**Chemical Reaction Engineering**

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## Lecture No. #23

## Gas-solid Catalytic Reactions – Nonisothermal effects

Friends, let us continue our discussion on gas-solid catalytic reactions, and today we will wrap up this discussion; in the last session, we were looking at nonisothermal catalytic reaction in the pellet. That is heat effects are not negligibly small; and therefore, depending upon the type of reaction, namely if the reaction is exothermic, then temperatures inside the catalyst pellet will be higher than the bulk temperature; whereas, the concentration will always be lower, and if the reaction is endothermic then temperature inside the catalyst pellet will be lower than the temperature at the bulk.

Now, if both concentration and temperatures are lower, as is the case with the endothermic reaction - the rate of reaction will be lower, inside the catalyst pellet compared to that in the bulk. But for exothermic reactions, if the temperature is high even though concentration may be low; the higher temperature may result into rates of reaction inside the catalyst pellet, higher than those occurring at bulk condition. And hence, the effectiveness factor which is the major of our observed rate to rate if, at the bulk condition could be greater than one; that is one aspect that we had seen in the last session.

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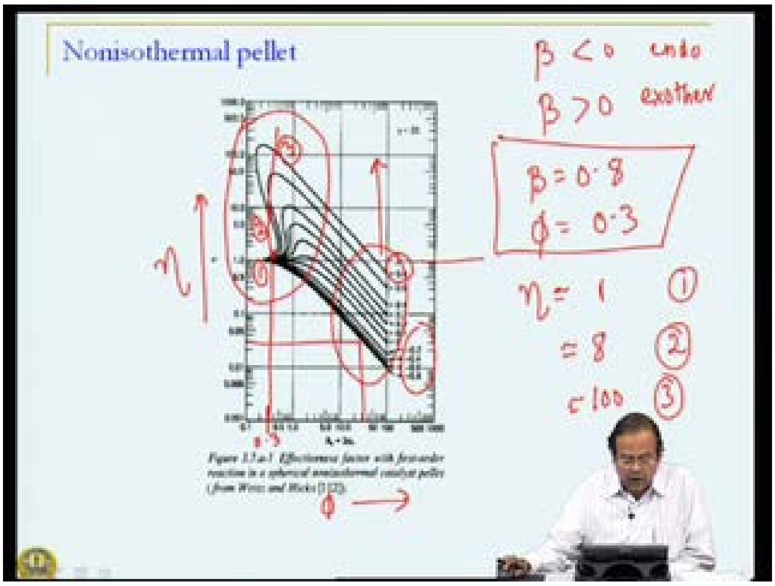

Nonisothermal pellet

So, let us look at it one more time. So, what we were saying is this is our thiele modulus on the x axis, this is our effectiveness factor on the y axis, and we characterized our reaction whether it is exothermic or endothermic by looking at a parameter value beta, the pratter number which is a measure of maximum temperature rise, if this number is less than zero, we have endothermic reactions.

And if reactions are endothermic, as is the case with all these case is over here. So, the effectiveness factor is uniformly less than one, as we are increasing the thiele modulus. But if reaction is exothermic; that is beta is greater than zero, then we have effectiveness factor greater than unity; this is our unity level. So, you have effectiveness factor greater than greater than unity, and the reason for which I just now mentioned; that conditions inside the pellet, namely temperature makes being higher than the bulk, it ensures that the rate of reaction, inside the pellet is higher than that in the bulk, and leading to average values also being being higher.

Now, there is another feature of nonisothermal pellet which is also apparent in this figure. And we will spend some time looking at that behavior - that behavior is namely, let us say that I have my thiele modulus value 0.3, you could choose any value, but suppose it is 0.3; and then at this thiele modulus value and beta value let us say 0.8, I have three possible values of effectiveness factor. In fact, what what I am saying is for beta equal to 0.8, thiele modulus equal to 0.3; I could have effectiveness factor which is close to unity that is my solution one over here.

Effectiveness factor which is almost equal to 8 or 9, let me put some value 8 which is my solution 2, and effectiveness factor which could be as high as 100. This is my solution three. So, for same value of reaction conditions - I could in principal have 3 different values of steady states. A behavior which is characterized by multiple steady states; everything else is same - it is a same catalyst pellet, the properties of the catalyst pellet are same; my my thiele modulus or diffusional resistances whatever it is, it is same the reaction, heat of reaction everything is same, but then how come we do not have a unique solution. If you look at solutions in this regime, these are all unique solutions; given a value of thiele modulus. I have a effectiveness factor, but in this particular regime over here over here, there is a possibility of multiple steady states.

Now, why do these multiple steady state arise, when we have the nonisothermal nonisothermal reactor situation. The answer to this is not not very straight forward, but we can look at an equivalent equivalent situation, and try to try to understand why is this why is this behavior behavior so important.

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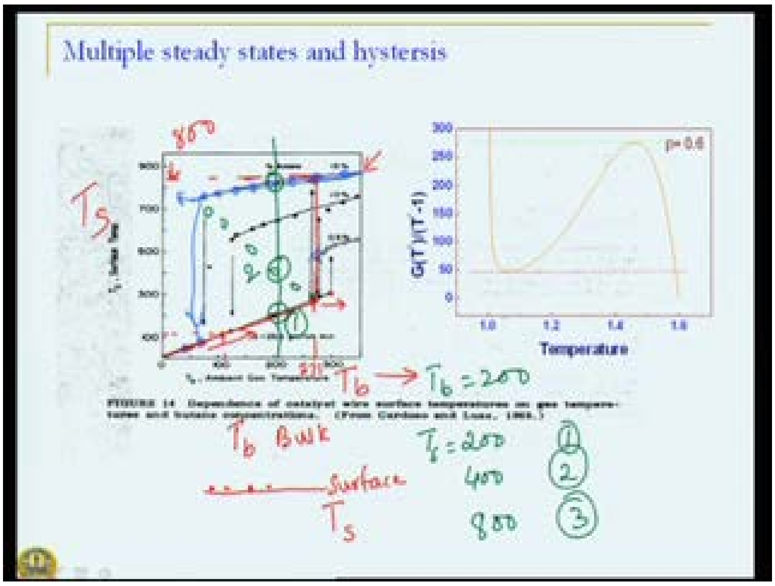

Multiple steady states and hysteresis

We will try to look at this example in a for for a slightly different example. And what what we are we are looking at, is the multiple steady state for a nonisothermal situation, catalytic reaction, but slightly slightly different. What is happening in this particular

particular reaction is butane, dehydrogenation to butene over a catalyst; and this catalyst is now, a wire catalyst - a thin wire; and the elements are only on the catalytic elements are only on the on the surface of these wire. So, there is no diffusion to speak of; so what is important here is you have bulk, and then you have surface, and the entire reaction is is on the surface. So, there are only external resistances in this particular particular case. So, first let us let us look at look at, the the behavior that we see here. So, what we are seeing here, is a bulk temperature bulk temperature on the x axis, and surface temperature that is temperature actually on the surface of the catalyst T s; that is on the on the y axis.

So, what do we what do we see here. We see here the following following behavior. As I am increasing my bulk ambient temperature, as I am increasing my bulk ambient temperature, my surface temperature is increasing; and it is increasing in this particular manner. So, these are all the all the points, that we that we will get. This result is for different values of different values of butane concentration, so let us focus on one particular example over here. Now, if you notice these solutions, my bulk temperature is around hundred; the surface temperature is also around hundred. I mean approximately; that means, there is very little reaction that is taking place, because if the reaction was to take place, and it is a exothermic reaction, temperature should have been should have been higher.

Now, let us look at the solution at this particular particular point. As we are increasing our bulk temperature let us say beyond 275, suddenly we find that surface temperature is much higher; surface temperature is about 8 800 in the 8 range of 800. So what have we done, we have not we have done a simple experiment where we took butane, we took catalyst in the form of wire; and brought about the reaction, and then kept varying the bulk temperature. So, I started with low bulk temperature of 50, I found my surface temperature is also 50 and so on. So, I got the set of solutions, where surface temperature was almost same as the bulk temperature.

Now, after about increasing the bulk temperature beyond 275, and these are all approximate numbers; just to illustrate what is what is the idea here. So, after we increase the bulk temperature beyond 275, I found that my surface temperature was suddenly around 800; my wire became extremely hot. There was lot of reaction that was that was taking place; and then any increase in temperature beyond this, I got I got the same high high temperature. So let us say, this is one high temperature, this is another high temperature and so on. So, I had I had this.

Then I decided to reverse the direction of change in bulk temperature. That is I was at at this particular particular , this particular temperature 800. And bulk temperature let us say 300, almost 500 degree change. That means there is lot of reaction. So what I did was, we start now cooling the bulk. So from 300 I went to 275, 200 and so on and so forth, and I found that my wire was fairly hot still. It is about 750 degree centigrade, but when I lowered the bulk temperature beyond this 75 degrees or so; once again, I saw my wire was now cold or in other words what has happened is as, I kept on increasing my bulk temperature; I travelled along this line, my solutions were along this line, at some point the temperatures suddenly increased, and then as I kept on increasing the temperature I followed this blue line. When I reversed the direction that is kept on lowering the bulk temperature, I got this solution, and then suddenly temperatures dropped down.

Now, how does this relate to multiple multiple steady state. What is not seen, because this is experiment is that there would have been alternate alternate set of solution, and we will see that when we do an mathematical analysis, some set of solutions over here. Which you cannot get in a numerical in a experimental situation, but they are there; and I will I will illustrate that to you, in in just few minutes. But what what therefore, it implies is let us say that we had a bulk temperature of 200.

At this bulk temperature of 200, I had a possibility that my surface temperature is also 200, so my bulk temperature is same 200; surface temperature is 200, solution one or it could have been somewhere over here, I mean this is just an approximate value, but believe me that solution is there, around 400 that is solution 2 or this value which is about 800 solution 3.

A behavior which is similar to what we saw in the previous previous scenario; that is same value of bulk conditions. I could have three different values of my surface temperature or 3 different ways in which my wire will be present or 3 different extent of reactions. Hardly, any reaction a whole lot of reaction to 3, hardly any reaction in 1, and intermediate intermediate in 2.

So now, let us try to understand or analyze this situation. This is easy to analyze and therefore, we we will analyze this. But I want to again draw an analogy with the previous scenario; that is same conditions three different solutions 1, 2, 3. The reason for both these solutions is same, the reaction is exothermic; only here, we are looking at internal mass an energy transport limitation, we will illustrate this same idea with external mass transfer limitation, which is relatively easy to easy to look at.

So, let us try to go back and look at this look at this scenario, and try to develop the energy and mass balances; so that, so that we have we get a clear understanding of what is happening.

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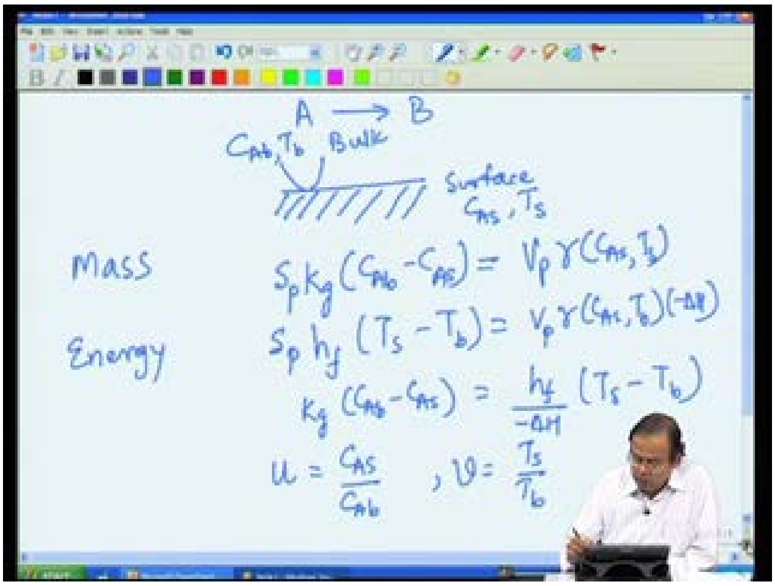

Mass $\quad S_p k_g (C_{Ab} - C_{As}) = V_p r(C_{As}, T_s)$

Energy $\quad S_p h_f (T_s - T_b) = V_p r(C_{As}, T_s)(-\Delta H)$

$$k_g (C_{Ab} - C_{As}) = \frac{h_f}{-\Delta H} (T_s - T_b)$$

$$u = \frac{C_{As}}{C_{Ab}}, \quad v = \frac{T_s}{T_b}$$

So let us say, that we are looking at reaction A going to B; it is taking place on the surface of the catalyst. Now, this is not a porous catalyst, but it is a it is a, it is not a non porous catalyst, but it is a non porous catalyst, that like a wire. so just to illustrate. So this is my surface, this is my bulk. So, my concentrations here would be C Ab, temperature would be T b, on surface it is let us say C As, and surface temperature T s. So, concentration will decrease from C Ab to whatever value, and temperature will increased if it is a exothermic reaction.

So let us first write the mass balance for this, mass balance. What is happening on the surface, the material is diffusing; so film theory, so our rate of mass transfer is K g into C Ab minus C As; and we want to express it, this is per unit surface area; so let us say surface area per per a gram of or per unit volume of volume of catalyst or this is our surface area, and this must be same as the rate at which reaction is taking place on the surface. So, at these conditions C As and T s multiplied by the volume of the, to keep the units consistent.

So this is my mass balance; we can immediately write a similar energy balance, which says Sp into h f into Ts minus Tb equal to same rate, but now energy is involved so into minus heat of reaction delta h. So, now if we, if we divide these two equations; so what we have achieved, is we have written mass and energy balances. And you will see, now similarity with with our approach, when we talked about when we talked about mass and energy balance for internal diffusion. Because the approach is same; the physics is different, but the approach approach remains the same. So, now if we look at these two equations, I can I can divide this first equation by second equation, and do a rearrangement; and what what we will get is K g into C Ab minus C As will be equal to minus delta h or rather sorry…

We will get h f divided by minus delta h into T s minus T b. So, just combine this mass and energy balance balance together. Just as we did earlier, let us define our dimensionless concentration as C As by C Ab. so that, everything goes between 0 and 1, and T s by T b. So if we if we do that, then we can write our mass and energy balances, which we have defined over here, in terms of dimensionless dimensionless quantities, and we will essentially get by by taking these two equations together.

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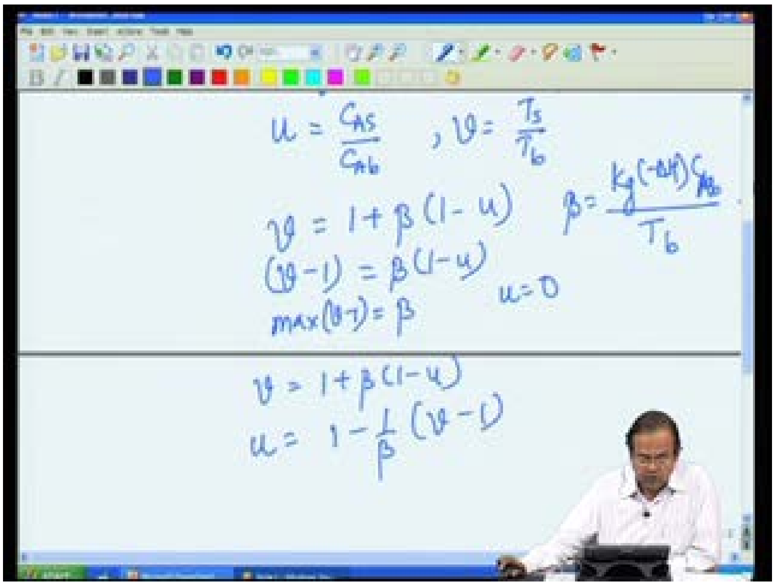

$u = \frac{C_{AS}}{C_{Ab}}$ , $\vartheta = \frac{T_s}{T_b}$

$\vartheta = 1 + \beta(1-u)$ $\beta = \frac{k_g(-\Delta H)C_{Ab}}{T_b}$

$(\vartheta - 1) = \beta(1-u)$ $u = 0$

$\max(\vartheta - 1) = \beta$

$\vartheta = 1 + \beta(1-u)$

$u = 1 - \frac{1}{\beta}(\vartheta - 1)$

We will get V equal to 1 plus beta into 1 minus u, where beta is now kg minus delta h C b by C Ab by bulk temperature; u is the dimensionless concentration, V is the dimensionless temperature. What is this beta? Beta once again, is is has a has a significance, similar to pratter pratter number. Because if you look at, when u is 0, temperature at the surface is different from the bulk or we can write V minus 1 which is temperature difference as beta into 1 minus u; so, beta is the maximum value of V minus 1, because that is when u is 0. And what is V minus 1, surface temperature minus bulk temperature divided by bulk. So that is the dimensionless delta t. Now, you will realize the same thing that we talked about, when we looked at internal internal diffusion.

So now, we can we can go back to our mass balance and energy balance equations, and instead of temperature we can write in terms of concentration or other way round u as 1 minus 1 by beta into v minus 1; they are both trying to tell us tell us the same thing.

Last time we looked at in terms of concentration. So, let us try to look at look at the whole whole behavior in terms of terms of temperature now. So, let us go back to go back to our go back to our energy balance which we had over here; this energy balance, but now, if we write it in terms of dimensionless quantities u and v, and in particular writing u as in terms of in terms of v, then we get the following. Let us let us try to work it out, and see how we how we get that.

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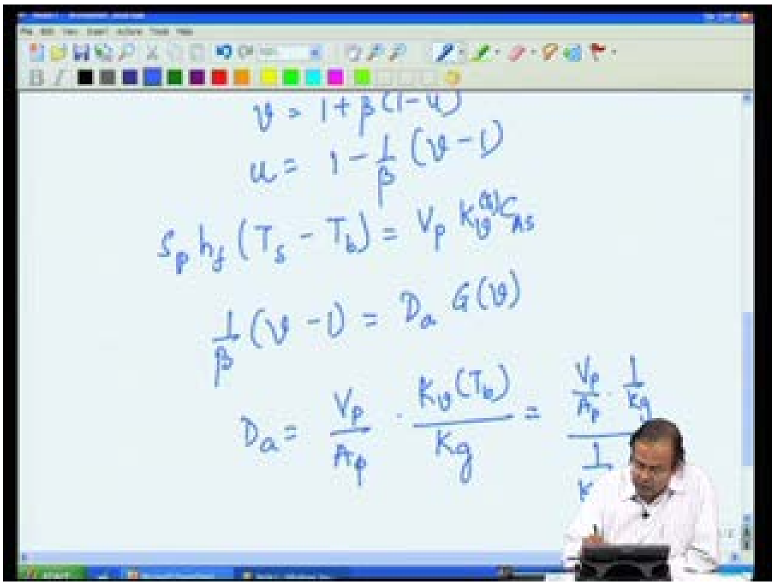

$$v = 1 + \beta(1-u)$$

$$u = 1 - \frac{1}{\beta}(v-1)$$

$$S_p h_f (T_s - T_b) = V_p K_v^{(s)} C_{As}$$

$$\frac{1}{\beta}(v-1) = D_a G(v)$$

$$D_a = \frac{V_p}{A_p} \cdot \frac{K_v(T_b)}{K_g} = \frac{\frac{V_p}{A_p} \cdot \frac{1}{K_g}}{\frac{1}{K}}$$

So, we have S p into h f into T s minus T bulk equal to V p into let us say rate constant K v into rate of reaction C As; this is all at temperature temperature of the of the surface. So, if we now do all this rearrangement, we are we are left with the following. If we rearrange these equation by taking u, v, and so on; we will get one by beta into V minus 1 equal to Damkohler number D a into G of V. What are these Damkohler number? Beta is what we have already defined over here, it is a measure of temperature increase. Damkohler number it it it works out to be V p by A p into K v evaluated at bulk conditions divided by the mass transfer coefficient. Which we can we can write in a in a manner that we wrote earlier, V p by A p into 1 over K g divided by 1 over K v.

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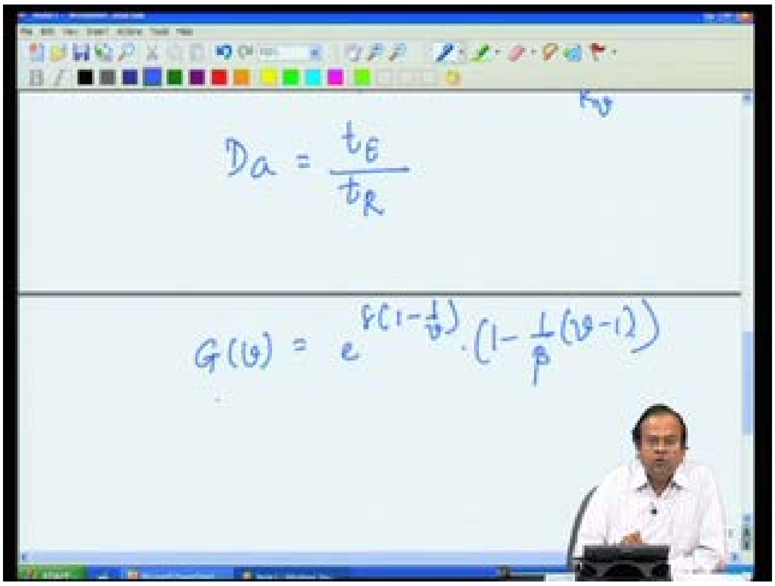

And what is V p by A p 1 over K g, that is the time scale for external mass transfer, and 1 over K v is the time scale for reaction. So, Damkohler number D a is a measure of or a rating parameter for external mass transfer resistance to external external reaction rate or kinetic kinetic rate, the time scales. Similar, to thiele modulus which we defined earlier; which was comparing the internal diffusion process to reaction process, here since we have looking at only external, we have we have this particular particular expression.

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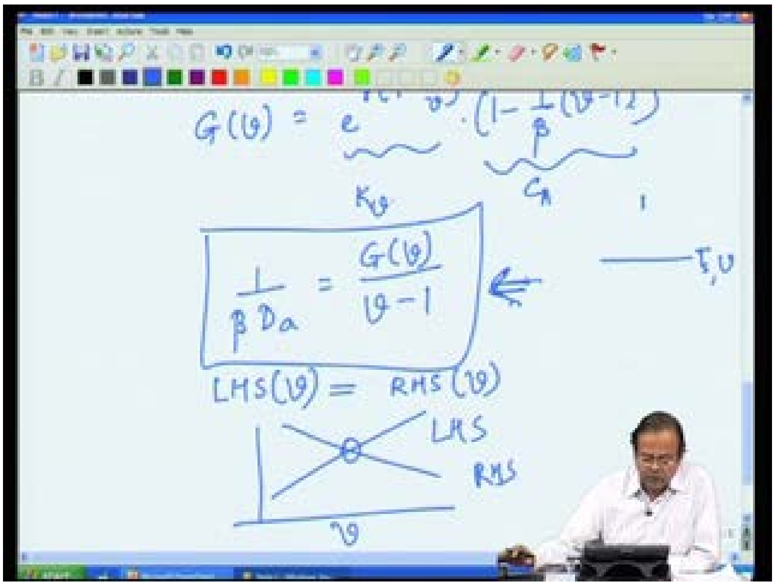

Now, what is this G of v? This G of v is a little involved function of of v, but but mathematically G of v is e raise to gamma 1 minus 1 by v into 1 minus 1 by beta into v minus 1. This is actually the dimensionless form of a reaction rate. And you can see that this is from coming from K v, and this is coming from concentration C A. In respective dimensionless dimensionless form; so let us let us put this two together, so what what these equation equation is doing is our mass and energy balance; so let us let us rewrite that energy balance differently, so we get one over beta into Damkohler number as G over V divided by V minus V minus 1.

So, the let me let me recap once again, we have a catalyst surface; temperature here is T s or in terms of dimensionless quantity V, the bulk condition is one, and the energy balance gives us by doing all these algebraic manipulations that we talked about basically, what we did was we wrote mass balance, we wrote energy balance, defined dimensionless quantities, and put all these things together. Finally, we ended up with a single solution, a single equation in terms of dimensionless temperature. So, the solution V, that is the dimensionless dimensionless temperature is given by this particular particular equation. So now let us try to see, what happens to this what happens to this solution. How does how does temperature changes as we are changing beta and Damkohler number.

So, let us let us look at that look at that solution, and what are we essentially looking at. We are one way of solving a equation, this is a equation, this this is a equation in single unknown V; so once we know the value of beta and Damkohler number, we can solve this solve this equation for a value of V, numerically you can solve it. Remember this G of V is not a simple expression. So, you may not get analytical solution, but certainly numerically you can solve it. But there is a graphical way of also solving this solving this equation, and which makes it easy to to understand; you know as they say, one picture is worth thousand words. So, how do you how do you solve this graphically; typically this is how it is done.

Look at this right hand side, and left hand side. So, this left hand side is equal to right hand side is the solution of this equation. There is only one unknown V, so why not we plot right hand side as a function of V, left hand side as a function of V, and then the solution of these equation must be the intersection of these two curves. Right hand side equal to left hand side; so typically, I am not saying for this equation; let us say that this is my left hand side, this is my right hand side as a function of V. So, the solution L H S equal to R H S must be the intersection intersection point. We will apply the same logic to our energy balance, and try to see how is the solution emerging.

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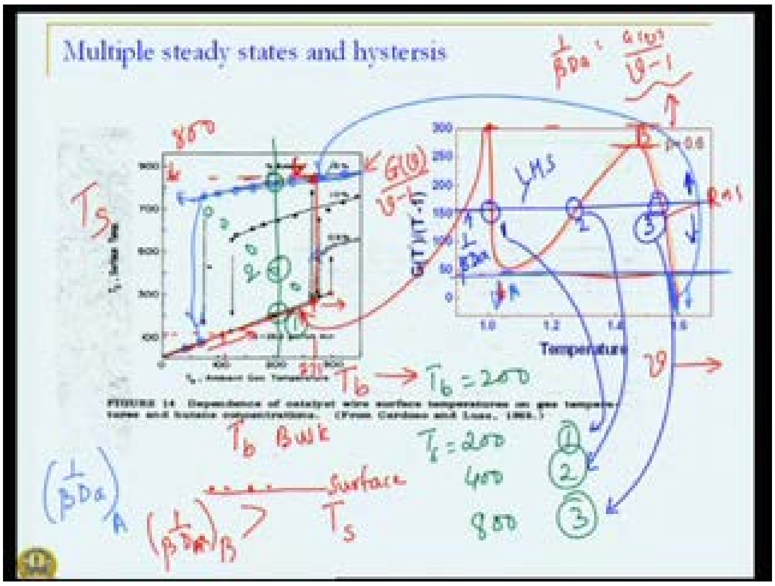

Multiple steady states and hysteresis

So, let us look at this look at this plot over here, so what we are seeing here is that what we are seeing there, is is the solution of dimensionless temperature, against see our equation is one over beta into Damkohler number equal to G of V divided by V minus 1. So, our right hand side as a function of V is plotted over here, G of v divided by V minus 1, and this solution is is of this particular particular form.

Why why this particular form. The reason being that this this is coming from our rate rate of rate of reaction; as our temperature is temperature is, let us say v is 1; the solution has a infinite value, this this particular. And as we are increasing temperature, it has this this kind of kind of set. Now, what is our left hand side; so this is my right hand side. What is my left hand side? Left hand side, if you look it is a constant, it is does not depend on V, the left hand side. So, left hand side as a function of V is just nothing but a straight line. So this is my left hand side, for a given value of one over beta into Damkohler number.

So now, now we can see that for a given value of Damkohler number, I could have possibly 3 solutions. 3 solution 1, where if you look at look at just mathematically; solution 1, the temperature is very close to unity; that means coming back to this example, this particular line; where bulk temperature and surface temperature is almost close to unity. Solution 2 intermediate, and solution 3 where temperature dimensionless temperature is fairly fairly high. Now, we see the connection between the experimental observation, and why we are getting this multiplicity of steady state. The only thing remaining that is that is required is here we change the bulk temperature, here now what do we change - we change this constant. So this line will go up or down, depending upon the values of one over beta into Damkohler's number.

So now, how is Damkohler number related to bulk condition; if you if you look at this Damkohler number definition over here, Damkohler number depends on temperature K v of T b. So, temperature bulk temperature will influence Damkohler number, what about what about beta beta also is influenced by the bulk temperature; over, because there is… So, in changing bulk temperature is equivalent to changing one over one over beta into Damkohler number. So, dependency of beta on Damkohler number is or beta into Damkohler number will be proportional to K g of T b divided by T b.

So, if you change bulk temperature, you will change the Damkohler Damkohler number into beta. So, now, we know how that bulk temperature change is equivalent to equivalent to change in this one over beta a. So, let us look at what happens when your one over beta a, beta value is at this lower limit. At this lower limit; then what happens, any bulk temperature or any one over beta a value in this region, there is only one solution of high temperature. That means, which branch we are looking at we are looking at, high temperature high temperature branch.

Any to be consistent with with the color we use for the first figure; so what we are saying, is let us say that this is the critical value of beta. Let us say that critical point e. So, any value of one over beta D a at a point, and any lower value; this is a tangent, the flat line is tangent to this curve, at this particular point. So, if you are looking at any solution over here, any solution and any beta value below here, there is only one solution; and that is of a high temperature. So, this is my high temperature regime, which corresponds to this particular particular solution. What about other way round? Any let us say this is another critical point beta, so let me now erase few things it is getting crowd it.

So, any any let us say this point b; so any beta D a D a Damkohler number at point B, and greater than that; that means, on this regime. So, where is my solution - my solution now will be only close to unity that means, this particular particular regime. So, any any any parameter value, any parameter value lower than this particular, lower than this particular critical limit, anything lower than that I am on the upper branch. Anything above this upper upper limit this green line over here or red line over here, any value of parameter above this I am at a lower branch. And in between these two values, you see there are 3 solutions; it turns out that this particular solution is inherently unstable, the only solutions you can experimentally get is solution 1 and 3; that is a characteristic of typical 1, 3, 1 multiple multiple steady state. This is called 1 3 1, because if you change this parameter one over beta D a, we go from 1 steady state to 3 steady states to 1 steady state again. So that is why, it is called 1 3 1; the intermediate 1 is typically inherently unstable.

So this is a behavior which is typical of non isothermal catalytic reactions, illustrated even with the experimental scenario; we will come back to this behavior, when we talk about reactors which is little little later on. So, what we what we have seen so far, and we will conclude with this the discussion on non catalytic reaction, and we will now initiate discussion on non catalytic gas-solid gas-solid reactions. So, let me let me refresh ourselves of what we saw in the session on gas-solid catalytic reactions.

We started by saying that, whenever there are more than one phase, we have boundaries and therefore, whenever there are boundaries; there are resistances to transfer both for mass as well as energy. Given this fact, how does these resistances or how does this mass and energy transport process influence my reaction; that was the focus of our discussion for last several sessions. So, we started looking at external mass transfer and energy transfer limitations, in internal mass and energy transfer limitations. We started our discussion, basically with a first order irreversible reaction in an isothermal pellet, following a simple first order first order kinetics in a slab geometry.

Here, the idea was to see, how does mass transfer limitations influence the rate of reaction. And we saw that whenever there is a resistance to mass transfer, as is the case in a porous catalyst, the concentrations inside the catalyst pellet are lower than the bulk and therefore, rates of reactions are lower. In order to characterize how important or how much is the extent of mass transfer limitation, we define the thiele modulus; which is a ratio of time scale of diffusion to time scale of reaction. So if diffusion time scales are longer than the reaction, that means diffusional resistances are stronger; and therefore, thiele modulus which is the ratio of these two time scales has a high value. And if thiele modulus has a high value, we get a indication that this is a situation of mass transfer limitation.

Now, under these conditions, the concentrations inside are significantly lower than the bulk; and therefore, the average or observed rate that you get is also significantly lower than that in the in the bulk. Now, when the rates are lower, how do we characterize them. So, we characterize them by taking the ratio of this, and calling it an effectiveness effectiveness factor.

Now this effectiveness factor therefore, has a value which is close to unity, if thiele modulus is small and it has a value which goes as inverse of thiele modulus - if the thiele modulus value is large. Typical low, small value and large value ranges are… thiele modulus less than 0.3, we say that diffusion is not important. Thiele modulus greater than 3 diffusion certainly is important, and it is a transition between these 2 limits. So this was as far as the slab geometry all these conditions, the reaction was was considered. We then went on relaxing the constants 1 by 1, we saw that even if your geometry is spherical or cylindrical or irregular, you still have a same behavior. We relaxed first order reaction consideration, and looked at general kinetics and you still get a pretty much similar similar behavior.

We considered, how do we determine whether mass transfer limitations are important or not by defining observable thiele modulus, and working getting a experimental measurements to get the value of that thiele modulus, and determining the extent of extent of mass transfer, energy transfer limitation. Now, the whole idea of defining this thiele modulus was that for first order reactions, we saw that thiele modulus depends only on on or rather effectiveness factor depends only on thiele modulus. So, if you know the value of thiele modulus, you can find out what is the observed, rate even without knowing what conditions prevail inside the inside the catalyst pellet.

So this idea has been extended for for several other situations, where the this solution may not be exact. The idea being that, you conduct conduct experiments by considering different extent of diffusional limitations; so thiele modulus being different or for that matter bulk conditions being different, and measure the observed rate. And these relationships between observed rate, and thiele modulus is more or less unique. So, when you actually do your reactions in a big reactors, if you have the same value of thiele modulus, one hopes and by and large one does get the same observed reaction rate, even if the reactor may be of a large size.

So that is a that is a idea; and it is basis is the results are exact for a simplified situation, that is how engineers work. You try to get exact solutions under simplified conditions, and then hope that at least in the small neighborhood of this simplified problem, this approximation or these conditions still hold good. Alright, then we finally, also relaxed the constraint on temperature, namely the reactions are non-isothermal or conditions are non-isothermal; so the temperatures can increase or decrease, and then we saw 2 distinctive behaviors, namely particularly for exothermic reactions. For endothermic reactions the behavior is not so interesting; in the sense that already depressed reaction, because concentrations are lower or depressed even further, because temperatures are also low.

But interesting situation arises for exothermic reaction, because depression due to depression in rates due to concentration depression or lowering of rates due to concentration depression depression is sometimes more than made up by increase in temperature; and therefore, we have observed rates more than that one can get on the bulk conditions. Not only that, you sometimes can get three different steady state values for the exactly identical operating conditions. Something which we tried to explain by looking at case of only external energy transport and mass transport limitation, which is little easy for analytical manipulations, compared to internal diffusion. So, this in short completes our discussion on gas-solid catalytic reaction, and in the next session we will start discussion on non-catalytic reaction; that will be the subject matter for our next session, thank you.