Mathematical Modelling and Simulation of Chemical Engineering Process
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Lecture 28
Modelling Pore Diffusion and Reaction

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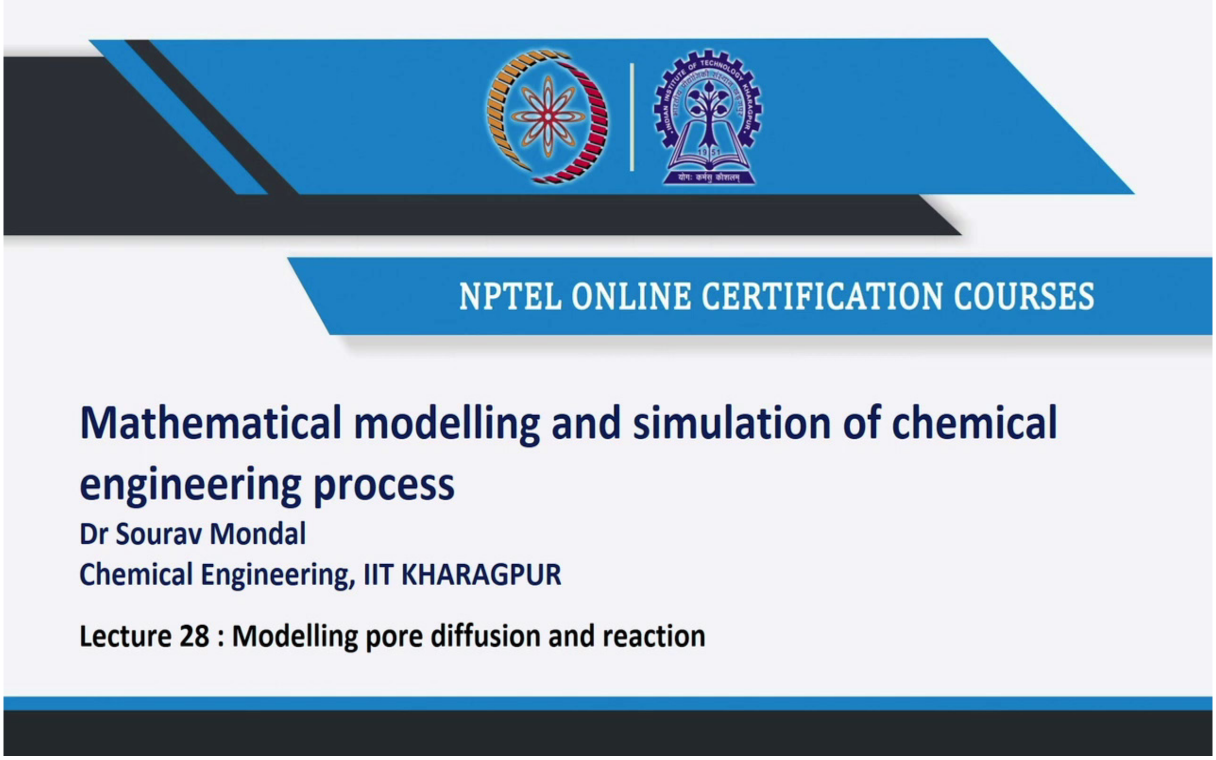

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Mathematical modelling and simulation of chemical engineering process

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Lecture 28 : Modelling pore diffusion and reaction

Hello, everyone. In this lecture we are going to see that how the pore diffusion or how the pore level phenomena in the catalyst particles or in any porous medium where there is a possibility of a reaction or adsorption taking place, can be modeled.

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CONCEPTS COVERED

- ❖ Pore diffusion and reaction
- ❖ Simultaneous reaction and diffusion

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So let us say that you consider, if you, if you just recall the motivation or the inspiration from the last class, we have said that in the in the catalyst particles there are innumerous pores, and it is the exposed pore surfaces where, on which the reaction happens. So there has to be some diffusion inside the pore before this reaction takes place on the surface of the pores.

So, reaction, we are, we are now looking at, we are now going to have a more microscopic view on this phenomenon and try to understand that reaction essentially does not happen in the entire region of the pore or entire void space, it only happens at the exposed surface areas or the surface of this catalyst. The more is the exposed surface area, the better is the reaction performance or the catalytic activity.

So there has to be a diffusion through which the particles or the mole, sorry, not particles, the molecules will enter into that pore space and then the reaction will happen at the walls. So, this is like, we are trying to relax the assumption in the last class what we have considered that reaction happens in the entire of the catalyst particle, which is like if the particle is extremely porous and instead of considering only the pore surface areas, we consider the entire bulk of the catalyst there the reaction happens.

But now we are trying to have a more microscopic view, particularly in the situations when the particle is not so porous. This is generally more applicable in the situation and particles, the porosity of the particles is not too much and pore diffusion plays a big role in the reaction because until the molecules diffuse inside the catalyst or essentially, into the pores, there is no possibility of reaction.

And again, after reaction, the particle again has to diffuse, the molecules again has to diffuse out, whatever reaction products, whatever has performed, it has to again diffuse out. There is no possibility of convection there, it is only diffusion as the primary mode of mass transfer inside those pores.

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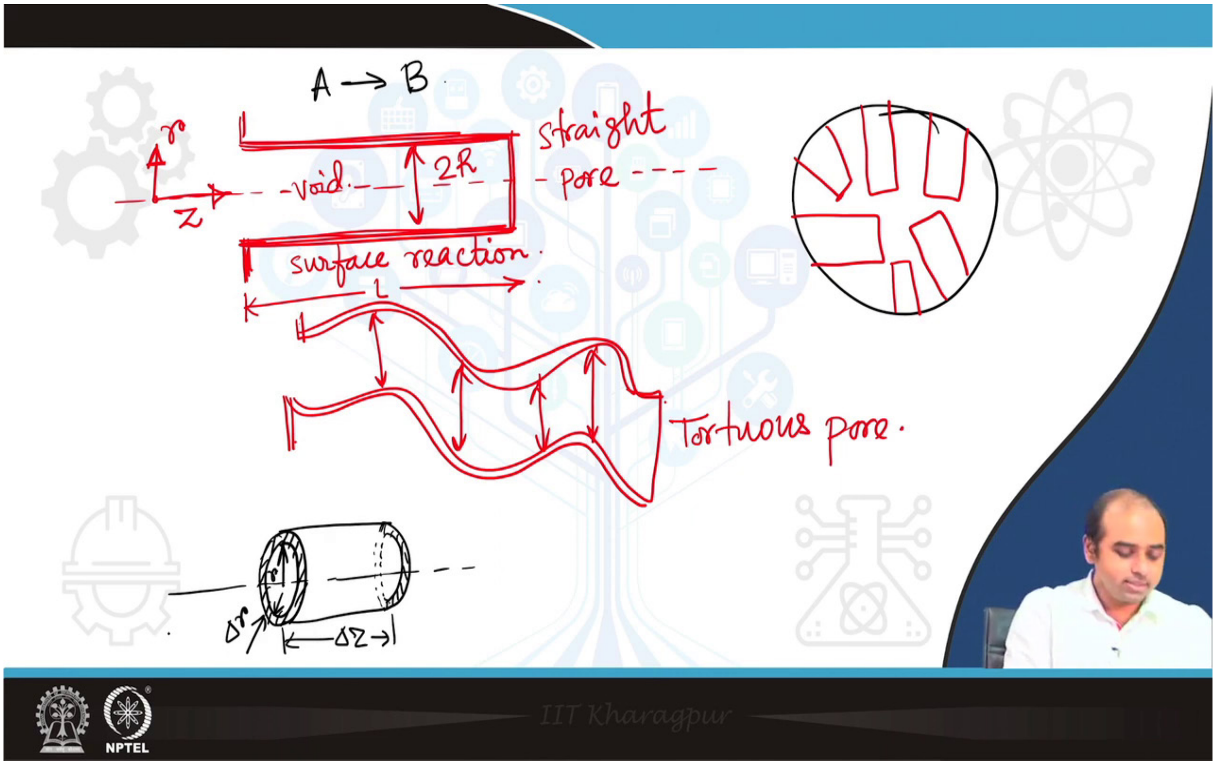

So, if you consider a catalyst particle, so I hope I can give you a microscopic view here. So, let us say this is a catalyst particle. So, the, you can, the pores which originate from the, the surface, something like this. Of course, the pores are not so well, they do not have so much of well defined path, and there is a certain factor of tortuosity which plays a big role.

So, tortuosity is the, the, is the factor which tells you that what is sort of the ratio of the curved or the tortuous path taken by the molecule with respect to the, the straight path. So, if you, if you, if the pore shape is not straight and it is like very much curved and curvy pathway is there, the tortuosity is going to be higher.

So instead of connecting two points by a straight line, if you connect it with the curve and it is a very curvy linear pathway, that total length of that path will be more. So, like the more is the tortuosity, the more is the exposed surface area which interacts with these molecules, or there is more availability of the exposed surface area on which the reaction can actually take place.

So, more tortuosity it is essentially better because you can fit, you can increase the exposed or the pore surface area within a small volume if the path of these pores are extremely tortuous. But there is, one drawback is that, the, so the, if the total particle volume is fixed, and if the path is more tortuous, so essentially, the pore, the diameter of the pores, not on the surface, but inside these paths, so these are like long cylindrical spaces, so that will be lower.

So, if that is lower, again, that will affect the mobility of the molecules or diffusion of the molecules into this tortuous path, even though, it experiences higher or more availability of the reaction sites. So, there is a tradeoff. Higher tortuosity does not always lead to high, higher reaction rates or higher catalytic activity because it also depends on the diameter of these tortuous path or the cylindrical pathways through which the molecule can essentially diffuse and get transported. So, there is a tradeoff between these two.

So, in this case, let us consider as sort of a geometry of this sort of a straight cylindrical geometry, and just for the sake of simplicity. So, if you want to simulate or you want to model the diffusion and the reactions in a tortuous path, so tortuous path can be like this, something like this if you want to model. Then it is, this is something which can be modeled using numerical calculations.

So please note that the surface of these, these walls, these walls of the pore, so this is like a pore, and I can say this to be straight pore, and this is like a tortuous pore. So, this surface, it is essentially on these surfaces that the, this is, this is the void space. So, this surface, on over the surface the reaction actually takes place. So, which is also true here. So, it is the, the pore surfaces which is responsible for the catalytic reaction.

So, you can see that the tortuous path can have higher surface area compared to a straight path. But again, to fit more number, again in, in a, if the total volume is constrained or it is fixed, then this, this diameter, this is what I am talking about, this diameter, this diameter has to be reduced. And if that is reduced, that will affect the mobility of the molecules or the movement of the molecules inside these pores. So, there is a trade-off.

So now in this sort of cylindrical arrangement or let us say a straight pore, in this case it is something which we are trying to consider. Let us say the radius, diameter is 2 R. This is the z direction, this is the r direction to the problem. Let us say the length of this pore is capital L. And we consider a simple, first order reaction which is taking place on the surface of these pores.

So now, how do I, how are we going to write the mass balance? So, diffusion is happening both longitudinally as well as radially in this cylindrical pore. So, if I consider a small elemental section of delta r and delta z, it will have a, a view of something like this.

So, this distance is delta z, and so this is, I hope all of you can see my drawing, is r. And this thickness is delta r. So, along the small elemental section having this element of delta r thickness and this length of delta z, we are trying to write down the species balance.

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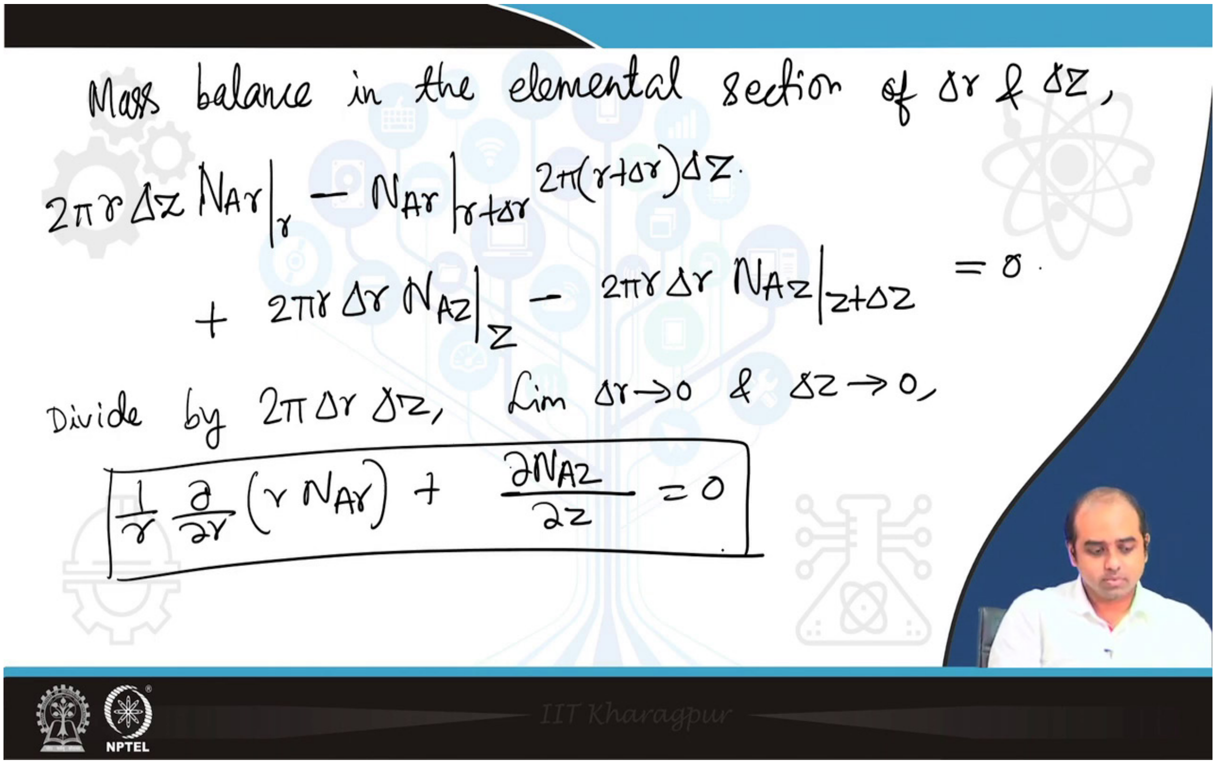

Mass balance in the elemental section of δr & δz,

$$2\pi r \Delta z\, N_{Ar}\Big|_{r} - N_{Ar}\Big|_{r+\Delta r} 2\pi(r+\Delta r)\Delta z.$$

$$+\ 2\pi r \Delta r\, N_{Az}\Big|_{z} - 2\pi r \Delta r\, N_{Az}\Big|_{z+\Delta z} = 0.$$

Divide by $2\pi \Delta r\, \delta z$, Lim $\Delta r \to 0$ & $\delta z \to 0$,

$$\boxed{\frac{1}{r}\frac{\partial}{\partial r}\left(r N_{Ar}\right) + \frac{\partial N_{Az}}{\partial z} = 0}$$

So, mass balance in the elemental section. So, the radial part is N A, sorry 2 pi r del r, 2 pi r del z, then we are having N A r at r. Similarly, we are having N A r r plus delta r. Of course, 2 pi r plus delta r is there delta z. And then for the z direction, we have 2 pi r. So please take care of the, the, these areas over which the z direction and the r direction fluxes are the projected surface area along the r and the z directions.

So, when the flux, this diffusion or the, this taking place along the z direction, it is the surface area of that elemental section of delta r, which is 2 pi r delta r. And when the, this diffusion is taking place along the r direction, it is a cylindrical surface area. So that is 2 pi r into delta z. So, these are the two surface area in the direction of the respective fluxes.

So now, please note that this is something we have written in the, the cylindrical space where only diffusion is taking place and there is absolutely no reaction. The reaction takes place at the boundaries. So those conditions will come as a boundary condition. So, before we move to the boundary condition, we just take the limits of delta r delta z tending to 0.

So, limits of delta r tending to 0 and delta z tending to 0 will give us the equation 1 by r. This is the equation of the, from the balance of the mass fluxes we have. So, what about N A r and N A z? Let us write them out.

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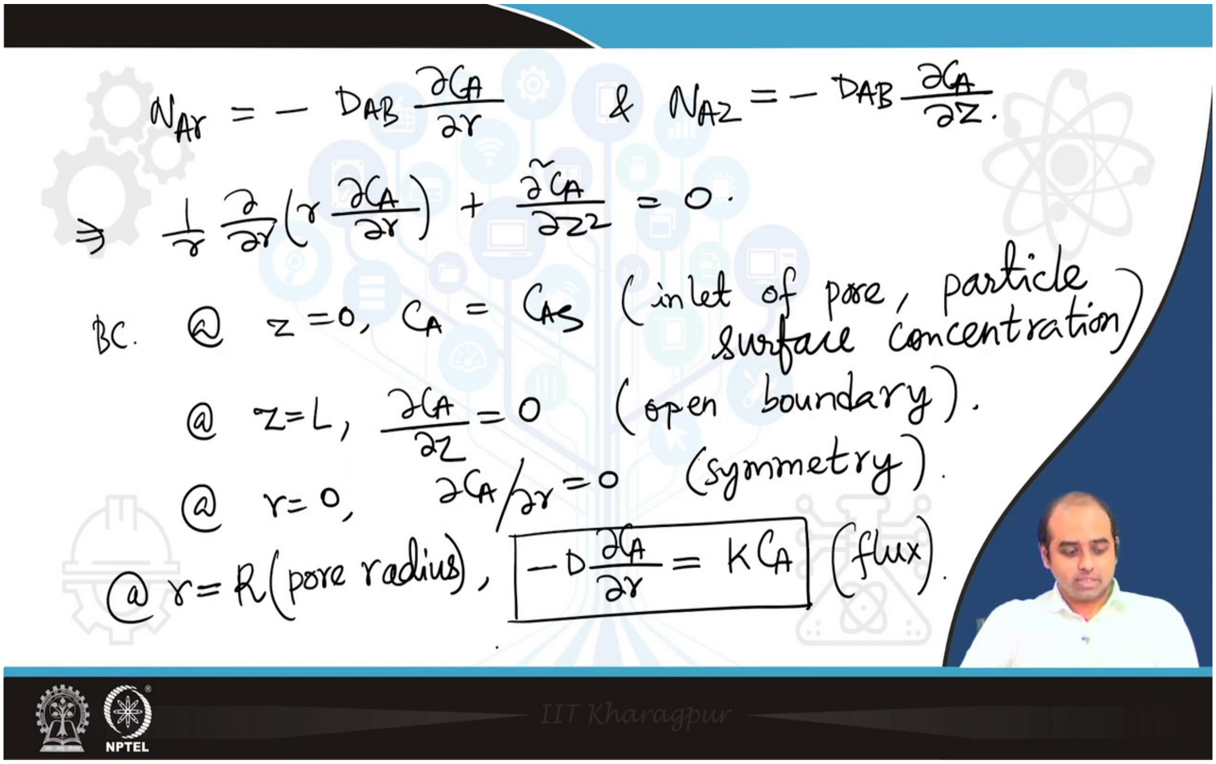

$N_{Ar} = -D_{AB}\frac{\partial C_A}{\partial r}$ & $N_{Az} = -D_{AB}\frac{\partial C_A}{\partial z}$.

$$\Rightarrow \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_A}{\partial r}\right) + \frac{\partial^2 C_A}{\partial z^2} = 0.$$

BC. @ $z=0$, $C_A = C_{AS}$ (inlet of pore, particle surface concentration)

@ $z=L$, $\frac{\partial C_A}{\partial z} = 0$ (open boundary).

@ $r=0$, $\partial C_A/\partial r = 0$ (symmetry).

@ $r=R$ (pore radius), $\boxed{-D\frac{\partial C_A}{\partial r} = K C_A}$ (flux).

So ideally N A r is this. And that is for N A z. So, if I replace these flux quantities, I will have, so the second order in z and second order in r, it is an elliptic PDE. So, the boundary condition is very important. We write, at z is equal to 0, this C A is equal to C A S which is the inlet of the pore, and this is inlet of the pore and this is the surface condition, not the pore surface, but the particle surface condition, which is exposed, which is same concentration, which is something that is related to the overall macroscopic packed bed reactor calculations.

Because please, remember all the pore mouths are essentially exposed or is, is appearing on the particle surfaces. Otherwise, it cannot enter, the pore opening is invalid. So, this concentration at the pore mouth or at the entrance of the pore is related to the concentration in the bulk or in the macroscopic domain, which is something to be considered, related to the packed bed conditions. At z is equal to capital L, we say that d

C A d d z is equal to 0, it is sort of the open boundary. At r is equal to 0, you have d C A by d r is equal to 0 which is a symmetry condition.

Now, the important one is that r is equal to capital R. So capital R is the pore radius. So this is the pore radius. At that point, you have the diffusive flux that is from the Fick's Law d C A d r is equal to the first order reaction K C A. So this is the flux balance by the reaction. So this is the important boundary condition where we are equating the, the diffusive flux or the flux is equal to the rate of reaction there, and this has to be balanced at steady state.

So now, I think this is the equation framework which is something you can solve by explicitly by separation of variables. It is elliptic equation, and this is something you should definitely try out. So here I am just going to give you another, a different approach to solve this problem by the method of area averaging.

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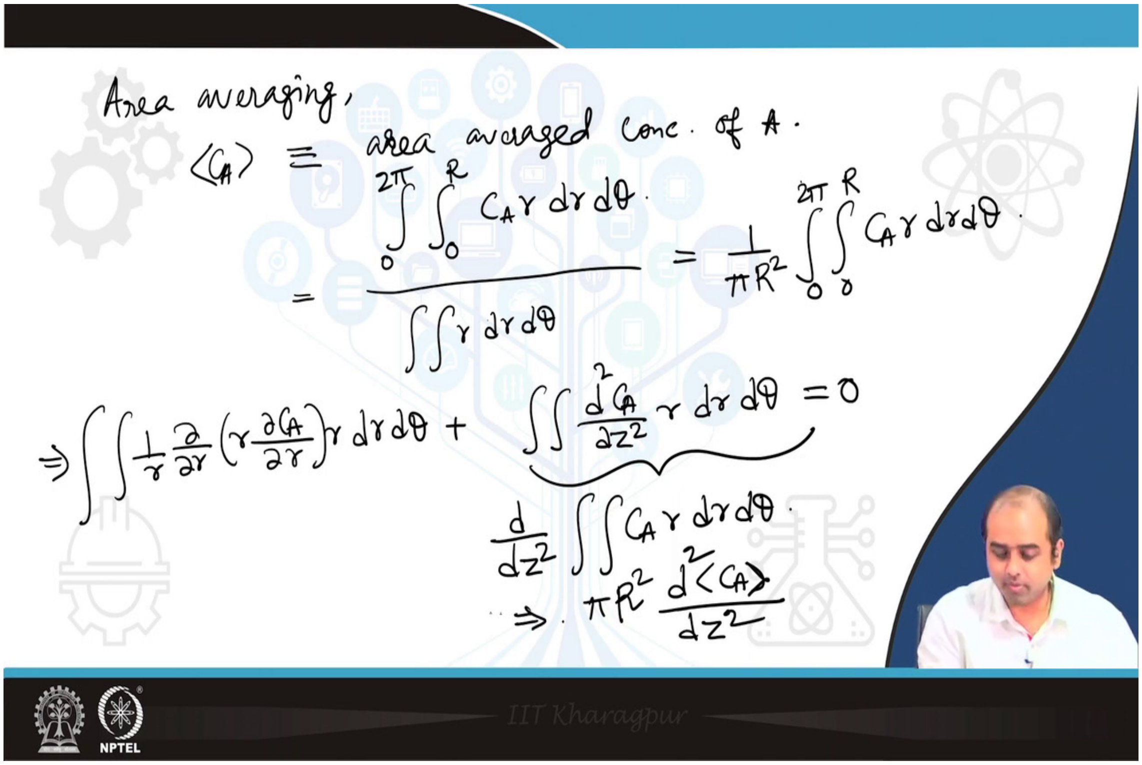

Area averaging,

$\langle C_A \rangle \equiv$ area averaged conc. of A.

$$= \frac{\int_0^{2\pi}\int_0^{R} C_A r\,dr\,d\theta}{\iint r\,dr\,d\theta} = \frac{1}{\pi R^2}\int_0^{2\pi}\int_0^{R} C_A r\,dr\,d\theta$$

$$\Rightarrow \iint \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_A}{\partial r}\right) r\,dr\,d\theta + \underbrace{\iint \frac{d^2 C_A}{dz^2} r\,dr\,d\theta}_{} = 0$$

$$\frac{d}{dz^2}\iint C_A r\,dr\,d\theta$$

$$\Rightarrow \pi R^2 \frac{d^2\langle C_A\rangle}{dz^2}$$

So what is this area averaging technique? Let us define this average area C A, something like within this brackets, area averaged concentration of A. So of course, we have assumed theta symmetry and phi symmetry, but if that is not the case this is just the, if you can write, want to write it for a generalized system, then we can write it for across the theta cross section also. But this is not required in this case because the concentration, whatever we are dealing with, has theta symmetry, but I am just trying to write down the generalized version.

So, this area averaged is the cross sectional area averaged. So, when I say this area average concentration, it is averaged across the radial cross section. So, this is, so if I apply this technique of averaging in the main equation, what I will get? So, this is my equation. Let us say, I try to average out the radial dimension, that is the idea.

Similarly, I also want to do this radial averaging on this term also. So, this is, I can write down, I can take out the derivative del del d d z square here, and I can write something like this. So, which is equal to pi, sorry R square. So, it is nothing but the average, the double derivatives in the z direction of the averaged C square. Now, what about the left part?

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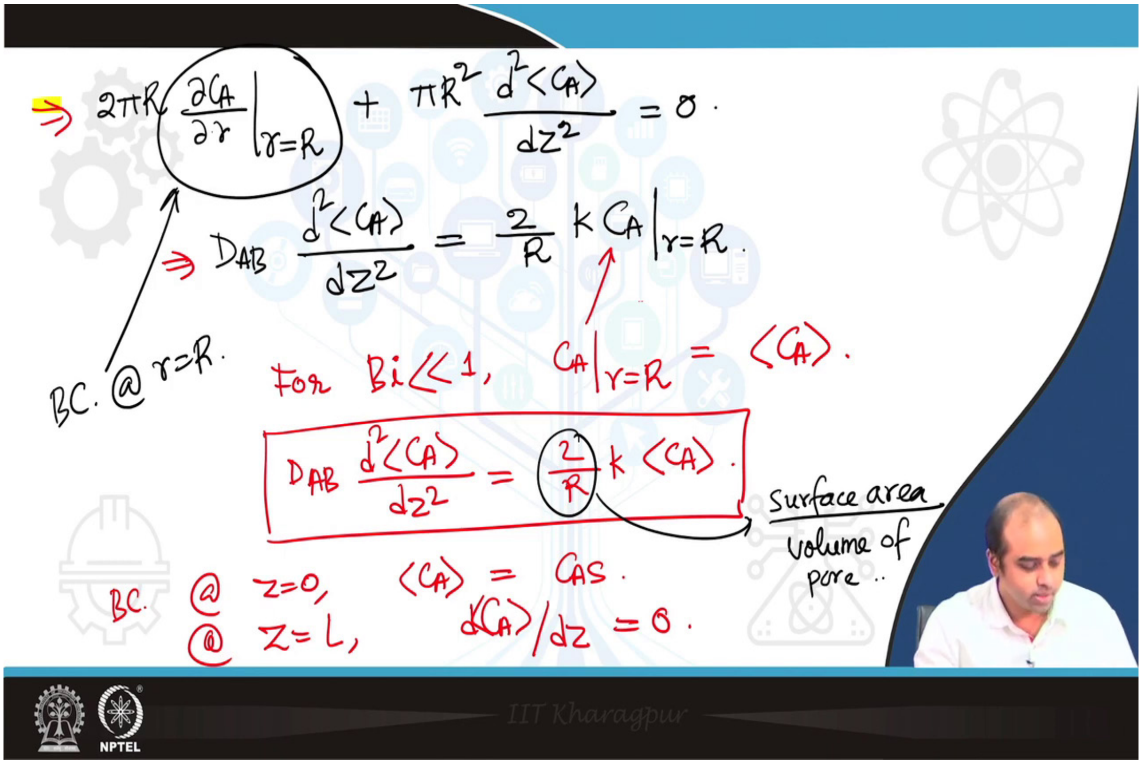


$$\Rightarrow 2\pi R \left.\frac{\partial C_A}{\partial r}\right|_{r=R} + \pi R^2 \frac{d^2\langle C_A\rangle}{dz^2} = 0.$$

$$\Rightarrow D_{AB}\frac{d^2\langle C_A\rangle}{dz^2} = \frac{2}{R} k \left. C_A\right|_{r=R}.$$

BC. @ $r=R$.

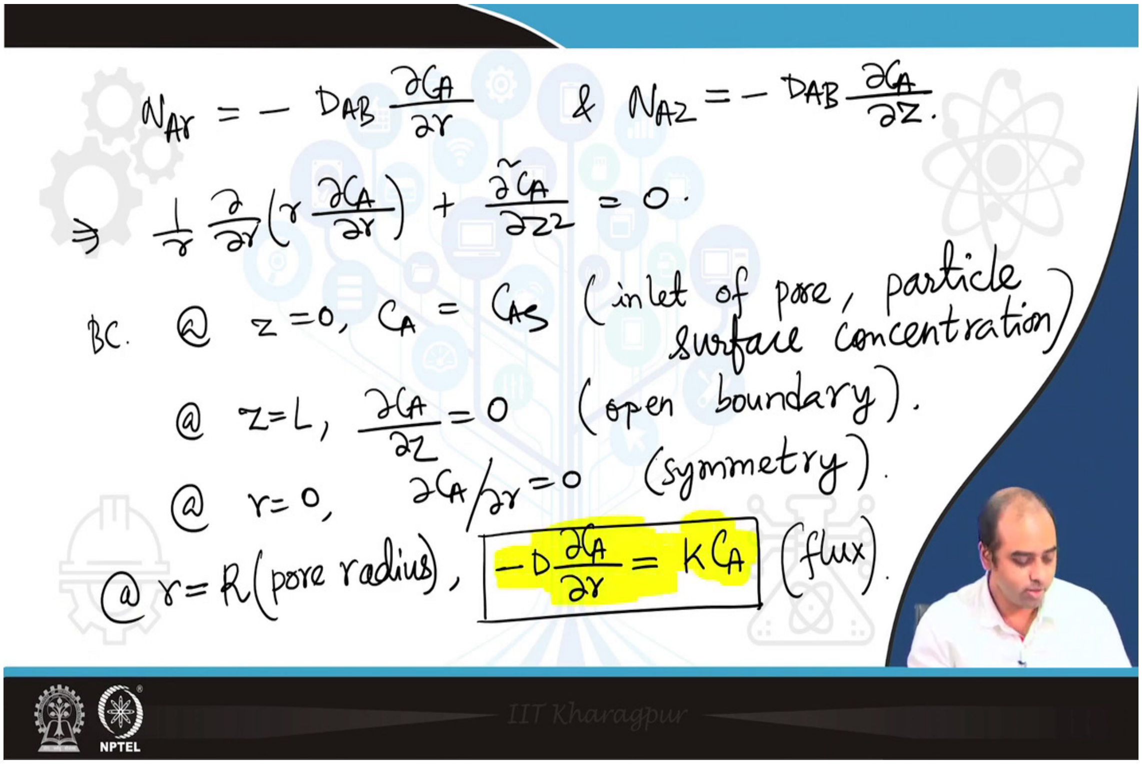
For $Bi \ll 1$, $\left. C_A\right|_{r=R} = \langle C_A\rangle$.

$$\boxed{D_{AB}\frac{d^2\langle C_A\rangle}{dz^2} = \frac{2}{R} k \langle C_A\rangle.}$$

$\frac{2}{R}$ → surface area / volume of pore..

BC. @ $z=0$, $\langle C_A\rangle = C_{AS}$.

@ $z=L$, $d\langle C_A\rangle/dz = 0$.



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@ $r=R$ (pore radius), $\boxed{-D\frac{\partial C_A}{\partial r} = kC_A}$ (flux).

So for the left part, we can write by doing one averaging, we can write 2 pi r, something like this, doing one averaging, one integration. This will remove one of the derivatives, and everything will be determined at C r, plus you have pi R square, this quantity. Now, please note that this condition is something which we can apply from the boundary conditions at C d del C A del r. So, this is something I can replace from the boundary condition.

Boundary condition at r is equal to capital R can be replaced, and we already have seen that boundary condition. Just to remind you, so this is the boundary condition, at, sorry, at r is equal to capital R, the flux boundary condition we have. So, this, I am just replacing in this equation because this evaluation is at r is equal to capital R from the integration in the previous step.

If you do this integration once here, you will land, and remove one of the partial derivatives and the other derivatives needs to be validated r is equal to capital R. So that is the boundary condition using which, I can, I can replace that. And so, from here, using the boundary condition, I can get this equation, in terms of this value of C A at r is equal to capital R.

So for, for Biot number or typically for distributed systems, it is reasonable to assume that the flux, not flux, the concentration profile can be assumed that whatever the surface concentration we have is more or less equivalent to the radially averaged flux con, radially averaged concentration.

So, it is based on this assumption only we can replace that this, this term here and we get this equation, this transformation, this modification. But please note that this is valid only for the case of Biot numbers, very small in sort of problems, where this radially averaged concentration is considered to be almost equivalent to the surface concentration. But I must say that this is not the general case everywhere.

But there are certain situations where you can make this assumption. And if you are able to make this assumption or if you find this to be practically possible quantity, there is a possibility on this, then it is, then it is okay to make this assumption, and we proceed from there and resulting into a normal ODE. So, this is, this averaged C A, what we see here is ODE. This average C A is now written down as an odd differential equation with respect to z.

So, what about the boundary condition in terms of z? So, at z is equal to 0, we have to consider the radially averaged C A as C A naught, so which is something I would write, prefer to write as C A S, the surface concentration. And at z is equal to L, we write this in terms of the z boundary condition. So please be informed, please be aware that this quantity is nothing but the ratio of the surface area to volume of the pore.

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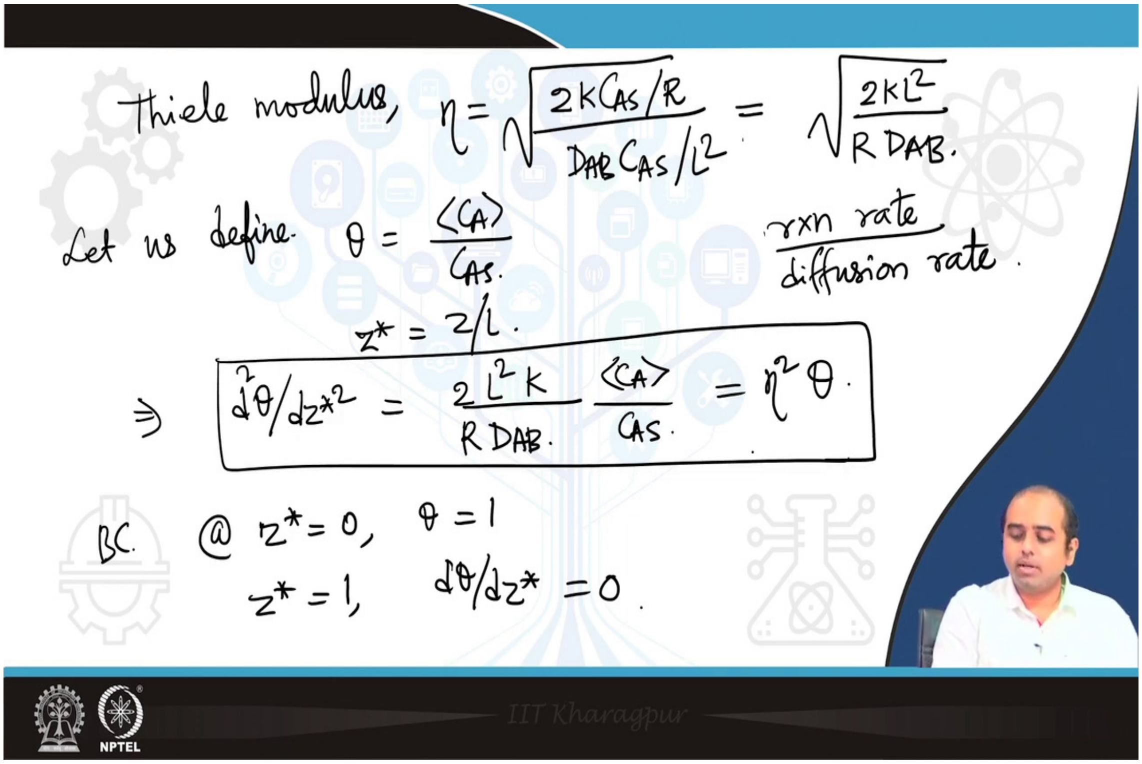

Thiele modulus, $\eta = \sqrt{\frac{2kC_{AS}/R}{D_{AB}C_{AS}/L^2}} = \sqrt{\frac{2kL^2}{R D_{AB}}}$

Let us define $\theta = \frac{\langle C_A \rangle}{C_{AS}}$

$\frac{\text{rxn rate}}{\text{diffusion rate}}$

$z^* = z/L$

$$\Rightarrow \boxed{d^2\theta/dz^{*2} = \frac{2L^2K}{R D_{AB}} \frac{\langle C_A \rangle}{C_{AS}} = \eta^2\theta}$$

BC. @ $z^* = 0$, $\theta = 1$

$z^* = 1$, $d\theta/dz^* = 0$

Anyway, so I think all of you are used to the convention of Thiele modulus. So let us introduce that here. Let us define this Thiele modulus as 2 K C A naught, sorry, I should not write C A naught, I should write C A S. So, this can be written down as 2 K L square. So, this is the, all of you, I am sure, know this reaction rate by diffusion rate. So, with this introduction of the Thiele modulus, and let us say I define theta is C A by C A S, and some z star as z by L.

So, I can non dimensionalize this equation into this way, d theta by d z star square is equal to this quantity 2 L square K by R D A B. And this is nothing but square of the Thiele modulus. So, the boundary condition at z star is equal to 0, we have theta is equal to 1, and z star is equal to 1, we have d theta by d z star to be equal to 0. So, all of the solution to this equation, right?

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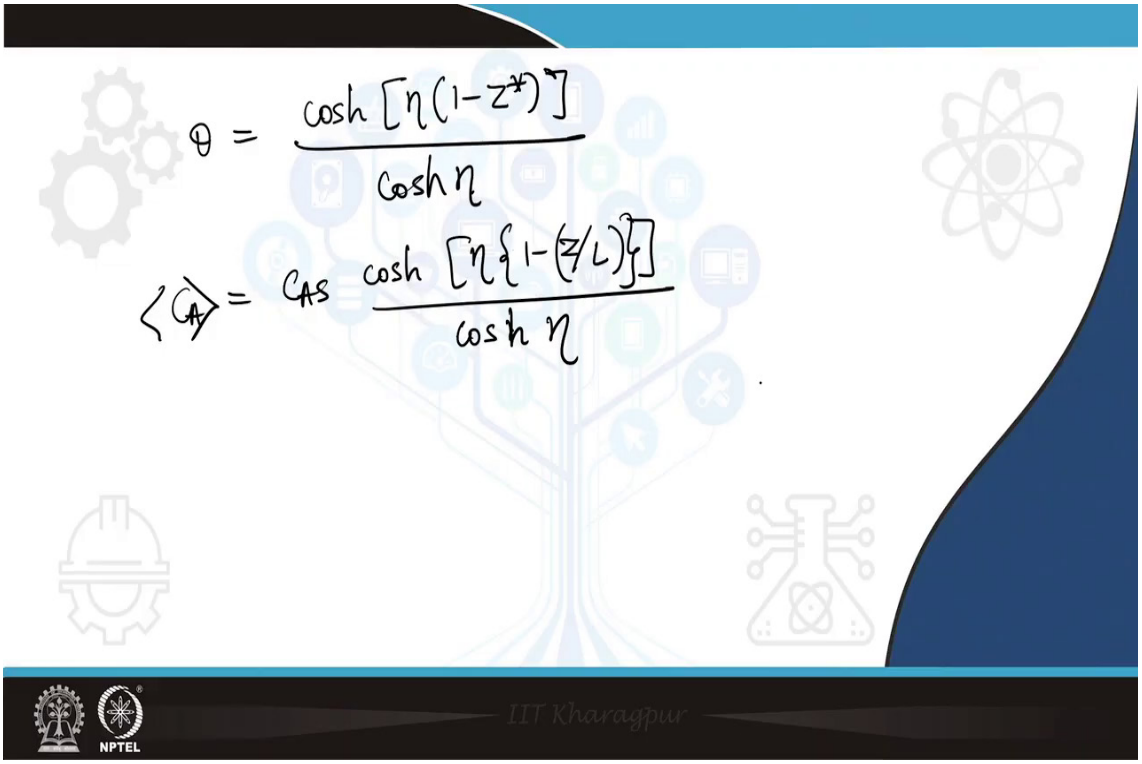

$$\theta = \frac{\cosh[\eta(1-z^*)]}{\cosh\eta}$$

$$\langle C_A\rangle = C_{AS}\,\frac{\cosh[\eta\{1-(z/L)\}]}{\cosh\eta}$$

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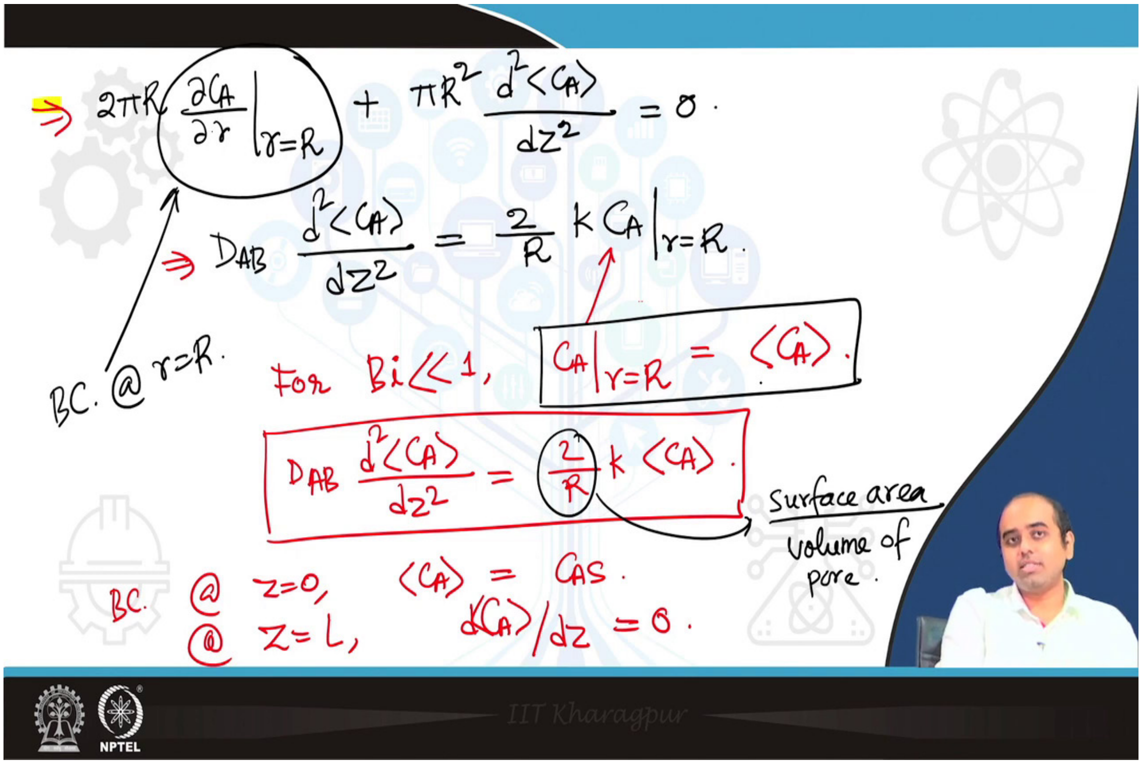

$$\Rightarrow 2\pi R \left.\frac{\partial C_A}{\partial r}\right|_{r=R} + \pi R^2 \frac{d^2\langle C_A\rangle}{dz^2} = 0.$$

BC. @ r=R.

$$\Rightarrow D_{AB}\frac{d^2\langle C_A\rangle}{dz^2} = \frac{2}{R}\, k \left. C_A\right|_{r=R}.$$

For $Bi \ll 1$, $\boxed{\left. C_A\right|_{r=R} = \langle C_A\rangle.}$

$$\boxed{D_{AB}\frac{d^2\langle C_A\rangle}{dz^2} = \frac{2}{R}\, k\,\langle C_A\rangle.}$$

$\frac{\text{surface area}}{\text{volume of pore}}.$

BC. @ $z=0$, $\langle C_A\rangle = C_{AS}$.
@ $z=L$, $d\langle C_A\rangle/dz = 0$.

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So, this equation has a solution in terms of using, this boundary conditions, using these two boundary conditions, you can easily write the solution in terms of sin h and cosine h and work out the boundary condition and you will get something like this. So, this is the concentration profile. And theta is, of course, C A by C A S. So, I can write C A as C A S cos h eta is the Thiele modulus, this is z by l. Sorry, cos h eta.

So, this is the concentration profile, this C A average concentration profile, inside the pore of the of the catalyst. And please note that this is of, this idea of Thiele modulus and everything is originated based on this very critical assumption or consideration that we have made. And this is true when Biot number to the problem is small or particularly for a very small diameter pore.

If the pore diameter is not small then you cannot make this consideration and this idea of area averaging will not work. And subsequently, the concept of Thiele modulus et cetera, is not applicable. So, this is one of the very important assumption or consideration behind the applicability of this Thiele modulus and then the, those effectiveness factor and everything.

But please realize that this is true in most cases where the pore radius is very small. And how small? That is, for that you have to consider, work out the equivalent Biot number. Even though Biot number is generally defined for the case of heat transfers, but you can also work out the Biot numbers for mass transfer considering the mass diffusivity and mass, this rate of diffusion and, similar, analogous to the heat transfer case, you can also work out the mass diffusivity for Biot number, Biot number based on the mass transfer scenario.

So, it is only when this Biot number is very, very small, and that is likely the case when the pore diameters is very small and slender, this assumption or this criterion works, and then you can proceed with this area averaging calculation and finally leading to the idea of the Thiele modulus and everything.

So, I hope I could give you a glimpse of the, in the pore scale analysis, and particularly, this is a situation where we see that the reaction which takes place at the boundary or at the surface of these pores and not in the bulk of the pore. So, this is something to understand and realize that when we are trying to consider the intraparticle mass transfer, it is very essential to understand that where is the, where is the effects or where is the mass transport more vital. Is it in the entire region of the catalyst or inside the pores? And accordingly, we have to choose the corresponding calculations.

So, I hope all of you understood the idea behind the, this mass transport as well as combined reaction systems. So, in the next class, we will talk about enzymatic reactions, as these are very important class of reaction problems. Thank you. I hope all of you found this lecture useful.