Chemical Reaction Engineering

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Lecture No. #22

Gas-solid Catalytic Reactions - Diffusion and Reaction III

Friends let us continue our discussion on heterogeneous gas-solid catalytic reactions. But this time let us bring in external mass transfer along with internal mass transfer playing an important role when the reaction is taking place.

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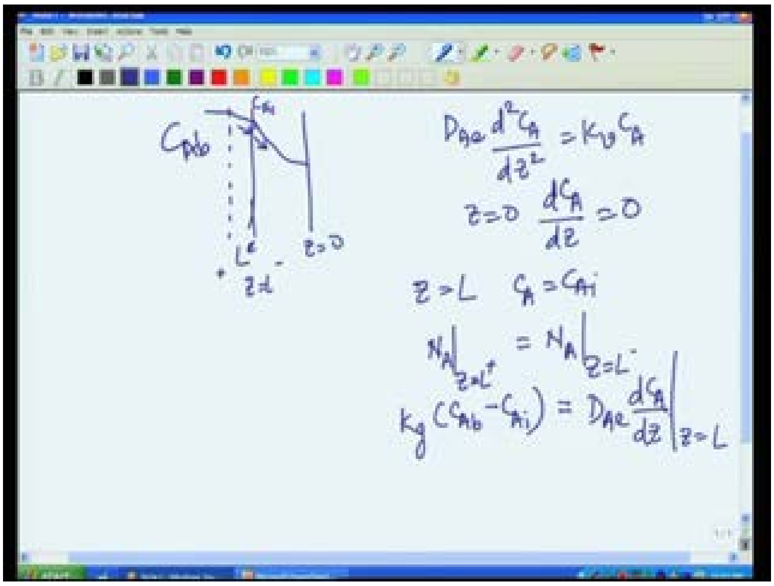

$$D_{Ae}\frac{d^2C_A}{dz^2} = k_v C_A$$

$$z=0 \quad \frac{dC_A}{dz} = 0$$

$$z=L \quad C_A = C_{Ai}$$

$$N_A\Big|_{z=L^+} = N_A\Big|_{z=L^-}$$

$$k_g(C_{Ab}-C_{Ai}) = D_{Ae}\frac{dC_A}{dz}\Big|_{z=L}$$

So, what we considered so far was a slab geometry catalyst half width L is a diffusion reaction and so on. But we assume that our concentration at the surface of the catalyst is the bulk concentration. So, now let us say that there is a external mass transfer resistance, and we will use film theory to characterize this external mass transfer resistance, which says that there is entire resistance to mass transfer is located in this boundary layer mass transfer boundary layer, and beyond this point the concentration is the bulk concentration C Ab. So, there is a diffusional resistance. So, there is a surface concentration, let us say C Ai, we do not know what that concentration is, but this is how, now, the scenario will look like. That is diffusion reaction gas-solid catalytic reaction in presence of internal diffusional resistances and in presence of external diffusional resistances. So, we are bringing now these two ideas together.

Now, if we look at our mass balance within the catalyst, the balance is same as before. There is no change in the mass balance, because whatever has happened is in the change changed condition that we have assumed now outside the surface of the catalyst. So, mass balance inside the catalyst is same with boundary condition at z equal to 0 being symmetric boundary condition namely d C A dz equal to 0. But now the boundary condition at z equal to L at z equal to L which earlier we said that concentration is C Ab. Now, we are saying that, that is not the bulk concentration; it is some concentration C Ai and which I do not know, so I cannot really use this as a boundary condition. But, I do know that since the surface has no capacity to store mass, the flux of A coming from the bulk to the surface of the catalyst must be same as the flux of A going inside the catalyst. Or in other words, if I call this z equal to L, two sides of it minus and plus, then the flux of A at z equal to L plus that is coming from outside must be same as the flux of A that is entering the catalyst catalyst surface.

What is the flux of A L plus coming from outside? Earlier we used boundary condition film theory, so this is the flux which is driving force C Ab minus C Ai multiplied by the mass transfer coefficient. And what is going inside is characterized by the diffusive flux, so this must be equal to at z equal to L. So, this gives me my boundary condition that I require for for the solution of these mass balance equations.

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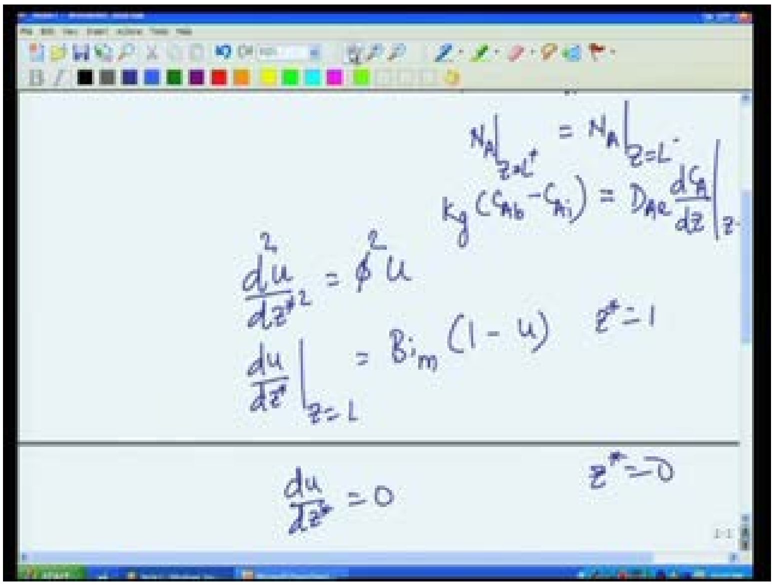

$$N_A\Big|_{z=L^+} = N_A\Big|_{z=L^-}$$

$$k_g(C_{Ab}-C_{Ai}) = D_{Ae}\frac{dC_A}{dz}\Big|_{z}$$

$$\frac{d^2u}{dz^{*2}} = \phi^2 u$$

$$\frac{du}{dz^*}\Big|_{z=L} = Bi_m(1-u) \qquad z^*=1$$

$$\frac{du}{dz^*} = 0 \qquad z^*=0$$

So, now I can make use of this two this two this two balances as well as the boundary condition and in terms of our dimensionless dimensionless quantities. We can once again write our mass balance equation as d square u d z star square as phi square u, I am assuming a first order first order reaction and d u d z star at z equal to L equal to Biot number for mass transfer into 1 minus u at z star equal to 1, and d u d z equal to equal to 0 at z star equal to z star equal to 0. So, this is a symmetric condition at the boundary at the centre point. This is the boundary condition.

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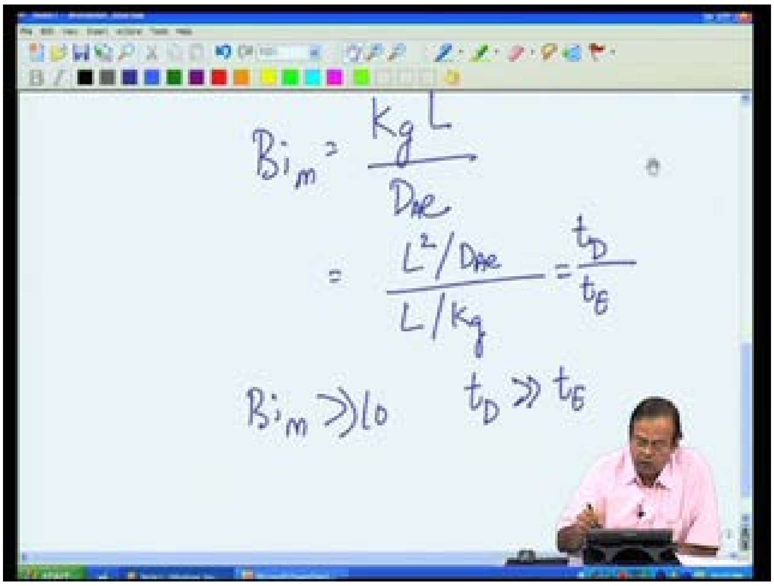

$$Bi_m = \frac{k_g L}{D_{Ae}} = \frac{L^2/D_{Ae}}{L/k_g} = \frac{t_D}{t_E}$$

$$Bi_m \gg 10 \qquad t_D \gg t_E$$

What is my Biot number? My Biot number, if you write everything in terms of mass transfer coefficient and so on. Our Biot number works out to be K g L by D e, K g is the mass transfer coefficient - external film mass transfer coefficient, L half width of the catalyst and D e - the internal diffusion diffusion coefficient or D Ae if you if you keep the notations. This Biot number we can also write keeping our tradition of writing it in terms of characteristic time as L square by D Ae divided by L by K g. And you can immediately see L square by D Ae is same that we defined earlier, characteristic diffusion diffusion time t D, and L by K g is the characteristic external mass transfer time. This involves diffusion coefficient inside the catalyst pellet so that is D Ae, this one is external mass transfer mass transfer coefficient.

So, Biot number actually characterizes what is what is the role played by diffusion internal diffusion, we service the role played by the external diffusion. So, if Biot number is very large, Biot number is very large very, very large, let us say larger than 10 that that would that would mean the time for external diffusion internal diffusion is very time scales is very, very large compared to external external time time time scales for external diffusion. So, Biot number tending to infinity would be the case when external mass transfer is not important, only internal diffusion is important.

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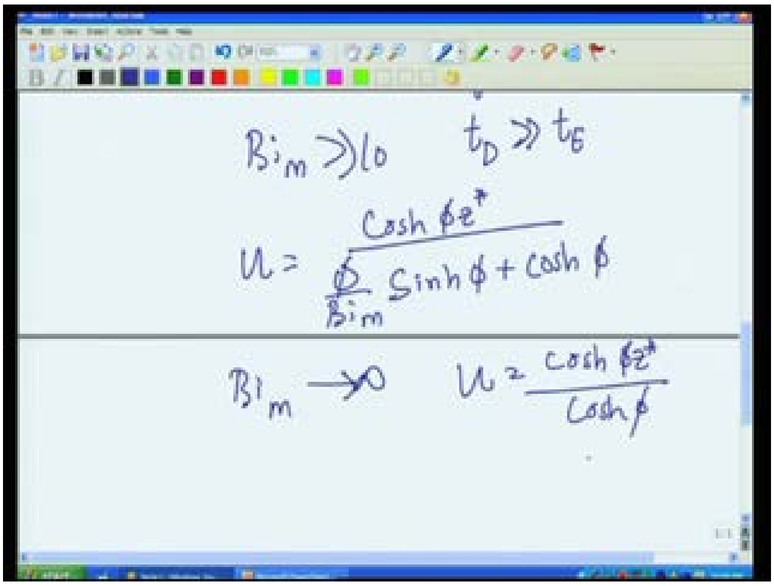

$$Bi_m \gg 10 \qquad t_D \gg t_G$$

$$u = \frac{\cosh \phi z^*}{\frac{\phi}{Bi_m}\sinh\phi + \cosh\phi}$$

$$Bi_m \to \infty \qquad u = \frac{\cosh \phi z^*}{\cosh\phi}$$

In fact we could solve these mass balances with appropriate boundary condition and so on, and then write the solution for u as cosh phi z star by phi by Biot number…

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In fact, this is the how concentration will vary and you can immediately see, when Biot number is tending to infinity, the solution u becomes cosh phi z star by cosh phi which is the same solution if you do not consider external diffusion at all and that is that is what we said just few minutes few minutes back.

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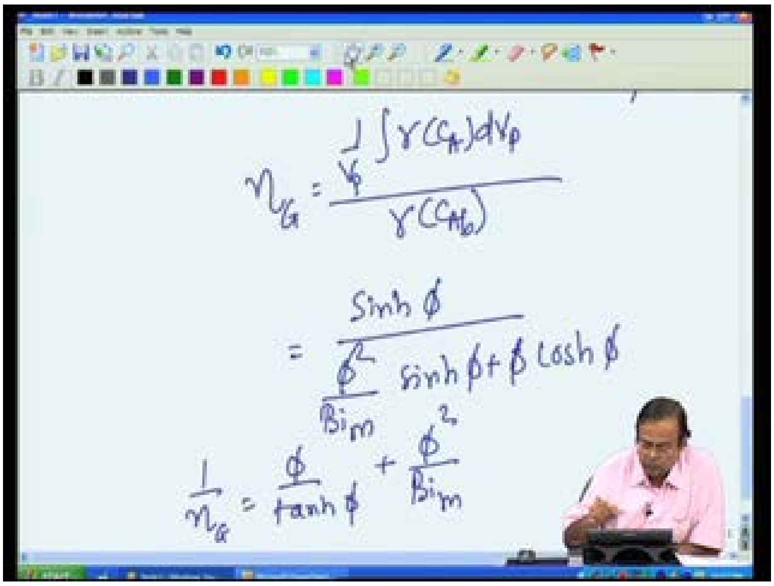

$$\eta_G = \frac{\frac{1}{V_p}\int r(C_A)\,dV_p}{r(C_{Ab})}$$

$$= \frac{\sinh\phi}{\frac{\phi^2}{Bi_m}\sinh\phi + \phi\cosh\phi}$$

$$\frac{1}{\eta_G} = \frac{\phi}{\tanh\phi} + \frac{\phi^2}{Bi_m}$$

In fact, if we now define our define our effectiveness factor, the similar manner as we had defined defined earlier that is the effectiveness factor as 1 over v r of C A dv p are divided by r of C Ab. For this particular case, we can we can simplify this solution as or we can obtain this solution and write it as for example, we can write eta G as this is we are considering only first order kinetics, we actually can write which upon rearrangement actually gives us…

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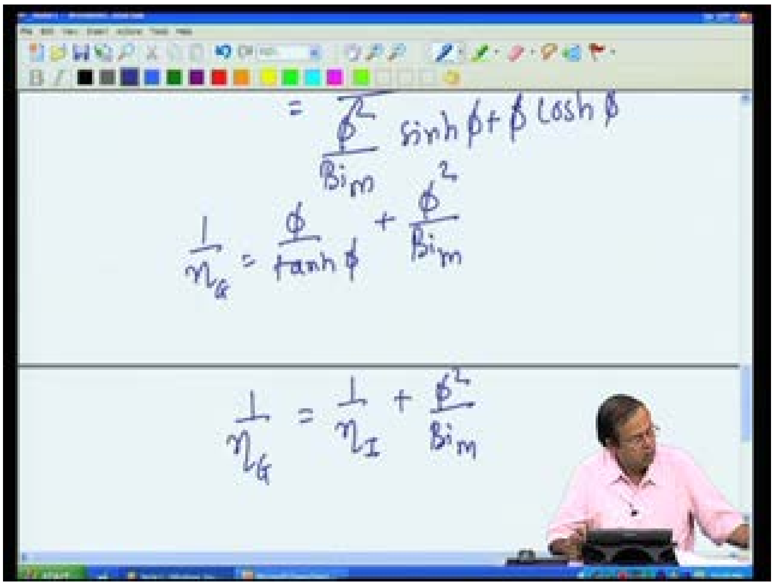

$$= \frac{\phi^2}{Bi_m} \sinh\phi + \phi\cosh\phi$$

$$\frac{1}{\eta_G} = \frac{\phi}{\tanh\phi} + \frac{\phi^2}{Bi_m}$$

$$\frac{1}{\eta_G} = \frac{1}{\eta_I} + \frac{\phi^2}{Bi_m}$$

Now this particular particular solution is interesting, because it further then we can write this as the inverse of effectiveness factor is 1 over or inverse of internal diffusion effectiveness factor, because if you recall tan phi by phi was the effectiveness factor if when we considered only diffusional resistance - internal diffusion. So, inverse of that plus phi square by Biot number by m. So, once again if Biot number is infinity, we get effectiveness factor same as internal internal diffusion diffusion resistance. Now, this is this is as far as single reaction in an in an catalytic gas-solid catalytic reaction is concerned.

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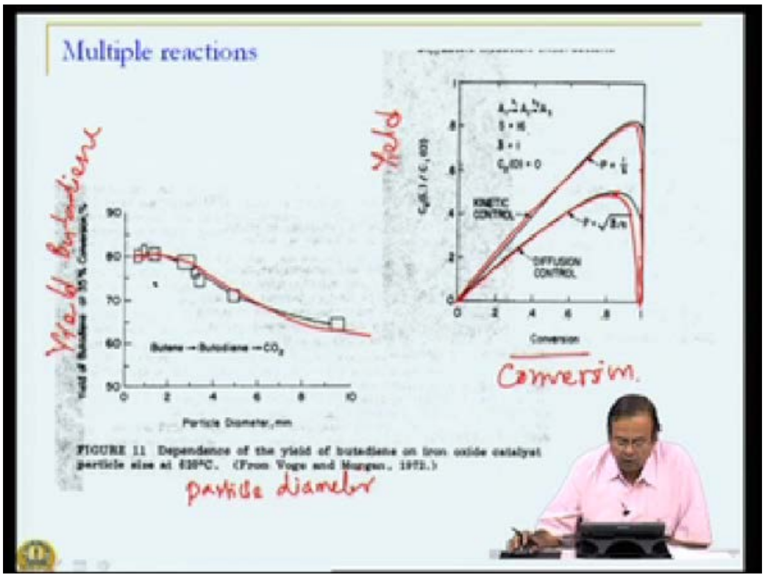

Multiple reactions

FIGURE 11 Dependence of the yield of butadiene on iron oxide catalyst particle size at 620°C. (From Voge and Morgan, 1972.)

Now, we see some several other interesting results or implications, if we have if we have more than one reaction or multiple multiple reaction. For example, if we look at typical typical example of multiple reactions such as A going to B going to C, the example shown here is butane going to butadiene to carbon dioxide, and what we see here on the x-axis is the particle diameter particle diameter and this is yield of butadiene yield of yield of a butadiene. And under identical conditions these experiments have been done except the catalyst particle size is is is increased.

Now, if you see typical result what it shows is initially at lower particle ranges the yields are fairly constant, but as particle size increases the yield is actually decreasing of butadiene. That means, more and more butadiene is going to carbon dioxide which which otherwise stopped at butadiene level. Now, why should particle size matter? It matters because this is a catalytic reaction, larger particle size imply diffusional resistances are stronger, and in this particular case increased diffusional resistances led to the reducing of reducing of yield. And in fact that is precisely what is shown here for the reaction scheme such as a 1 going to a 2 going to a 3, and what we have here is conversion and yield diagram. This is what we earlier had seen when we talked about kinetics. So, without any diffusion limitations, if this was a homogenous reaction or even if it was a heterogeneous reaction the diffusional limitations were not there. The yield conversion diagram was for example something something like this.

Now, same reaction same conditions, but for some reason the diffusional resistances became important such as particle size increasing. We see that under diffusional control regime, the yield conversion diagram has now shifted. And in fact yield is generally lower under diffusional control regime compare to compare to compare to the the reaction control regime. Now, why is this all happening? Although one can go into details of each one of the cases individually, I will just give you a broad outline us to what is what is happening.

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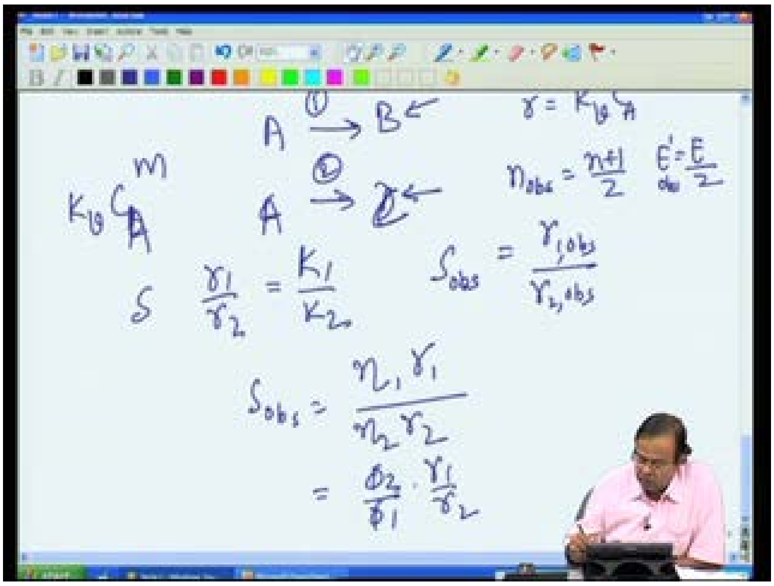

Now, let us go back to our our reaction single reaction scenario. And we saw that for example, if there is a reaction of a kind A going to B, and if this let us say that this is a this is a reaction is power law kinetics. Then we saw if diffusional resistances are strong we get n observed which is n plus 1 by 2 and E observed that is activation energy observed is E by 2 or E observed is E by 2 the true activation energy by 2, and we saw this few sessions earlier. The point is that if you have a diffusional resistance, the dependency of rate on concentration is no longer the same as dictated by the true kinetics, diffusional limitations falsify the kinetics and mass (( )) all right.

Now, let us say that we have another reaction B going to C which is following the kinetics C B raise to m. So, we have a series reaction A going to B, B going to B going to C. And depending upon the kinetic rate constants as well as order the impact that diffusional limitations will have on this process will be different than the impact that diffusional limitations will have on this particular particular process. To give you a to to to illustrate illustrate this point; let us take a simple example. Let us just say that we are interested in looking at if this is reaction 1 and this is reaction 2, what is a ratio of r 1 to r 2? Or let let let me take simple example, because this example is also not simple enough for what I want to illustrate. So, what I am going to say is that I instead of considering B going to C, I am going to consider a reaction C going to D completely unrelated reaction or A going to C, if you want to relate it. So, let us say A going to C. So, we have reaction

A going to B, A going to C. So, this is like a desired reaction, undesired reaction kind of kind of scenario. So, let us say that we are interested in looking at r 1 by r 2.

Now r 1 by r 2 which will tell us the selectivity of B over C and so on, under diffusional control regime, so this is under under strong let us say reaction controlled regime. This would have been simply k 1 by k 2. If we assume both m and n are same that is orders are orders are same. Now, the same thing so let us call this selectivity, same thing under diffusional limitations will be r 1 observed by r 2 observed, which in case diffusional limitations are very strong diffusional limitations are very strong I can I will have to write s observed as eta 1 into r 1 divided by eta 2 into r 2, eta 1 and eta 2 are let us say respective effectiveness factors which under strong diffusional limitations is phi 2 by phi 1 into r 1 by r 2.

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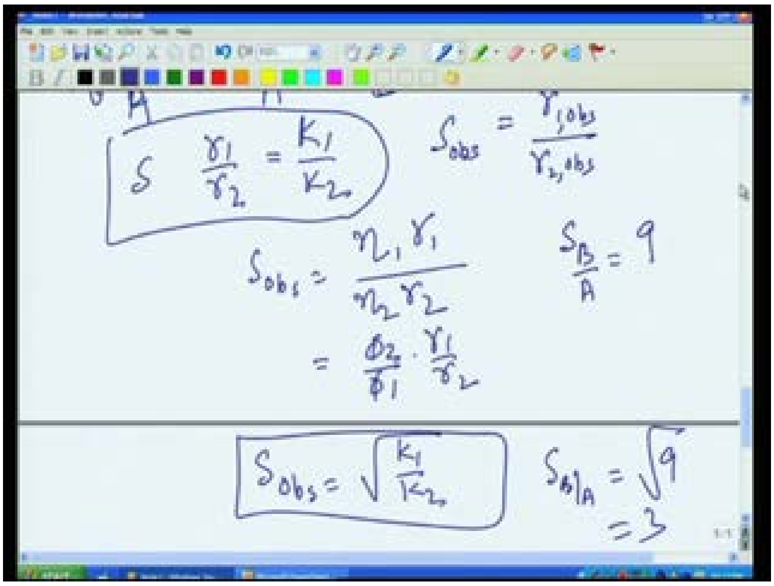

$$\boxed{S \quad \frac{r_1}{r_2} = \frac{K_1}{K_2}}$$

$$S_{obs} = \frac{r_{1,obs}}{r_{2,obs}}$$

$$S_{obs} = \frac{\eta_1 r_1}{\eta_2 r_2} = \frac{\phi_2}{\phi_1} \cdot \frac{r_1}{r_2}$$

$$S_{B/A} = 9$$

$$\boxed{S_{obs} = \sqrt{\frac{K_1}{K_2}}}$$

$$S_{B/A} = \sqrt{9} = 3$$

And if we now substitute our kinetic rate expression that is r 1 and so on. This now s observed becomes square root of k 1 by k 2. So, under no limitations of diffusion, selectivity was ratio of k 1 by k 2. Under strong diffusional limitations, it becomes square root of k 1 by k 2. So, selectivity of B over A let us put some numbers, let us say k 1 was 9 times k 2 was 9 under reaction control regime, same selectivity under diffusion control regime would be square root 9 or 3, a clear indication that diffusivity is now reduced. I mean diffusivity reduce the selectivity of the desired product.

Mind you, here we did not do anything about order of reaction. We assume the order of reaction to be same. You can imagine the kind of (( )) results we will get if the order of reaction also itself is different, then what effect it will have on differing differing selectivity's, yields and so on. We do not have enough time to go into details of all reactions schemes are at least simple reaction schemes. So, we will we will conclude this discussion of non-isothermal reaction by by noting that when you have multiple reactions, the influence of the on the desired reaction may be different and undesired reaction, and your selectivity's, yields all those could be could be very much very much different.

Now, at this point, let us recap what we what we have seen so far. We said we will look at slab geometry, but then relaxed that constraint by looking at cylindrical and other geometries and found that effectiveness factor relationship is fairly uniform. We said we will look at first order reaction, but we also looked at generalized kinetics where you get If I Thiele modulus which for example, in a power law kinetic situation depends on the bulk conditions and so on. We then said that we will we are considering only internal diffusion, but then relax that internal diffusion diffusion as well, and saw that if you have both external and internal diffusion things could be different depending on the Thiele modulus as well as as well as Biot number. Now, we also looked at what happens to the kinetics when when diffusional limitations are important, and how do we find out whether they are important or not by not knowing the true kinetics, but by just doing experiments observing the Thiele modulus and by looking at the value of this Thiele modulus, some judgment about the extent of of diffusional limitations can be can be made.

All these discussion was based on assuming isothermal situation. That means your your catalyst thermal conductivity is so large that if at all any heat is generated liberated it is dissipated very fast, there is hardly any any temperature temperature change. Or the heat effects with the reactions were itself very negligible. That is the heat of energy heat of reaction was let us say 4 less than 4 kilo calorie, I mean 4 is also fairly high number, less than 1 kilo calorie practically negligible, so that you could observe any any appreciable appreciable change. But in reality that is not always the case and we could have heat effects accompanied by the diffusional mass transfer (( )) or in other words, not only mass transfer, but energy transfer also now becomes an important important issue while looking at gas-solid catalytic catalytic reactions.

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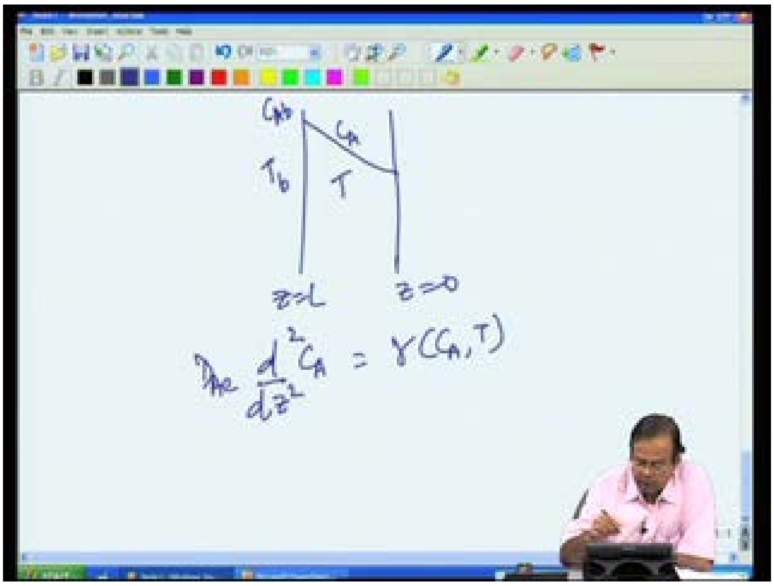

$$D_e \frac{d^2 C_A}{dz^2} = r(C_A, T)$$

So, what essentially essentially we are saying is that we have now our catalyst and this time we will just focus on internal resistances. Again slab geometry everything is everything is everything is same; concentration at the surface is bulk and it is decreasing. The temperature at the bulk is also T b, and inside concentration is C A, temperature is T and it is either same or same or different. So, now we have to set up set up mass balance and energy balance equation to account for this temperature variations, so that we will we will know how what is likely to happen as far as temperature inside the catalyst is concerned. So, let us write down our mass balance equation which is same as before, because mass balance equation is a mass balance equation. And let us keep it in the form of rate, which is we do not know what that rate is at the moment, but we will we will come back to that rate in just a minute. So, we are looking at our mass balance equation.

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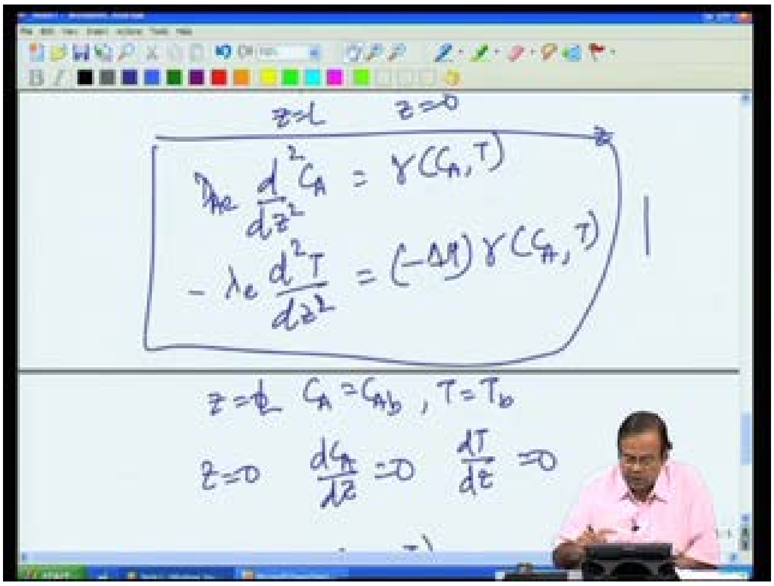

$z=L \quad z=0$

$$D_{Ae} \frac{d^2 C_A}{dz^2} = r(C_A, T)$$

$$-\lambda_e \frac{d^2 T}{dz^2} = (-\Delta H) r(C_A, T)$$

$z=L \quad C_A = C_{Ab}, T = T_b$

$z=0 \quad \frac{dC_A}{dz} = 0 \quad \frac{dT}{dz} = 0$

Now, just as we have our mass balance equation, we also can write energy balance equation in a very similar manner and we will end up with the following. Lambda e is the effective conductivity, thermal conductivity of this catalyst. Once again effective, because remember this catalyst is not all solid block of same material. So, you cannot say that it is a thermal conductivity of a single material. It has the components of that material, but more importantly it has voids, which there is air; an air in general is a poor conductor. So, the thermal conductivity of the catalyst is several times less than the actual thermal conductivity of the catalytic material. So therefore, the heat transfer resistances become important, because it is they are not good conductors of of of of heat or their conductivity is rather limited.

Now, what are our boundary conditions? At z equal to 0, let us write down our boundary boundary condition at z equal to 0, the same condition as before; concentration is the bulk concentration, temperature is the is the bulk temperature at z equal to L sorry on the surface. What about z equal to 0? Symmetry, because same whatever we discussed about mass must also happen same similar manner about energy, because it is not that one end of the catalyst is insulated the other one is exposed, both ends are exposed equally. So, d C A dz must be 0, dT dz must be must be 0. So, we have these two mass balance equations and the required boundary condition, and we can solve them look at their solutions and so on. But before we look at their solutions, let us let us try to look at what is what is happening here. So, before we start looking at the solution of these equations, let us try to understand what is happening in this particular particular situation.

Firstly, we have reaction which is which is causing the change in concentration of concentration of A. So, we have we have let us say we have rate of reaction which is a function of C A and T. Now, concentration change is resulting into or because of reaction there is a there is a energy that is getting generated, and what is the rate at which this energy is getting generated, is the heat of reaction times the rate of rate of reaction. So, because the heat the the the the the reaction is is releasing heat and thermal conductivity is not very high or it is rather limited, the temperature is changing. Now, because temperature is changing, the rate of reaction will change, because rate is function of both concentration and temperature.

Or in other words, we have a feedback effect of this simultaneous variation of concentration and and temperature. And this effect of that is the change in concentration and change in temperature are related to each other. Because why is why is temperature changing? Temperature is changing, because heat that is generated. The heat that is generated depends on the rate of reaction. The rate of reaction also determines how concentration will change. So, in other words, how concentration changes and how temperature changes are related to each other. And we can mathematically see this relationship in these two mass balances itself.

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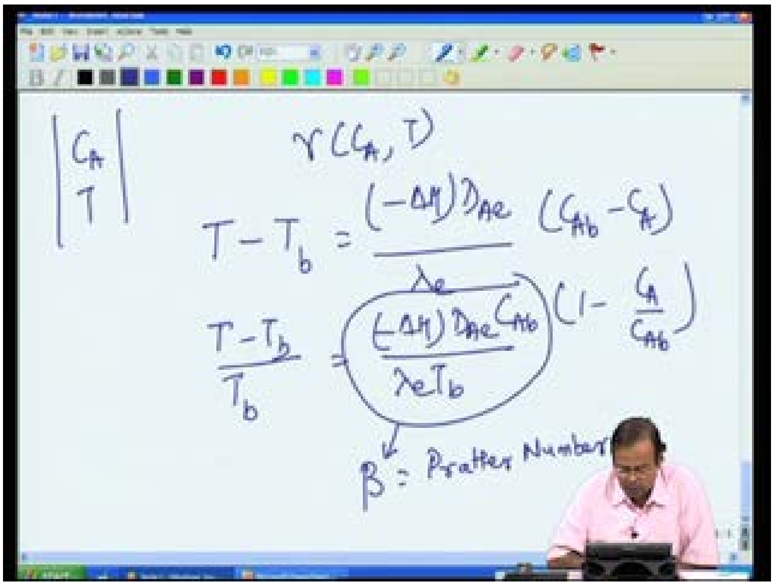

$$\left| \begin{matrix} C_A \\ T \end{matrix} \right|$$

$$r(C_A, T)$$

$$T - T_b = \frac{(-\Delta H) D_{Ae}}{\lambda_e} (C_{Ab} - C_A)$$

$$\frac{T - T_b}{T_b} = \frac{(-\Delta H) D_{Ae} C_{Ab}}{\lambda_e T_b} \left(1 - \frac{C_A}{C_{Ab}}\right)$$

β = Prater Number

More to be more precise, if we take this two mass balance equations and this two boundary conditions we can actually write T minus T bulk as minus delta h that is the heat of reaction D Ae by lambda e into C Ab minus C A. Or in other words, the concentration and temperature variations inside the catalyst pellet are actually related to related to each other.

Now, what does what does this this particular relationship relationship implies? Let us let us look at this look at this little more closely. We can we can also write this in the form T minus T b divided by T b as minus delta h and the reason for this will become clear into C Ab 1 minus C A by C ab divided by lambda e into bulk temperature. This quantity over here if you look at its look at its dimension; this is dimensionless, this is dimensionless, so this number over here must be a dimensionless number, and it is indeed a dimensionless number given a notation beta and referred to as prattler number referred to as prattler prattler number.

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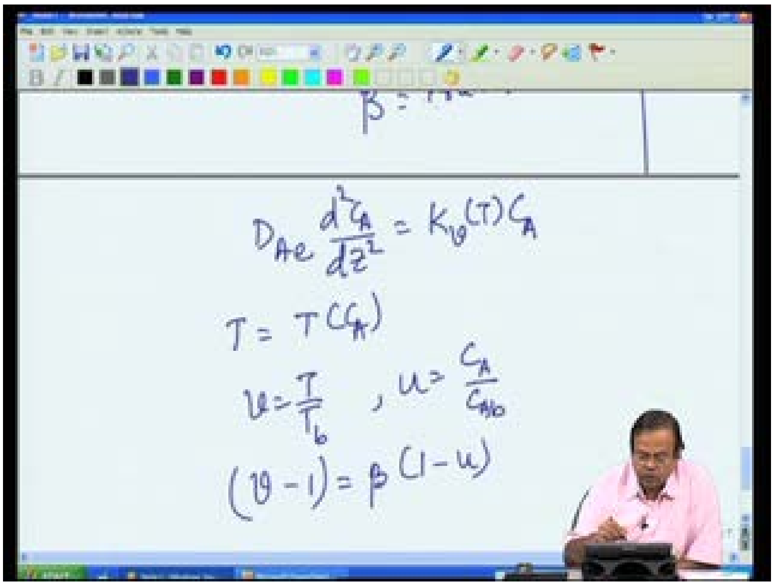

$\beta =$

$$D_{Ae}\frac{d^2C_A}{dz^2} = k_v(T)C_A$$

$$T = T(C_A)$$

$$\vartheta = \frac{T}{T_b}\ ,\ u = \frac{C_A}{C_{A0}}$$

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

Now, what is what is happening, we will we will we will come come back to that in just just a minute, but let me let me then go ahead and say that we are going to now look at the solution of these two equations, but what has happened? We have these two mass balance equations, but in reality we do not need two mass balance equations, because we just now saw that temperature is related to concentration. So, we can in principle in principle just consider mass balance equation. Let us say if you are considering a first order reaction, with the understanding that T is a function of concentration, what is that function? That is a linear actually that is a linear relationship which we just now defined. That is dimensionless, in fact if we work in terms of dimensionless quantities that is let us say we define T by T b as dimensionless temperature v, and we have this dimensionless dimensionless prattler number and our usual… So, if we define v as T by T b, u as concentration C A by C Ab then we have a nice equation v minus 1 is beta into 1 minus u, temperature in terms of concentration.

Let us also try to see what is the implication of this relationship. Let us say, what is this prattler number? What is what is what will happen if reaction goes to completion? If reaction goes to completion, this particular quantity will have it is maximum value namely 1. So, if reaction goes to completion C A is 0, so that means that is that is no more reaction, so temperature cannot change further. So in other words, beta is nothing but the maximum temperature change that can occur in a catalyst. Because C A value 0 is the minimum value, so T minus T b that is delta T by T b non dimensionless temperature difference. The maximum value of which is beta. So, beta has a significance that it represents the maximum temperature change that can occur because of energy and mass transfer limitations.

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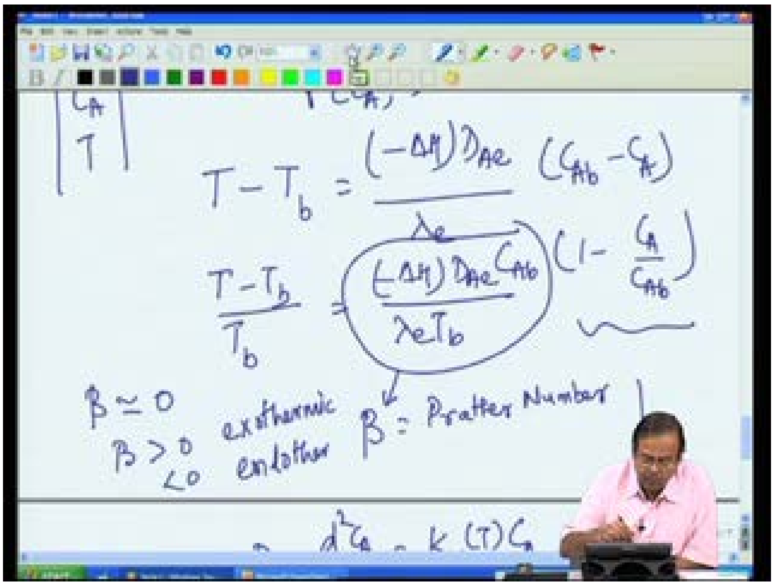

$$T - T_b = \frac{(-\Delta H) D_{Ae}}{\lambda_e} (C_{Ab} - C_A)$$

$$\frac{T - T_b}{T_b} = \frac{(-\Delta H) D_{Ae} C_{Ab}}{\lambda_e T_b} \left(1 - \frac{C_A}{C_{Ab}}\right)$$

β = Prater Number

$\beta \simeq 0$

$\beta > 0$ exothermic

< 0 endother

Now, what happens to value of beta? For example, if the reaction is isothermal, heat effects are heat effects are negligible, beta is 0. If it is an exothermic reaction, then we have delta h or heat of reaction which is negative and so beta is positive. So, beta is greater than 0 for exothermic reaction, and is less than 0 for endothermic reactions, because delta h is now positive. So, by according to definition of this definition of this definition of this prattler number it is either positive or or negative.

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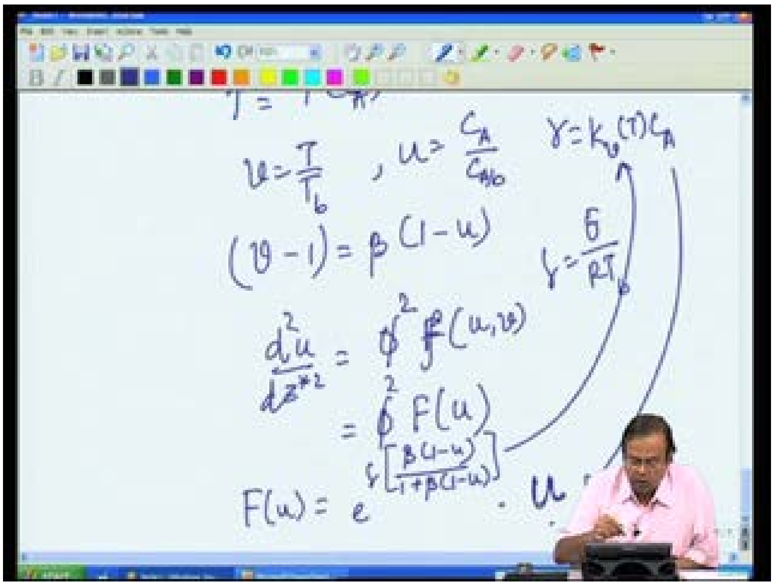

$\vartheta = \frac{T}{T_b}$, $u = \frac{C_A}{C_{A0}}$ $r = k_v(T) C_A$

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

$$\frac{d^2u}{dz^{*2}} = \phi^2 f(u,\vartheta)$$

$$= \phi^2 F(u)$$

$$F(u) = e^{\gamma\left[\frac{\beta(1-u)}{1+\beta(1-u)}\right]} \cdot u$$

So, now let us say that we make these equations dimensionless by using this dimensionless variables, and we can actually write our our mass balance equation, because we need only one now.

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So, some function F which we can write in terms of function of u alone, because temperature can be substituted by by in terms of concentration, where this function F of u is e raise to gamma… Into u, gamma is activation energy by RT b, another parameter that will come. This u came remember our kinetics is r is equal to k v of T into C A. So, this u come dimensionless u because of concentration. This term you can identify with k v term, because if we assume Arrhenius rate form, you will get this kind of dependency on temperature and all we have done is for dimensionless temperature we put the we put the in terms of dimensionless concentration. So, these are our mass balances and now let us let us we also define in a similar manner the effectiveness factor.

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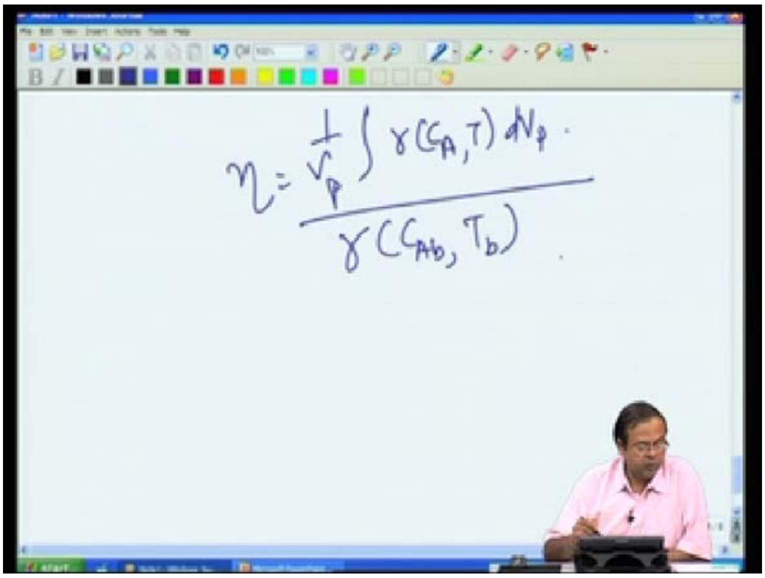

$$\eta = \frac{\frac{1}{V_p}\int r(C_A,T)\,dV_p}{r(C_{Ab},T_b)}$$

Now, the only difference that we have to make here is that effectiveness factor which is 1 over v p integral r C A of dv p divided by both diffusional resistances and energy transfer resistances are negligible, what would be the rate? So, our rating now parameter is the observed rate (( )) what rate would have been if none of the diffusional limitations or energy limitations were were present in the present in the system. So, one can actually numerically solve, it is not possible to solve it analytically, but let us look at the look at the solution of this equation.

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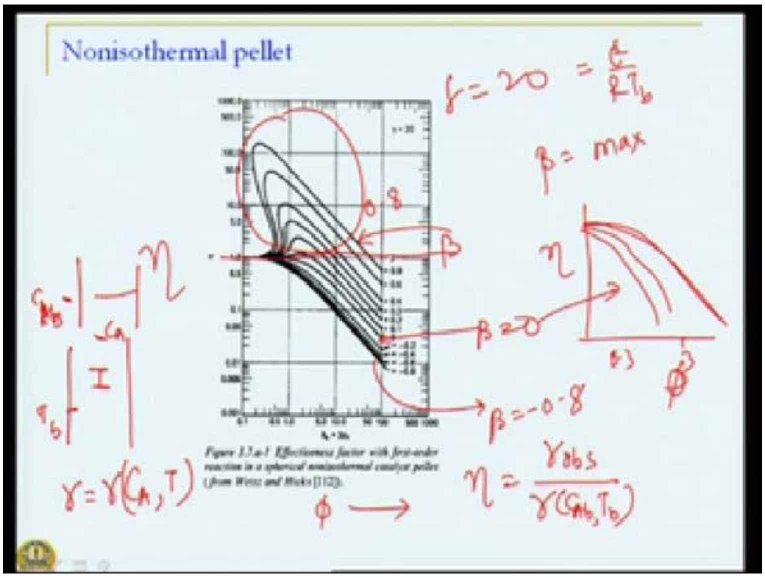
Nonisothermal pellet



So, what we are seeing here is actually the effectiveness factor for first order reaction in a spherical catalyst. But if it is a cylindrical or sphere we or slab we know the results are results are similar. So, what we see here is Thiele modulus and effectiveness factor eta for a given value of gamma equal to 20, because now effectiveness factor is a function of Thiele modulus gamma and beta. Gamma is E by R T b and beta as you know we said that is a maximum temperature temperature rise. So, what we see here is for different value of beta, so for example this is a solution for beta of 0.8, this one over here is for beta of minus 0.8, and these are values going from 0.8 at 1 extreme to minus 0.8 at at other extreme. So, we have these different different values, somewhere in the middle is the solution when beta is 0 that is what our isothermal isothermal case is.

So, now if we if we look at this behavior of non-isothermal pellet. I will just put on the side a typical sketch for isothermal which we had seen earlier eta versus phi, and this was about 0.3 and somewhere 3 over here. We see that there are some differences and similarities. Of course, when beta is equal to 0 that says what the solution is. So, this is no surprise that it is it is similar. In fact for all beta values negative, the solutions are almost similar to that. In fact they are lower and lower as the beta value becomes negative. That means reaction is highly endothermic, it is more endothermic the beta value will be higher in magnitude with a negative negative sign.

So, effectiveness factor is actually decreasing, so diffusional resistances influence or energy resist transport resistances; for example, influence the the endothermic reactions in a severe severe manner. Because compared to compared to no energy energy transport limitations, the effectiveness factors are lower as we are getting endothermic reactions. But the situation is completely different, when we look at what happens when we have exothermic reactions. For exothermic reactions, in fact this is the boundary 1, for quite a few cases this entire region, the effectiveness factor is greater than unity. What does this what does this imply? Remember we had defined our effectiveness factor as r observed divided by r if no limitations existed. Now, this value being less than 1 is understandable, because if there are no limitations of mass or energy transport you get the highest rate, I mean that is a normal thinking. But look at what happens and that is indeed what happens when we have endothermic reaction. But look at what is happening when you have exothermic reaction.

When you have exothermic reaction, having mass transfer limitation is actually enhancing the reaction rate. Why is that? That is because you have I mean, how do we know that? That is because effectiveness factor is greater than unity. Effectiveness factor is greater than unity, if the reaction is exothermic and we have we have reaction rates inside the catalyst pellet or the average of those higher than higher than (( )). Now, why is this why is this happening? To see that let us go back to our let us go back and and look at look at what is what is actually happening here.

Remember our rate is a function of concentration and temperature. Now, if reaction is exothermic, temperatures are higher than the bulk by depending on, so this is the temperature inside the catalyst, this is the bulk and it is value is high. Concentration is always lower than the bulk. So, if this is the bulk bulk value, the concentration here is always low than the bulk. But look at what is happening to look at what is happening to temperature. Temperature inside the catalyst pellet will be higher than the bulk temperature if there are heat transfer resistances. So, what what what does that do?

Inside the catalyst pellet, temperature is higher, and remember how temperature dictates rate of reaction; Arrhenius rate dependency highly non-linear. So, increase in temperature, we saw that example I think in the beginning. A 10 degree increase can double or triple your reaction rate or change it by several order of magnitude depending on the activation energy of course. So, if the temperature inside is higher than the bulk condition, the rate of reaction inside is also higher than the bulk condition if the reaction is exothermic. And hence the effectiveness factor or the observed rate can be higher than the rate in absence of energy and mass transfer limitations. So, this is one clear advantage of having energy and mass transfer limitations if if if reaction is exothermic.

We can argue the same thing if reaction is endothermic temperature inside the reactor inside the catalyst will be lower than the bulk. So, not only the concentration will be lower, but temperature also will be lower. Implying that the rate of reaction inside the catalyst pellet will be low both because of concentration and temperature being low, so making situation worse than not having having the same temperature as bulk. So, endothermic reactions suffer because of mass and energy transfer limitations, and exothermic reactions may benefit if there are in mass at energy transport reaction - a transport limitations.

So, this is just to give you an idea as to what happens when we have when we have these these exothermic non-isothermal situations. There is one small point which we will try to cover, because if you look at if you what happens is actually there is a possibility of multiple steady states in a in a catalyst, and we will concentrate on that in our next session before moving further. Thank you.