do we do that we do that by noting that at point E and F what is happening Q G is equal to Q R and the slope of this two lines is equal. That means not only the generation rate and heat removal rate are equal but the rate of change of generation heat generation with temperature is same as rate of heat generation a heat removal with temperature and so using to this two equations we can actually find out corresponding values of let us say critical temperature one, critical temperature two. Let us call that that point as theta c prime and if we do little bit of mathematics this actually results into a quadratic equation and we end up with theta c for example, being gamma by two this parameter gamma was define in the previous session namely E by R T zero.

And knowing this value and also realizing that we have our Semenov number Semenov number. So corresponding to this we will get the slope of that line and let us call that slope as one over psi c where psi c as we know from the definition is. Now we also know

we also know that we can write concentration in terms of pressures partial pressures. If you assume ideal gas for example, and there is a critical value psi c or in other words we can we can therefore find out the relationship between this curves with a known value of psi c. Now defines a face plane behavior or the separate in the face plane of P 1 0 and T 0.

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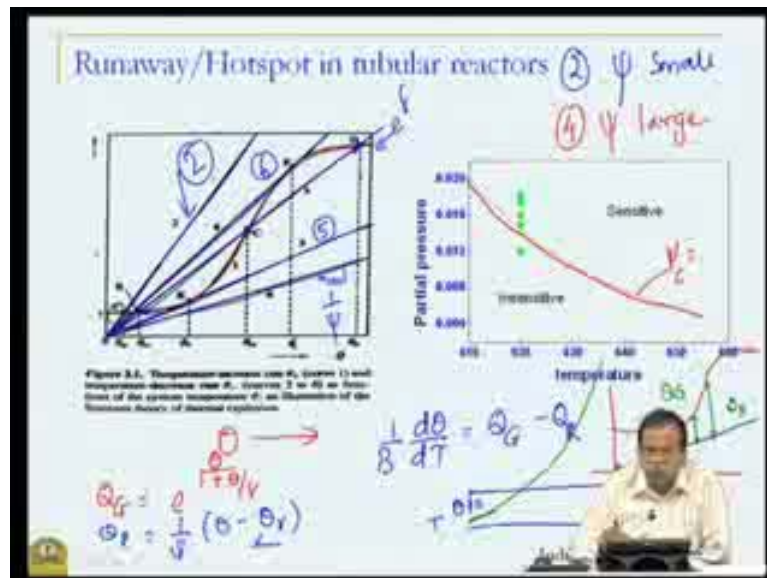


So let us try to look at that so that relationship for psi c that psi c equal to whatever in terms of P 1 zero and T 1 zero. Now we get this separate tricks and if the combination of P 1 zero and T 1 zero is such that we our psi value is in this regime. We have a runaway reaction or sensitive region and in this regime we have an insensitive region. So this gives us a kind of kind of operating guidelines as to what inlet temperatures and pressures should be avoiding anything in this region is a recipe for recipe for disaster. Now going back to our example we said that we neglected the reaction altogether.

So in plotting this we said that this term is unity this particular one. Now let us just qualitatively try to see what will happen as the reaction proceeds and how do we get that that hotspot. So to do this I am going to redraw this figure but I just want you to notice the following fact. If this is my line Q G with x equal to zero x equal to zero. Then for a different value of x my Q R curves remain same but my Q G will have a lower value. So for x I am just going to take it will it will still start with value lower value and it will have lower curve.

So I want to keep that in mind for example, this will be let us say x for 0.1. So in other words what is going to happen to our generation curve as reaction is proceeding is that this generation curve is going to shift downwards. So let us ==let us== keep that that information in mind.

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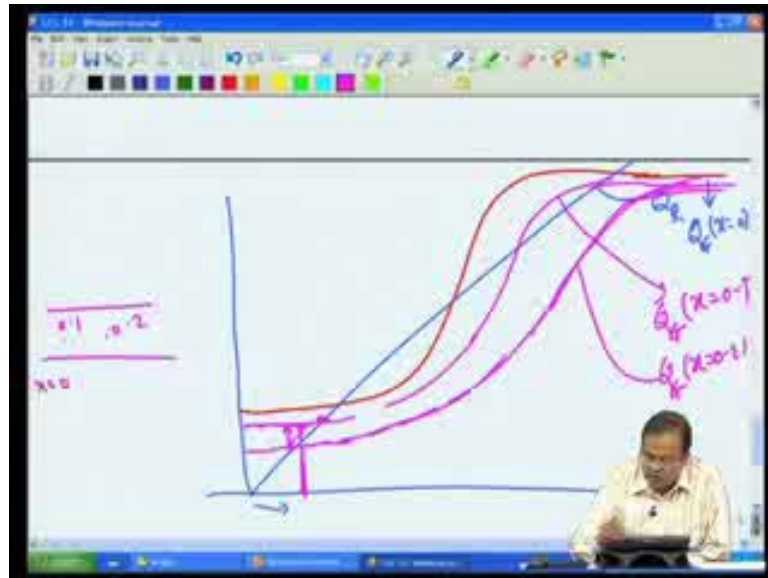


Let us now try to ==try to== look at ==look at== an operation what will actually happen in a ==in a== plug flow reactor when the reaction is taking place. So let us say at the start of my reaction this is my generation curve and my operating line was something like this. So I will just put just for sake of argument. So this is my value of psi so this is my Q R curve and this is my Q G curve with x equal to zero. So initially my temperature rise is limited because as my temperature is increasing my heat generation is coming closer to heat removal. So what I am going to do is draw progressively lines with==…==

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So let us say that this is Q G of x equal to 0.1 this is of 0.2 and so on. Now you have to imagine the following situation my temperature is increasing. So is my conversion so for example, from start if my operating point or in to somewhere along these reactor. See this is my x equal to zero that is my conversion and at some location x will become 0.1, 0.2 and so on and temperatures will also. Now let us ==let us== consider a situation where I am somewhere in the between this two regime. So what will happen my generation rate

has come down but still I will be near this operating point and my difference is still narrowing.

But now let me consider and situation where this is my temperature in the reactor this is my temperature in the reactor and my conversion is 0.2. So I have a curve which goes like this and this is this is my operating line. Now when I have this and let us let me clear this few things over here so that.

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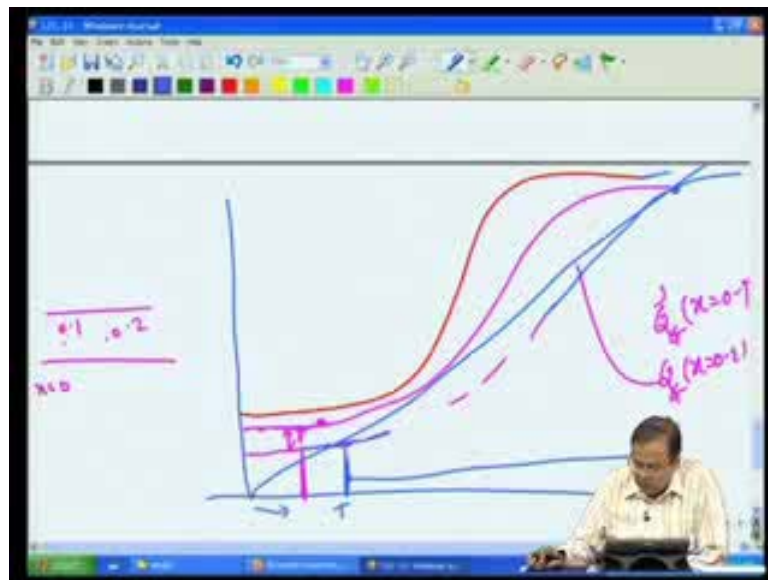


Let me show my operating line operating line and so if my if my if my if my temperature is let us say over here that is just for sake of argument and conversion is 0.2 then I see that this particular branch of intersection point has completely disappeared and only where point where intersection can occur is this high temperature. So what will happen my temperature will suddenly go to a go to a high value or a hotspot? But then once again as the reaction is proceeding as I said earlier that because conversion will be almost complete the rate of reaction will go to zero. So generation will also go to go to zero and once again our temperatures will come back.

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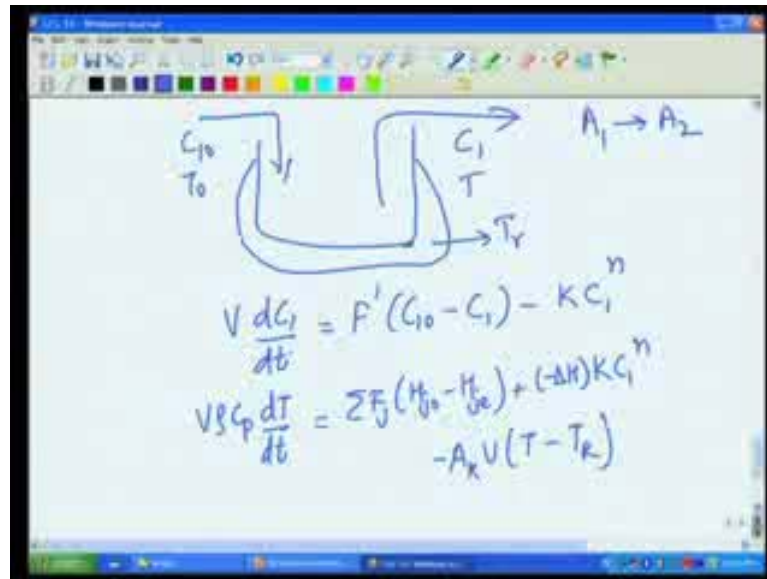


So this is this is what happens when we have we have a plug flow reactor. Now let us try to look at what kind of kind of scenario will emerge if we have we have a stirred tank reactor because we saw an example where stirred tank reactor also gives rise to multiplicity. So let us say that we have a stirred tank reactor a stirred tank reactor and some jacketed vessel so that we are trying to maintain the maintain the temperature. So let us let us try to write down the mass and energy balances for now stirred tank reactor by again taking A 1 going to A 2 an exothermic reaction as our model reaction and let us try to try to see what will what will happen.

So if I write my mass balance I have keeping the same notations as before that is F prime is my volumetric flow rate and my reaction is n th order reaction C 1 0 T 0 are temperatures here C 1 and T r temperatures at the out let T r is the temperature of the of the of the coolant. Once again I will assume that my properties are not changing with temperature and so I can write my energy balance in the following manner. I am just repeating what we had seen earlier that is each of this term on the right hand side first term is the energy transport due to convection. So material is coming in with certain enthalpy H j zero is living with certain enthalpy H j e.

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There is a second term which is representing the generation of energy because of reaction and the third term the removal of removal of energy. So to these mass balances to these mass balance and then we will we will write H j zero minus H j e as C p j minus T minus T zero and so on R T zero minus T and we will use the same dimensionless parameters as before n minus 1.

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In terms of these dimensionless quantities I can once again write my mass and energy balances in terms of these dimensionless quantities. So I am going to just substitute these quantities in this mass balance and do some rearrangement and we will get the following equation I am skipping this substitution part but you can you can try it out and see whether this is what we actually get. Our mass balance and for our energy balance for our energy balance we will get once again minus this particular quantity.

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Where did these term come from these term come from these A k u term, and that enthalpy term. But what is what is interesting to once again realize is that our energy balance is once again a balance between heat generation rate which is actually the same term as what we had we had before. And the heat the removal term, which is slightly complicated than before, but it has the same essence of representing how much energy is being removed from the system. There are two terms here, and both this term this one is obviously coming from the heat exchange or heat removal due to the jacketed fluid whereas this term is arising, because of heat removal due to the change in the enthalpy of the of the system, so convective energy removal.

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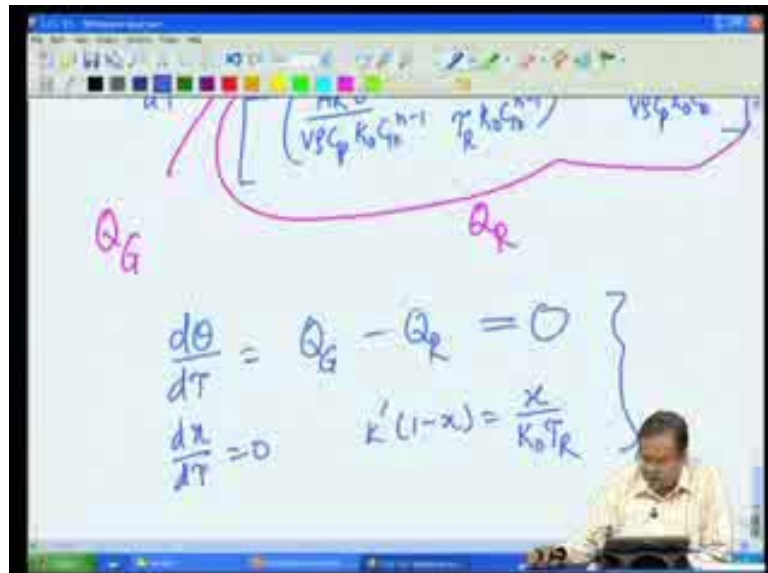


But the point is once again we can write as Q G minus Q R and as you know in stirred tank reactor in stirred tank reactor we have a steady state so this is actually a precise description. This is our precise description or in addition to of course, our mass balance

dx d tau also being equal to zero which if we consider a first order reaction will give us this particular relationship.

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So now if we combine this to mass and energy balance we can actually represent our energy balance or Q G term by combining mass and energy balances and Q R term as. So if we want to now look at steady state behavior of this particular stirred tank reactor operation. We what we need to do we need to plot Q G as a function of temperature what is k prime k prime is coming from our reaction rate constant. So that is e raise to theta by one plus theta by gamma the same term that we had we had before so if we now if we now try to plot this behavior.

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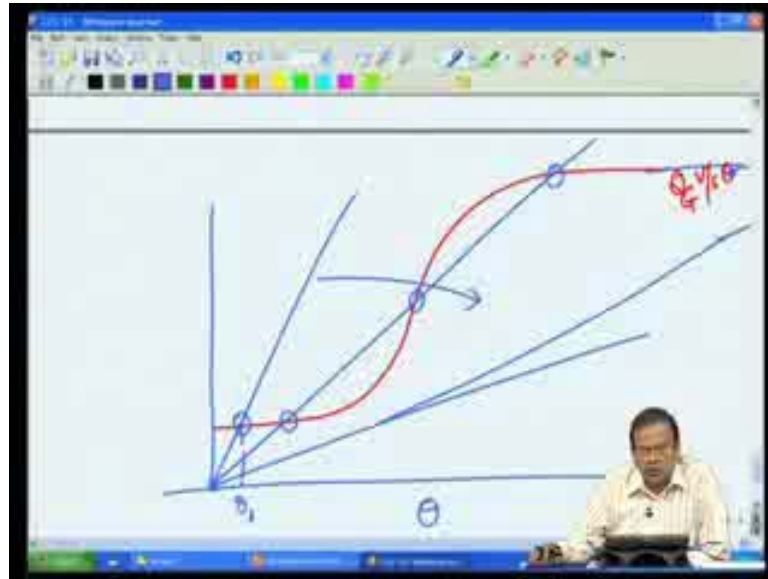


So let us try to once again do the same exercise temperature and heat generation rate it actually turns out that we have this very similar shape as before. So this is Q G versus theta and we have Q R which once again can be represented by straight lines with a slope equal to this particular value so this the slope of Q R versus theta and this is of course the intercept, which is a non zero can be a non zero value. But if we just scale it make a linear transformation we can show it to be starting from here.

So now let us see what happens here once again we see that if the slope of this line is high value slope of this line is high value then we have steady state temperature which is which is let us say steady state temperature one which is of a of a low value. But as we now what the is the slope of this Q R curve dependent on slope of this Q R curve is dependent on for example, area of heat transfer or heat transfer coefficient. So and of course, the other terms but if you just look at this two terms in particular it becomes clear to us that high value of this slope means high heat removal rate so high value of this slope means high value of heat removal term.

So when heat removal is very large compare to generation we have temperatures which are of low value. Now what happens if heat generation is as we change the slope of this line now how can we change slope of this line we can change the slope of this line by changing A k or u or I also by changing tau R value, which is the which is the residence time and we can change the intercept by changing the value of the coolant temperature.

Now what will happen when we change the value of the coolant temperature or the residence time such that the slopes go in this direction? So what happens here we have one steady state and then we have possibility of three steady states and otherwise of course, there will be only one steady state somewhere intercepting beyond this line.

Or in other words if we now let us say plot suppose we are changing we are carrying of adiabatic reaction. So what will happen for adiabatic reaction for adiabatic reaction this term is zero because there is no temperature of the coolant and so on. This term is also zero because there is no heat transfer mechanism so for adiabatic reactor Q R is simply one over tau r into k naught into theta. So let us say that we change the residence time and that is what the result we had seen earlier if we change the residence time such that we start from a small value to a large value. What will happen to the steady state? From small value to large value of residence time implies that the slope of this line is decreasing.

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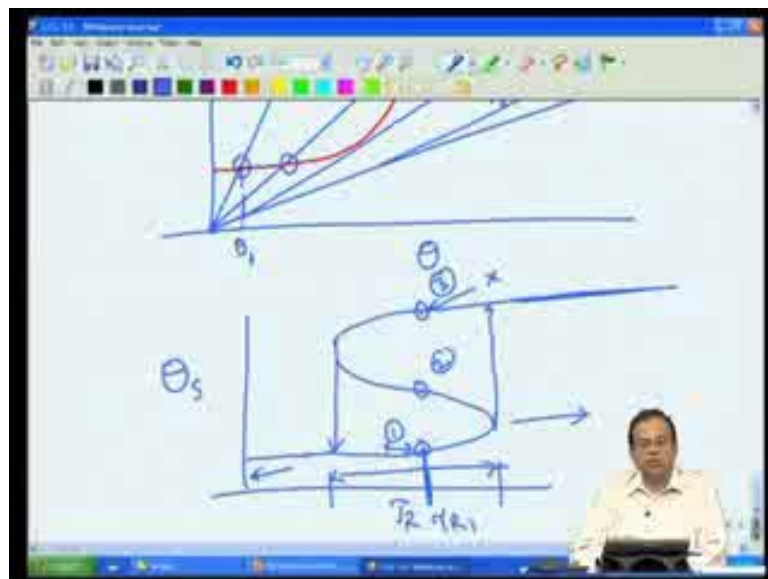


So what will we get? So we will get something like this if you are looking at steady state temperature theta s versus residence time tau r, when tau R is low we have only one steady state and so we will have this lower branch of steady state. As we as we keep increasing the value of decreasing the value of this slope or increasing the value of tau r what are we getting we are getting three different values of values of steady state. So this

particular point this point and this point and we will have a behavior which we which we saw earlier.

That is temperature so what will happen as we are changing the slope if you are increasing the residence time if we are increasing the residence time, then we will have steady state which correspond to all these intersection points where Q G is equal to Q R that means the lower branch lower branch. But if our residence time is such that our slope is below this line or our removal rate is below this line then what feasible solution we have we have a feasible solution only with a high temperature.

So this is that regime so here we have only in this regime we have only high temperature in this regime we have only low temperature solutions whereas, for the intermediate value of residence time we have possibility of three solutions and hence we will have this kind of kind of behavior with increasing residence time up to this point we are on the lower branch then suddenly we will shift to higher temperature solution behavior and if we are decreasing the residence time we will be on this particular branch of branch of solution. But after this point we will suddenly shift to a lower branch.

So what this what this implies this is for adiabatic reactor and one can argue a similar behavior when have even heat transfer that is that coolant flow rate or heat transfer area or heat transfer coefficient and so on. So what does this does this mean? This means that in a stirred tank reactor operation at steady state let us take this example of adiabatic reactor. What it means practically? It means that under certain range of our residence times we have multiple solutions that are three different steady states are steady states are possible let us say at this particular residence time tau R 1.

I have steady state one, steady state two and steady state steady state three. So there are there are question arises that which one of this which one of this steady state, we will get with our reactor. I mean how we know that whether we will get steady state one, steady state two or steady state steady state three. So that will depend on as we saw here what was our starting condition for example, if I started residence the reactor for residence time of tau R 1 and the inlet initial temperature of my reactant was something close to this point one. So suppose this was my inlet temperature then one can except that we will reach this particular steady state.

But suppose my inlet temperature was somewhere over here then you can expect we will reach steady state number three that is we will have this particular steady state. So it all depends on where you start your reactor. So in other word for stirred tank reactor even though you are interested in steady state what steady state you will get will depend upon where you start up your reactor and therefore, start up of the reactor is also an important aspect in deciding how the reactions will take place and what steady states we will get. The second question that that one would like to therefore, asks is what happens if I start over here at this particular value of temperature. Will I go to steady state number two? Because that appears to be closest steady state let us try to answer that answer that question in this particular manner.

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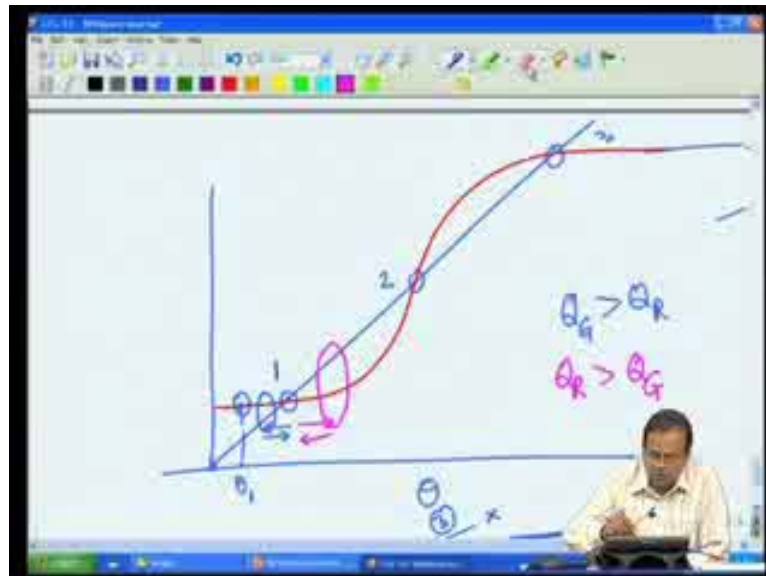


So let us say that this was my steady state one this was my steady state two and this is my steady state three and I am going to remove some of this material so that. We have only required now let us let us look at what is happening if I am at this particular steady state so this is my temperature versus temperature versus this Q G curve and let us say that my from this particular steady state I am slightly away from that steady state and slightly away from steady state in this direction. So if I am away from this steady state in this direction what do I see here if you focus on this I see that Q G is greater than Q R.

What does that mean that means heat generation rate is higher than heat removal rate? So what will be happening in out reactor if generation heat generation is higher than heat

removal temperature will increasing. So we will start moving in this particular direction. Till such time that I come to this particular value of steady state where Q G is equal to Q R. Now let us see what happens if I make if I am away from that steady state temperature in this particular direction. So in this direction what is happening my Q R is greater than greater than Q G.

So what will happen to my temperature the removal energy removal rate is higher than energy generation. So temperatures will start falling and I will once again come back to this particular steady state. Or in other words at this particular steady state any perturbation in the temperature either temperatures becoming lower than the steady state value or higher than the steady state value the dynamics of the process will ensure that we are driven back to that particular steady state or in other word this perturbations will die out.

Let us try to see what happens at steady state three or in other words and the same thing can be said in other word other way that this steady state is just inherently stable steady state that is any perturbation that you carry out from in the in the positive direction or in the negative direction will die out and we will come back to the steady state we will look at what are the formal definitions of a steady state inherently stable steady state and so on little later.

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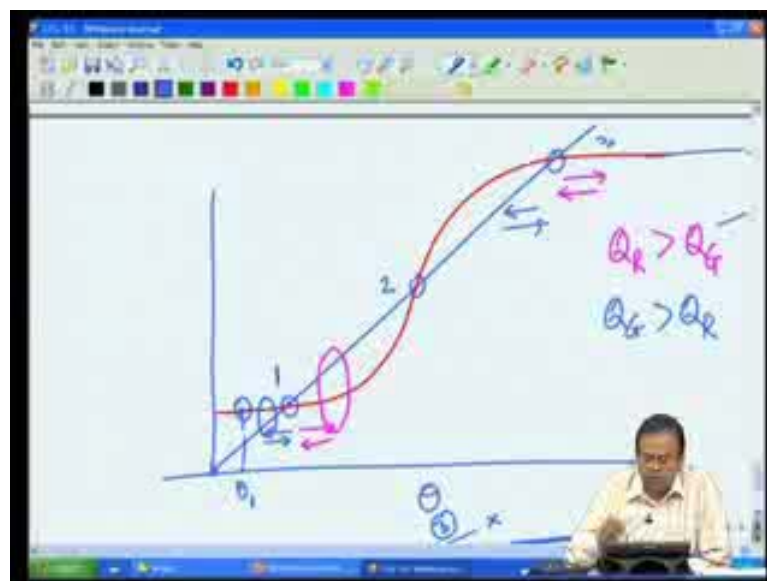
But let us try to look at what will happen at steady state three. So let us come to steady state three and let us say that we make a perturbation once again in the directions in this particular direction. What is happening there? Once again Q R is greater than Q G; Q R is greater than Q G. So we will come back to this steady state if we make a perturbation in this particular direction Q G will be greater than greater than Q R or in other words our we will go back to the same steady state or in short this steady state number three is also and stable steady state whereas, one is also stable three is also stable. So let us try to look at what happens at steady state steady number two.

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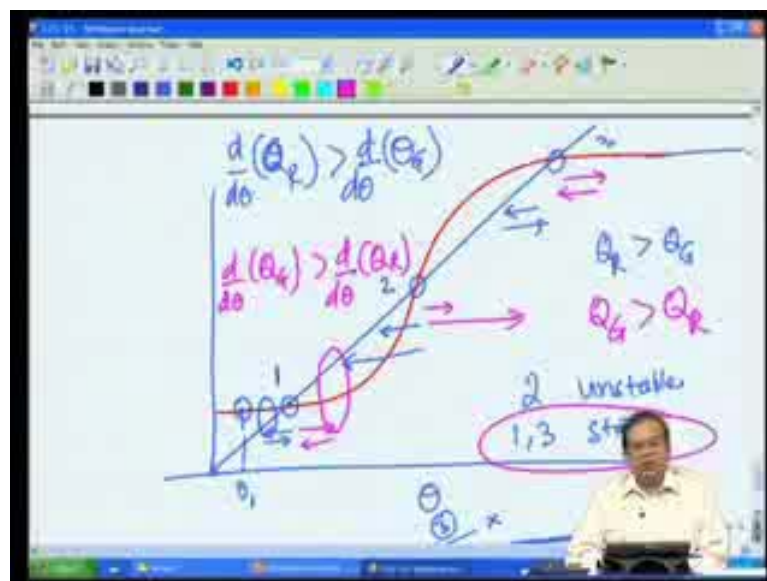


So let us say that I make a perturbation so that temperature goes down. If temperature goes down corresponding to this steady state what do I see I see my Q R is greater than Q G. This blue line is above this red line so what has happened in this particular case. When my temperature has gone down my heat removal rate is in excess of heat generation rate. So what it means my temperature will go down even further. How long will it keep on going down till I come to this particular point? Because here we saw if we decrease the temperature it will try to increase it once again.

Now what will happen if I increase my temperature? If I increase my temperature I see that Q G is higher than Q R, now Q G is higher than Q. So what will happen? Generation is rate of heat generation is more than the rate of rate of heat removal. So we will have further increase in temperature and how long can this go on till we come to this point

three because here we saw that this is a this is a stable steady state. In short any perturbation at steady state number two is not going to die down; it is in fact going to amplify. We call such steady states as inherently unstable steady state.

So we have steady state two is unstable and steady state one and three are stable steady state. We will look at formal definitions and how we do this analysis in our next session. But before we close for todays session let us qualitatively try to look at or rather quantitative terms. What is this condition that is not satisfied at this particular point? So what is the feature of steady state one and three which is not there in steady state steady state two? We can look at this in the following manner let us look at what is happening at steady state steady state three.

If we increase the temperature Q R value is higher than Q G value that means the rate of change of Q R with temperature is more than the rate of change of Q G with temperature. Because at steady state three both Q G and Q R are same but increase in temperature Q R is Q R is higher or in other words at this point d d theta or of temperature with respect to Q R is more than d d theta with respect to Q G. I see that same is case at steady state one that is heat removal rate slope of heat removal line is more than the slope of heat generation line.

But is that the case at steady state number two I see the contrary at this condition d d theta of Q G is higher than d d theta of Q R. Because slope of this red line is higher than the slope of this blue line and red line is being the generation line and blue line being the removal line. So in short if my heat removal rate slope is more than the heat generation rate slope then I have steady state which is stable, this is that those point. So the condition that is required for steady state to be unstable for this particular example is the slope of heat generation rate is higher than the slope of heat removal rate.

We will see how with this condition is obtained in the more formal way when we look at stability of chemical reactors in our in our next session. So in todays session we essential saw how we what is the origin of this parametric so called parametric sensitivity behavior. Basically in exothermic or reactions in which reactors are operated in an non-isothermal manner this parametric sensitivity arises because of heat generation within the reacting system and if the system is not able to balance this heat generation with heat removal we are likely to situation is ripe for sensitive behavior.

Now what kind of behavior can we except for example, this give rise to multiplicity of steady state in a CSTR with some steady states being stable some being unstable. It gives rise to hotspots in tubular reactor where for small change in the inlet condition you will suddenly see the temperatures shooting up. Although we did not discuss it in detail but an analogy between plug flow reactor and a batch reactor would convince you that the same behavior must be responsible for explosions in the in the reacting batch reacting system such as methyl nitrate decomposition or hydrogen peroxide hydrogen and oxygen reactions.

So one has to be extremely careful in designing the reactors to avoid this sensitive region, having said this I should also point out it turns out that most of the times the operation which gives you maximum return on your reaction return in terms of productivity or yield is often very close to the sensitive region of operation. So on one hand from safety aspect you have you do not have to be in that region but from economy consideration or from profitability considerations you have to be we have to be close to that region, which implies that we must have extremely good control system so that we even accidently we do not go into that sensitive zone.

So for example, moment you realize that there is a decrease in coolant temperature or decrease in the flow rate. All these will have to be compensated accordingly, so firstly we should have good identification system, which will identify these deviations and secondly good control system which will effectively take care of such perturbation. Otherwise, we may land up into undesirable operating region. So, we will stop here for this session, and spend some time on looking at the stability analysis in general, and that of chemical reactors in particular that will be the topic for the next session. Thank you.