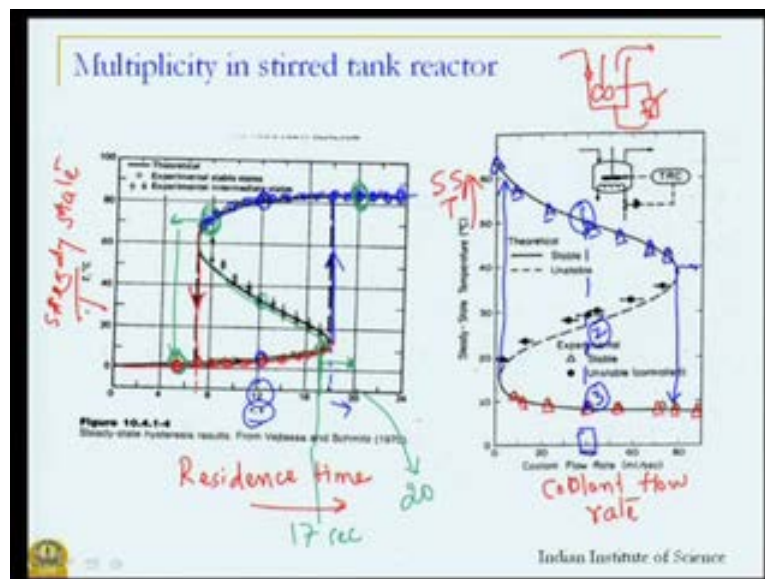


Chemical Reaction Engineering
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Lecture No. # 34
Parametric Sensitivity

Friends, in the last session towards the end we started looking at some design aspects. And particularly an example, of sodium thio-sulphate oxidation in stirred tank reactor adiabatic operation in which we saw we get multiple statistics. Same stirred tank reactor even if you are not doing an adiabatic operation, but let us say we are trying to do an isothermal operation.

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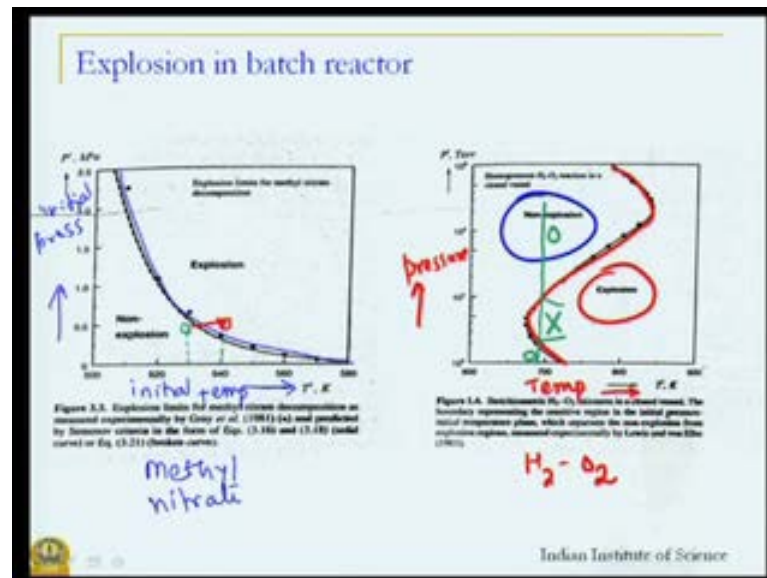
Then we can see in this next example, the following following behavior. What we are seeing on the on the right hand side essentially what we have is the stirred tank reactor. So, we have a stirred tank reactor and it is a continuous operation and there is some cooling that is that is taking place. So, that the temperature is temperature is controlled. Now what we are seeing results over here, are what happens when you change the coolant flow rate and what steady state temperature. So, steady state temperature in the reactor on the on the y axis. So, let us try to try to do an experiment where let us say that we start with very high value of coolant flow rate. Now when you have very high value of coolant flow rate you can expect the temperature to be lower, and this is what we get.

So, let us now do an experiment where we started with this point and then went on decreasing the flow rate wait for some time for steady state to attain and note the temperature. And this is what we will see if we keep on decreasing the coolant flow rate. If we start the experiment other way round that we keep very low coolant flow rate, then we may expect temperatures to be high, and this is what we can expect. So, very high temperature and then temperature progressively **progressively** decreases as we are increasing the coolant flow rate.

But, if we increase the coolant flow rate beyond certain value we now actually see a very low temperature. Or in other words the same hysteresis effect is seen over here, as well namely the for increasing the coolant flow rate we get progressively reducing the temperature, but at a highest level of temperature and at some points we suddenly see that temperature goes to a low value, it is again an exothermic reaction. So, you expect that temperatures low would mean, that very low reaction rates and therefore, very little conversion. So, what we see here is we suddenly go to a lower branch, but now again you start increasing the temperature we remain at a lower branch increasing the coolant flow rate we remain on this lower branch and then at some point we suddenly jump to a higher temperature branch.

So, then hysteresis effect similar, to what we had seen earlier in our adiabatic reactor. And also interesting is that suppose we fix our coolant flow rate at this value 40, then at this coolant flow rate we have multiple steady states possible. Number 1 number 2 and number **number** 3. So, question then arises that if you are trying to run an reactor with this value of coolant flow rate which of these three steady states will you get will you get high temperature low temperature or the intermediate temperature. Now it turns out and we will look at this behavior little later that number 2 is inherently unstable. So, if we do not if we do not control have a controller mechanism we will never get this number 2 it is called unstable steady state and only possibilities are 1 and 3. Of course, if you have a controller then you can artificially make that steady state stable and get those get those results. So, this is what happens typically can happen in stirred tank reactor

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Let us take another example of a batch reactor. And there are two examples shown over here the first example is methyl nitrate decomposition methyl nitrate decomposition and this is a batch reactor. So, what we are seeing on the x axis is the initial temperature **temperature**, and this is initial pressure initial pressure. So, on y-axis is initial pressure this is a gas phase reaction. So, initial pressure and on x-axis we have initial temperature. Now what we what we see over here, is an separate risk the name for this separate risk will become clear in a minute that is in this phase plane of initial pressure versus initial temperature, if your operating conditions are in this region; if your operating conditions are in this regions that is below this line than you have a safe reaction there is there is no reason to worry about.

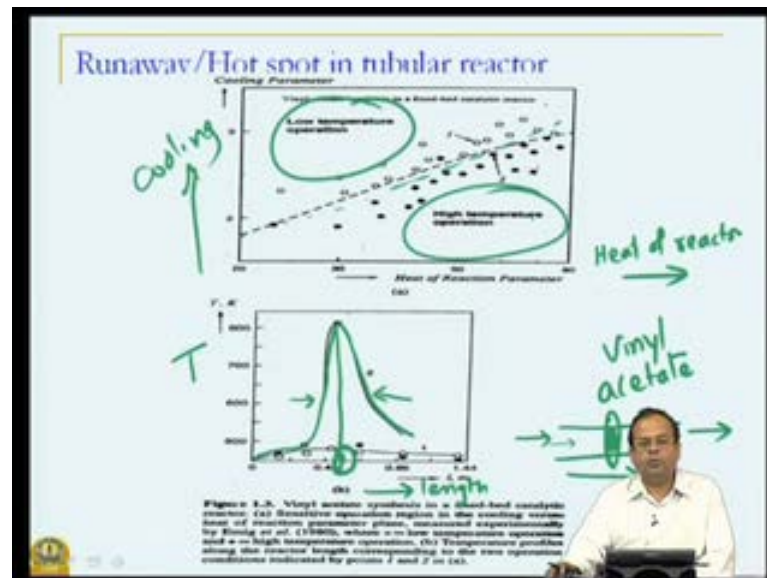
However, if your operating condition is in this particular region above this line then we have an explosion occurring in our reactor a disaster. And the reason why we call this line as separate risk is, because we can see that this line divides this phase plane of initial pressure and initial temperature into two different regions separate them into two different region safe operation and and explosion. Now one way of looking at such such situation is we say that we; obviously, do not start with those initial conditions where you have you have explosion. So, you always design here, but look at how sensitive this behavior is for example, let me let me just for sake of illustration let us say that we have chosen an operating condition over here.

Safe operation I have no cost to be worried, but something happens at the start of these reaction and temperature which was supposed to have been at this levels which is about 530 k incidentally happens to be 540 or 535 same pressure, but higher temperature. And now look at what has happened in our in our reaction. So, this is my new operating condition and this is now in a danger explosive range. So, a small out of 500 k or 530 k 10 is less than 2 percent error. Less than 2 percent error, but that can have disastrous implication for our reactor **reactor** operation. On the right is another example, where we are looking at hydrogen oxygen mixtures and combustion **combustion** reaction. This reactions are increasingly important, because hydrogen is being looked at as a fuel for the future, but look at what is likely to happen in such reactions. Again what we have here is initial temperature that is a start of temperature on x-axis and pressure on y-axis initial pressure on y-axis.

And once again we have a separate risk which divides this phase plane into two region of explosion and no explosion. And unlike in the previous example, these separate risk is crazy shape it is not the unmade it is not continuously going down what it means, is for example, if we have if we are starting somewhere over here, all these conditions up to these points are safe, but then we have unsafe region in this boundary and once again we have a safe region, or in another words this portion safe operation, this portion unsafe operation, once again safe operation. So, slightly different what it means, is we are looking at partial pressure. So, lower pressure and higher pressure is for a given temperature, but any intermediate pressure is a cause for concern, that is we will have an explosion.

So, this is another possible behavior in a in a batch reactor. And once again the sensitivity issue is also at play that is to cause changes from non explosive to explosive region, you do not need a huge change or operating condition difference. A small difference is enough to cross over the boundary between safe operations to a explosive operation.

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This is yet another example, and this time we are looking at tubular **tubular** reactor. And we are looking at a reaction of vinyl acetate synthesis. Vinyl acetate **acetate** synthesis in a in a tubular reactor and what we are looking at is on the x-axis is the length along the reactor. This is where my reactants are coming in; this is where my products are coming out. So, on x-axis looking at length and on y-axis I am looking at temperature **temperature** in the in the reactor. There are two different operation shown low temperature and high temperature operation, but we will we will right now look at a behavior which is of nature such that if you have a low temperature operation we are starting with temperature of about 400 k and temperatures will remains well below 500 k during the entire **entire** reactor it is about 450 k and so on, but something called high temperature operation we will try to analyze this situation in more detail.

In a high temperature operation if you you look at look at this behavior initially the temperatures are well controlled, but then something happens in our reaction and suddenly the temperature shoots up by about 300 to 400 Kelvin. And once again it **it it it** **it** comes **comes** down. Now if you look at this behavior of this of this temperature suddenly increasing. This is a cause for concern why, because if you look at this lobe of how rapidly this temperature is increasing it is too high it is almost infinitely large and. So, is the way in which it is cooling? Giving rise to an effect what is called as hotspot in a tubular reactor, if you look at this temperature rise it is almost like there is a region in

the reactor this particular spot where temperature is suddenly is very high let us say that point is somewhere over here.

So, below this temperatures are alright after this temperature are alright, but there is a hotspot in the reactor at this particular reactor at this particular location. And this behavior is like a spot behavior, because the slope the increasing temperature is almost infinitely large. Now one may argue that temperatures are coming down. So, why bother about this we have to be worried about this behavior for a simple reason. This magnitude what we see here increase is not a small magnitude it is about 300 k and just imagine a scenario in which your reactor is made up of a material which can withstand only about 700 k because you are going to operate it at 500 k or below 500 k.

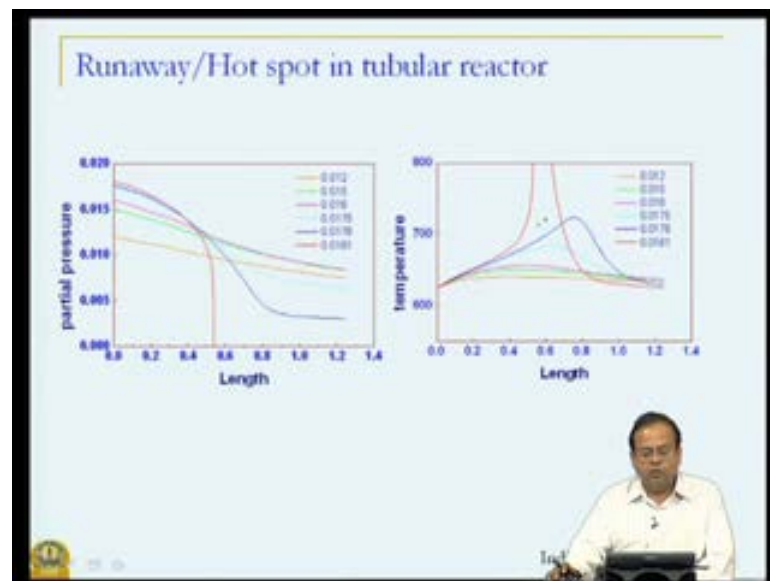
So, we thought to give a safe margin let us make a reactor which can withstand up to 700 k. And look at what will happen if you have a operation like this we will have temperatures reaching as high as 800 k, resulting into complete melt down of the of these material, because stability was or melting point was only about 700 and then we never know what will happen. If the reactor assure recipe for an accident, it is a matter of little consequence that temperatures also comes down, now why do they come down here they come down here, because in this particular this was a control experiment they come down, because by the time temperature reaches to such a high value your reactant is almost completely exhausted and therefore, you have you have reaction almost stopping almost instantaneously.

So, no heat generation anymore and you have a complete **complete** meltdown. On the top what you see is a plot in which this is called heat of reaction parameter, on x-axis and we will see what that parameter is in a in a minute versus cooling parameter. So, heating versus cooling and again a kind of separate risk, were these is my low temperature operation that is safe operation, this is my high temperature operation or something that I need to need to avoid once again. I will emphasis the fact that transition between this low temperatures to high temperature need not occur, because of some significant change in any operating condition. A small few percentage point change is enough for this behavior to take from. So, now let us try to understand what it that is making this operation so sensitive is.

Or in other words what we have what we have seen so far this tubular reactor batch reactor or stirred tank reactor three different types of reactor. So, we have covered all the basis is that a small perturbation in an operating condition can cause significant deviation from the normal operation or steady state system behavior. And such behavior is default to as parametric sensitivity of a chemical **chemical** reactor. Now all these results that you saw are experimental results that were carried out in a well controlled environment.

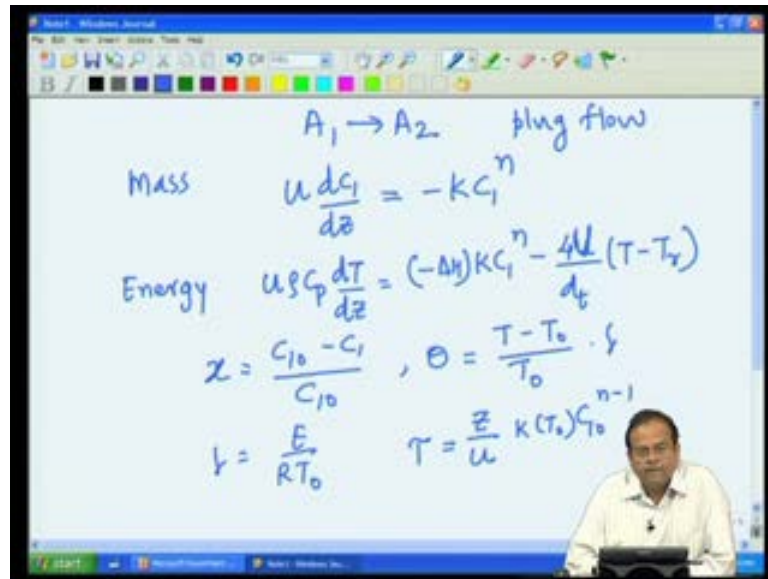
But, it is always not very easy to carry out these reactors where you cause an explosion and yet there is no damage. Just imagine how much safety precautions that you will have to do. So, mathematical analysis of the situation comes handy at least to see what is reason for this kind of sensitive behavior, and further more are there any operating parameter regimes where we can where we can prevent such behavior

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So, we will see that by doing a simple mathematical analysis, and let us try to **try to** look at these analysis for plug flow reactor and behavior of hotspot, because if you realize plug flow reactor and batch reactors I have are equivalent in time and space domains. Space domains for plug flow reactor and time domain for batch reactor they are they are equivalent. That comes out mathematically also, because your mass balance equation are almost identical except we have real time in one case and residence time in other case

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So, let us let us consider a reaction. A 1 going to a 2 in a plug flow reactor whether it is a catalytic reaction or otherwise right now we will not worry about that. So, for this particular reactor our mass balance using our slandered notation we can write $u \frac{dc_1}{dz}$ i am going to assume simple plug flow reactor ideal flow and so on. And just say that this reaction is is a n th order reaction the n th order reaction. So, this is my this is my mass balance. Let us put our energy balance we are carrying out an exothermic reaction and we are carrying out by cooling it. So, we can we can hope that there is a safe operation, but let us see what happens. So, we write the energy balance convective energy transport on the on the left hand side. The first term on the right hand side representing the heat generation, and heat removal rate. So, what am I writing my writing my balances for the concentration or the mass balance for the species a. So, c_1 is the concentration of A 1 in the reactor and energy balance which gives me how temperature will vary t as a result of generation due to reaction and removal due to the coolant which is flowing out side these tube.

So, we are removing this heat the diameter of the tube is d_t u is the overall heat transfer coefficient and T_r is the reference temperature for the coolant **coolant** flowing. So, with these two balances if you look at this balances there are too many parameters in this system. So, let us try to reduce the parameter space by few and it turns out that we will end up with two when we do this by looking at by looking at defining some dimension less quantities. Starting with x as dimension less concentration in this manner which is

nothing, but our conversion $C_1 - C_0$. That is the inlet concentration minus the exit concentration divided by inlet concentration. Let me define my dimensionless temperature as $T - T_0$ divided by T_0 .

Temperature T in the reactor minus what was there at the inlet conditions into gamma we will worry about what is this gamma. This gamma as $\frac{E}{RT_0}$ and residence time τ as $\frac{z}{u}$ into k at T into $C_1 - C_0$ raised to $n - 1$. What is this all this case $T_0 - C_1 - C_0$ raised to $n - 1$ and all that? How did we how did we get that we are going to define this in this manner. So, let us see what we will what we will get and I will just show few steps and show the final result.

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$$x = \frac{C_1 - C_0}{C_{10}}, \quad \theta = \frac{T - T_0}{T_0}$$

$$\gamma = \frac{E}{RT_0}, \quad \tau = \frac{z}{u} k(T_0) C_{10}^{n-1}$$

$$K(T) = A e^{-E/RT} = k(T_0) e^{\frac{E}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)}$$

$$= k_0 e^{\frac{E}{RT_0} \left(1 - \frac{T_0}{T} \right)}$$

$$K(T) = k_0 e^{\frac{\theta}{1 + \theta/\gamma}}$$

For example, our rate constant k which is a function of temperature we can write this as K we will typically write this for a example, as Arrhenius rate law, but we can also alternatively write this as by taking T_0 as a reference temperature. We just rearrangement to serve our purpose and what is the purpose will become clear in a minute. So, this we can write as K_0 and let us take which in terms of our quantity is that we have. We have defined dimensionless temperature for example, we can write this in the following manner. That is my dimensionless reaction rate rather in terms of this dimensionless temperature. So, now, this motivation for making this dimensionless will become clear for example, if I take my mass balance and instead of C_1 express it in terms of x I will end up with the following and appropriate **appropriate**

appropriate τ . So, all I am going to do is put these dimensionless quantities into these mass balances.

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$$\frac{dx}{d\tau} = e^{\frac{\theta}{1+\theta}} (1-x)^n \quad x(0) = 0 \leftarrow$$

$$\frac{d\theta}{d\tau} = B e^{\frac{\theta}{1+\theta}} (1-x)^n - \frac{\theta - \theta_f}{\psi} \leftarrow$$

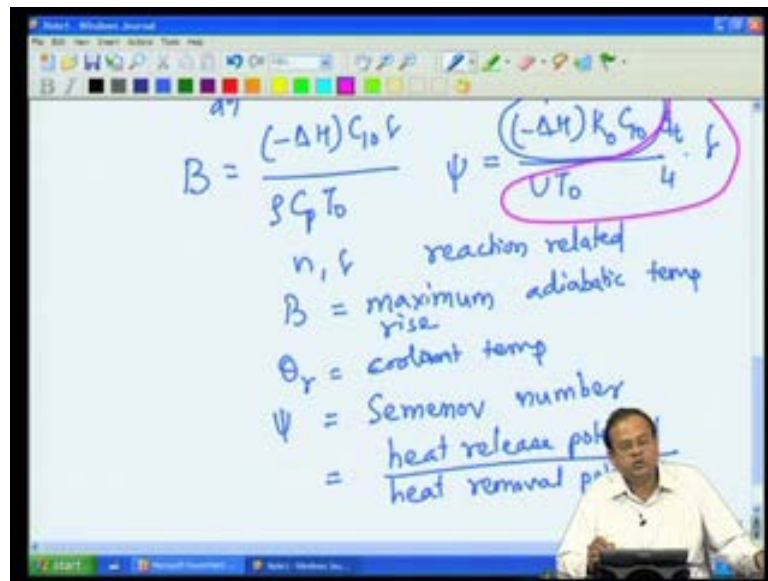
$$B = \frac{(-\Delta H) C_0 \gamma}{\rho C_p T_0} \quad \psi = \frac{(-\Delta H) k_0 C_0 d_t}{4 U T_0}$$

n, γ reaction related
 $B =$ maximum adiabatic temp rise

And I will get my dimensionless equation a mass balance as with concentration dimensionless concentration $x = 0$ at the inlet. Now if I do the same exercise and this is where the little bit of manipulation will come in, that is take this θ put it in this energy balance and put all other dimensionless dimensionless quantities. I get my dimensionless energy balance in the following manner. θ is my dimensionless temperature τ is my dimensionless residence time.

What is my B my parameter B as minus ΔH naught into $C_0 \gamma$ divided by ρc_p into T_0 naught? And my parameter ψ which is pairing in the second equation is minus ΔH $k_0 C_0 d_t$ by $4 U T_0$ naught. Now the reason for writing this in this particular manner is now will become clear. You look at look at this original mass and energy balance, how many parameters did we have there, if you if you consider $U, \rho, c_p, \Delta H, \text{heat transfer coefficient}, d_t, \tau, n$ and all rate constant and so on, but look at look at the behavior in terms of dimensionless quantities how many how many parameters **parameters** do we have in this energy balance and mass balance. We have n and γ , n and γ which are reaction related. B if you are if you remember little bit from our previous dissections is actually nothing, but maximum adiabatic temperature rise, That is that is a maximum temperature rise that you can expect, if the if you are carrying out an adiabatic **adiabatic** operation.

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Theta r is a dimension less cooling temperature or coolant temperature. And an interesting parameter is which is called as Semenov number. And if you look at this terms in this this actually is a ratio of heat release potential to heat removal potential. Why do we why do we say that, because if we actually look at lets down this write down this in form if you look at this is parameter for example, this term is the maximum rate of reaction multiplied by heat of reaction.

So, that is a heat release potential and if you look at the remaining term it is actually one can look at it as u into t not divided by four by four by d t which is actually nothing, but if you **if you** look at this heat removal term. Now what is the maximum maximum potential or it is a measure of heat removal potential $4 u t$ naught by d t and a gamma, because we have non dimensionlized d t in a particular way, but the point is that this parameter si major heat release or rate heats release with visa heat **heat** removal. So, what does a large value of si what would it mean, large value of is would mean, that heat release potential is much higher than heat removal **removal** potential.

Now, let us go back to this equation mass and energy balance and in order to simplify this analysis, we are going to make one assumption which is which is not strictly valid when the reaction is taking place, but is an good approach mission, because we find that this heat **heat** hotspot or these kind of behavior are occurring very early in the reaction. What do I mean, by that if you go back and look at **look at** our example, of this **this** reactor our hotspot is definitely at a early stage when the even before the midway point.

So, what we are going to say is that in order to look at at least qualitatively what behavior we can expect we are going to neglect this conversion phenomenon or reaction or we going to assume that x is very small; that means, not much reaction has occurred if that is the case than I can **I can** write my energy balance the same energy balance.

I am going to rewrite this energy balance by negating this $1 - x$ term, because this value is close to close to unit. So, that is why I said this is not an exact analysis, but is an good **good** approximation.

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The image shows a whiteboard with handwritten mathematical equations. At the top, the equation is $\frac{d\theta}{dT} = B e^{\frac{\theta}{1+\theta/\gamma}} - \frac{1}{\psi}(\theta - \theta_r)$ with $x \approx 0$ written to the right. Below this, the equation is boxed as $\frac{1}{B} \frac{d\theta}{dT} = Q_G - Q_R$. Underneath the box, the heat generation term is defined as $Q_G = e^{\frac{\theta}{1+\theta/\gamma}}$ and the heat removal term as $Q_R = \frac{1}{\psi}(\theta - \theta_r)$. To the right of these definitions, two specific cases are noted: $\theta = 0 \Rightarrow Q_G = 1$ and $\theta \rightarrow \infty \Rightarrow Q_G = e$.

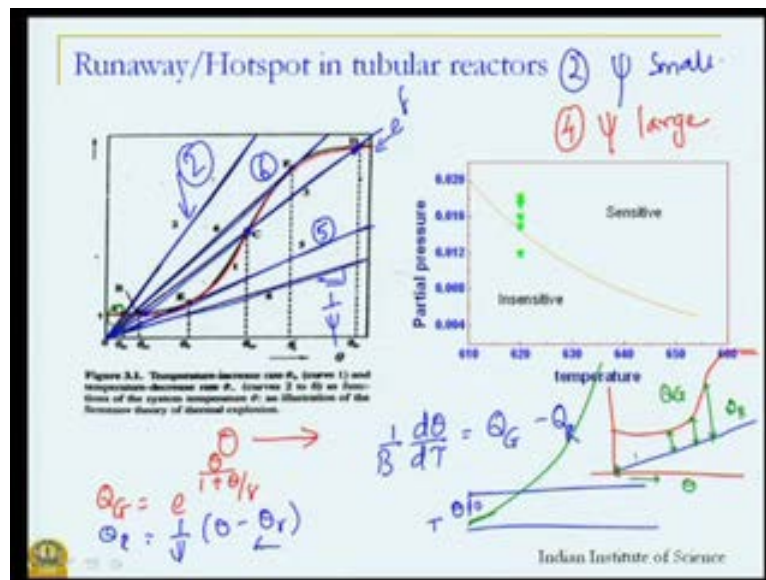
So, what we are going to say is that my energy balance is of this kind $d\theta/dT = 1/B \left[e^{\frac{\theta}{1+\theta/\gamma}} - \frac{1}{\psi}(\theta - \theta_r) \right]$. That is all I have done is in this particular **particular** equation in this particular **particular** equation I have neglected **neglected** x I have assumed it to be very small value. So, if we **if we** **if we** like we keep B on this side or you we do not like it at this poking let us bring B over here. Now if we see that since our θ behavior is gone I can now look at this behavior of the system since our x is gone, we can look at by simply looking at this θ equation. So, I have taken x to be very small value. So, once again this.

What is this term this is heat generation term. So, Q_G and what is this term heat removal term. So, Q_R and for sake of simplicity I mean, just to just to make things little more simpler I am just going to take B on one sides, because its common in both these factors and we are just font to say this is $Q_G - Q_R$ divided by b , but if I express Q_G as

just erase to theta by 1 plus theta by gamma I am I am still still. So, what is this energy balance trying to tell us it is trying to tell us what we expect actually? That change in temperature along the length of the reactor will be a result of imbalance between the heat generation and heat removal that is that is what we expect. So, if a generation is more than heat removal we can expect increase in temperature if heat generation is less than heat removal we can expect the lowering of temperatures along the length of the length of the reaction.

Now let us try to graphically see how this two terms depend on the temperature. So, if we look at this Q G term which we have said that this is just theta by 1 plus theta by gamma. What happens to this Q G term when theta is 0 that is we are temperature is at the inlet condition Q G is 1 right, because it is only function of theta and when theta becomes very large goes to infinity let us say, in reality we will never go to infinity this will be e race to gamma. So, Q G goes to e race to gamma. So, some kind of a saturation and what about Q R if you look at Q R which is one over si theta minus theta r. So, Q R is also function of dimension less temperature theta and we can we can see how it changes with theta the relationship is linear with the slope one over one over si.

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So, now, let us let us try to look at graphically how this two functions functions look like. What we are seeing here what we are seeing here is temperature theta on x- axis and a function Q G which was e race to theta by 1 plus theta by gamma which is shown by this red line red line over here. And function Q R which is one over si theta minus theta r

graphically we will look like straight lines which are these different lines that we see with the slope $1/s_i$. So, there are various these different lines but slope of this line is $1/1/s_i$. Now and what is our energy balance our energy balance is Q_G minus Q_R . So, on the y-axis we have two different types of heat rate one generation rate and one removal rate generation rate showed by red line with we saw earlier this limit is e^{γ} and value is one when θ is θ_0 . So, now, let us consider a situation where situation where.

We have s_i value very small; that means, slope of these line straight line for heat removal rate to be very large, and this is what this curve which shown as number 2 over here indicate. Now what does what this particular value of s_i indicates? So, what **what** we have at point 0.2 our s_i value is small. What does it mean? It means that our heat generation rate is much smaller than heat removal rate. So, now, let us try to imagine how this reactor behavior will take place if **if** our **our** temperature is as we proceed along the length of the length of the reactor. We start with θ equal with 0 θ is 0 at the inlet. So, we start over here. We see that Q_G is higher than Q_R . So, temperature will start increasing. So, I am just going to plot a simple sketch here just to just to illustrate the idea that how temperature **temperature** will increase, but what happens as my temperature is increasing I think I need to need to just enlarge the figure. So, that we are we are together on this. So, this is my heat line removal line and this one let me let me make it even more bigger. So, this is my heat **heat** removal line and heat generation line and let me show my heat removal line that this line 2 is at least little bigger.

So, we started our operation we started our operation somewhere over here somewhere over here. And we see that heat generation heat generation heat generation is heat generation is more than heat removal. So, temperature will slightly increase, but what is happening us temperature is increasing temperature increase means, what we are we are moving in this direction. As temperature is increasing the generation rate gap and the removal rate gap that is this gap is narrowing down; that means, what as we are proceeding as the reaction is proceeding in the reactor the rate of increase in temperature is going to go down, because generation rate and removal rate is gap is lowering; that means, these two difference is lowering. So, temperature increase will lower and it will keep on lowering or in other words temperature will never exceed these particular value whatever that value θ_m .

So, temperature will always remain below that particular value. In other words the temperature we will have a safe operation right, because temperatures would not rise. Now, let us consider an operating line such as four where Si value is large and the slope is small. So, let me try to use the same logic and without going into too much details let us try to see what will happen in the reactor let me just enlarge this figure for this case also. So, these are our heat generation curve and for sake of argument let us say my heat removal curve is something like this. So, let us see now how our temperatures will vary we start over here we see that the gap is large.

So, temperature will start increasing. So, as the reaction process this is Q_G and this is Q_R removal rate. So, what is happening as our temperature is increasing because this is my $\theta = 0$ and in temperature started increasing it appears that the gap is narrowing down, but we see that there is always a positive difference between heat generation and heat removal what it would mean, that if you look at this energy balance Q_G is always greater than Q_R ; that means, this temperature will always keep rising temperature will always keep rising something very similar, to what we saw when the hotspot occurs. That is if our parameter value Si very small we have a safe operation as shown over here, but if Si value is large; that means, heat generation potential is much larger than heat removal potential than what we see in principle is that the temperature will always keep on increasing. What about Si values intermediate we see that for Semenov numbers which are intermediate, we see that for some values such as 3 we can have 3 different values of intersection points and this 1 over 5 here and 6 here.

What are these two lines these two lines are actually tangent the straight line which are tangent to this curve they have their own significance and they in turn determine the critical parameter ranges that we talked about when we had these sensitive and insensitive regions. We will stop here for today, and continue this discussion in the next session where we will see how we determine those critical operating conditions and what happens actually when the reaction is also taking place, because this is all discussion based on no reaction taking place. So, that is a topic that we will start with in a next session thank you.