Mathematical Modelling and Simulation of Chemical Engineering Process

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Lecture 27

Modelling Intraparticle Transport and Catalysis

Hello, everyone. We are going to learn about intraparticle transport, I mean intraparticle mass transport during the reaction.

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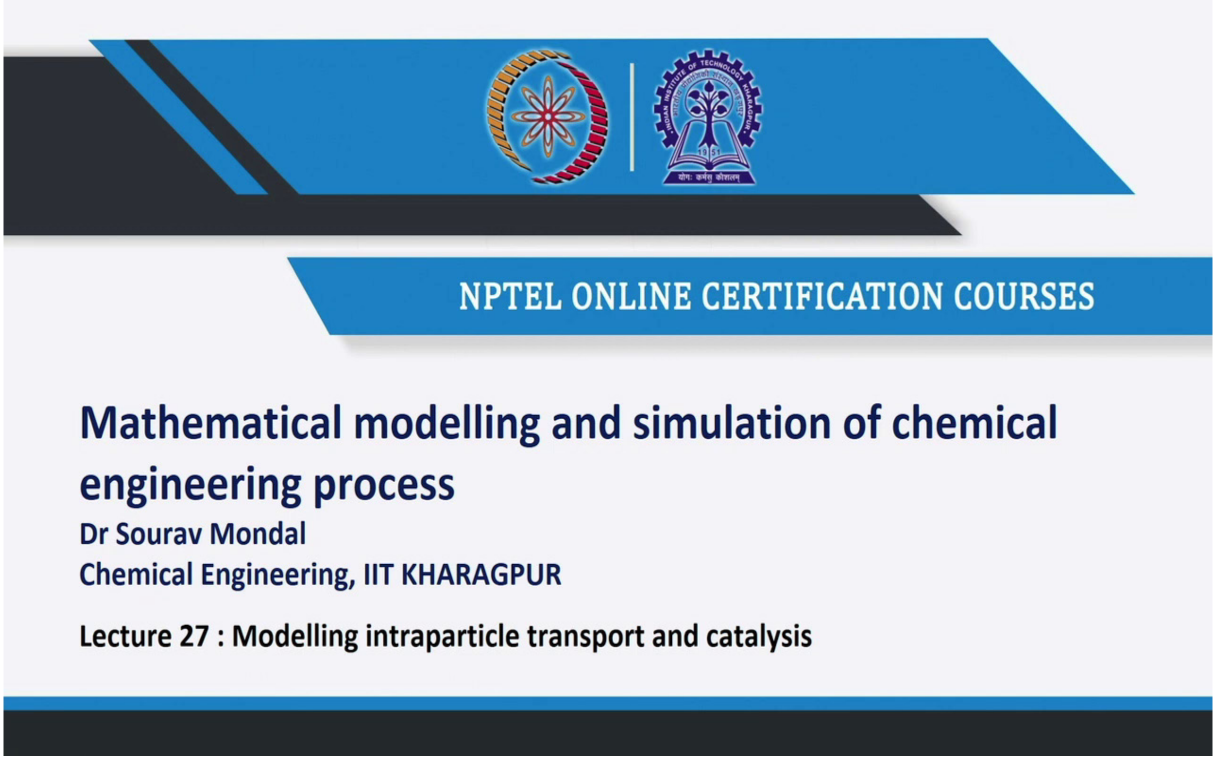

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Lecture 27 : Modelling intraparticle transport and catalysis

So in most packed bed reactor systems this is something which we often encounter, especially in the case of packed bed catalytic reactor systems. We often see that the mass transport inside the catalyst particle plays a big role in changing or in determining the overall conversion as well as the performance of the packed bed reactor.

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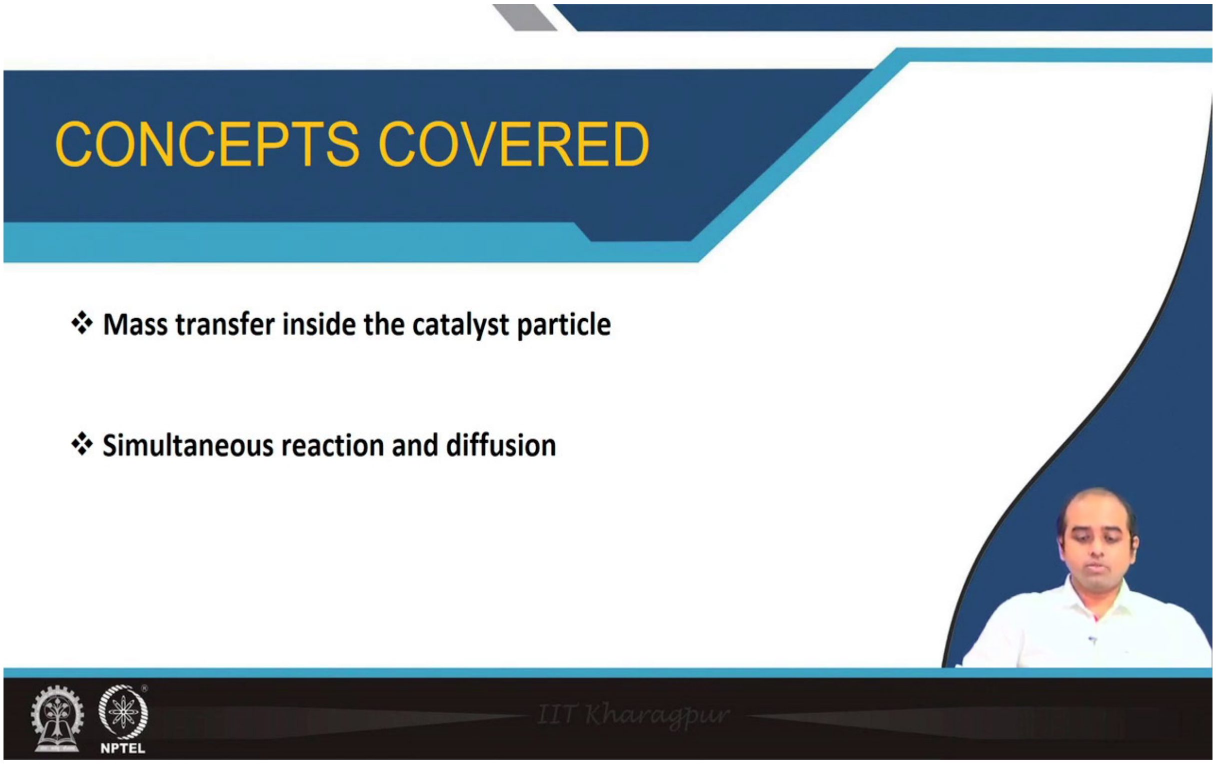

CONCEPTS COVERED

- Mass transfer inside the catalyst particle
- Simultaneous reaction and diffusion

So in the case of, so the intraparticle effects are important or let us say they are dominant when the rate of reaction at the surface, and this is something which we have already talked about in the last class when we tried to model the packed bed reactor, we said that the particle surface concentration which acts as the sink term to the main equation, is essentially governed by the, the particle level dynamics.

And then we have made an assumption or consideration that at steady state, the rate of disappearance at the particle surface should be equal to the, the rate of flux, convected towards the surface. But, and then subsequently, we also that the particle surface concentration is significantly lower compared to the bulk concentration et cetera because generally the reaction dynamics are much faster compared to the bulk scale diffusion.

Now, the question comes to the mind that what about diffusion inside the particle? Often, these particles are porous in nature and at the interior pores, there is a possibility of diffusion as well as reaction. So even if the reaction is faster it may happen that due to diffusion the particle, the concentration of the species, of the reactant species is not, not changing fast or the dynamics of the process is not entirely governed by the reaction inside the particle.

And accordingly it will affect the overall bed characteristics or overall the bed, catalytic packed bed reactor. So let us say if you have a spherical catalyst and we say that the particle is extremely porous and the reaction happens almost homogeneously inside the particle.

So please do not get me wrong here when I say it homogeneous. I mean that inside the particle, we do not consider any pore level effects. We consider that throughout the inside particle or in the bulk of the inside particle, the reaction happens. But overall, in the packed bed reactor, it is in the particles where these reactions happen. And this is true for extremely porous catalyst particles.

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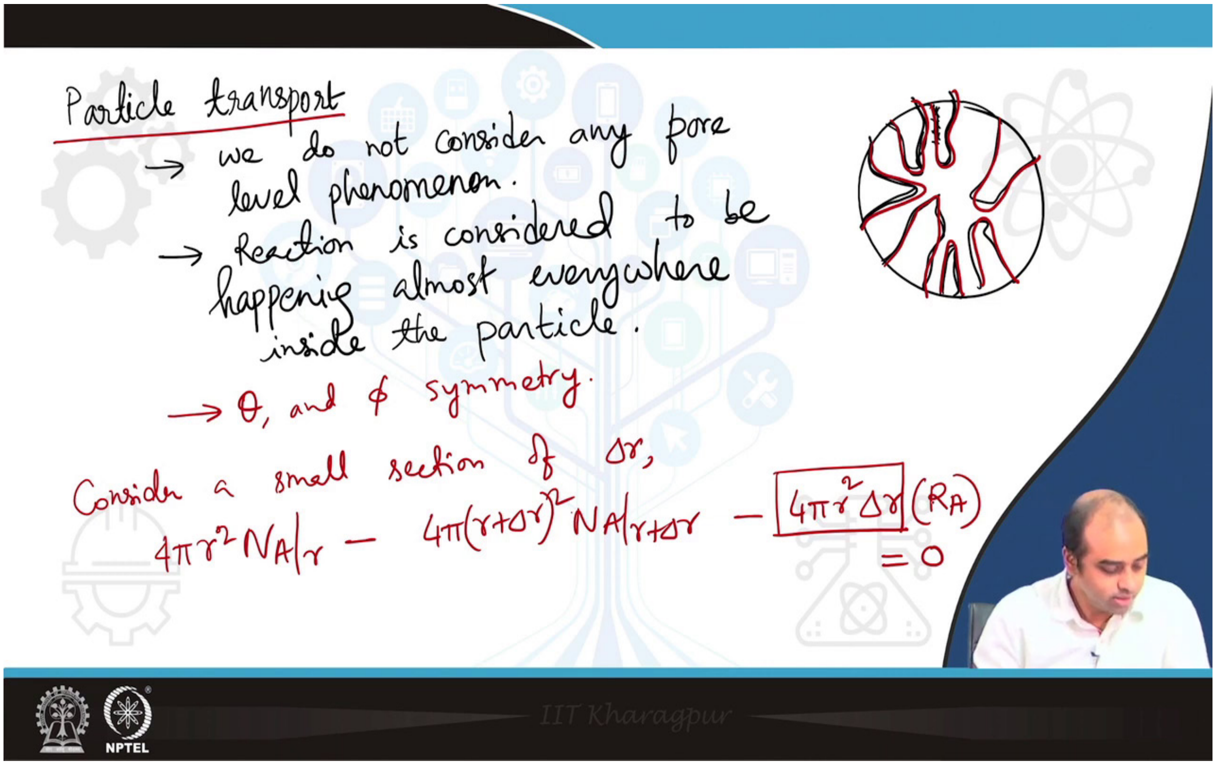

Particle transport

→ we do not consider any pore level phenomenon.

→ Reaction is considered to be happenig almost everywhere inside the particle.

→ θ, and ϕ symmetry.

Consider a small section of Δr,

$$4\pi r^2 N_A|_r - 4\pi(r+\Delta r)^2 N_A|_{r+\Delta r} - \boxed{4\pi r^2 \Delta r}(R_A) = 0$$

So let us say if you have a spherical catalyst or if you have a spherical particle where it may have certain pores like this, and essentially it is the reaction which ideally should happen at the interior of the pore surface, that is on the surface of the pores, that is something we are going to talk about in the next class.

But here, we are considering that these pores or whatever these pore networks are there inside this catalyst particle is so branched that you can consider, instead of, you can ignore these individual pore level effects, and you can consider that reaction is happening almost uniformly inside the catalyst particle.

This is a practical assumption in the case of highly porous catalyst particles, and you know that more the porosity of the particles is, the better is the reaction characteristics and better is its performance because it is the adsorption as well as reaction which takes place, is highly dependent on the porous surface area per gram of the catalyst particles.

So, in this case, for, for now we are considering that the particle transport is happening almost, almost homogeneously inside the, inside the catalyst particle. And we do not, for this moment we do not consider any pore level phenomena. So, we do not consider any pore level phenomena. Reaction is considered to be happening almost everywhere. That is not practically true, but essentially the reaction only happens at the exposed surface areas.

But you can make a consideration that if there is too much of branching or there is too much of pore network inside the particle, considering reaction at certain discrete points inside the bulk of the reactor can be assumed to be as like a uniform reaction which is happening at the inside of the particle. So, we can consider that almost everywhere this reaction happens in the bulk of the catalyst particle instead of considering only the, only the exposed surface area of the catalyst particle.

So that is a consideration we are not making here, and probably something we will look into the next class. So, with this idea in mind, considering that the particle has a radius of r we can write the elemental mass balance at a thickness of delta r, is not it? Again, we consider that this particle properties or whatever, this reaction properties or mass transport phenomena uniformly takes place in the theta and the phi direction.

So, we can assume that this mass transfer fluxes as well as distribution has theta and phi symmetry. So, we consider only the radial transport. So, consider a small element or a small section of delta r. We can write the fluxes in this way, is not it? This is the flux toward at the r and then we write down the flux that is coming out at r plus delta r. And this is subjected to the volumetric reaction.

So, flux in minus flux out is equated to the disappearance or the consumption by the chemical reaction, which is this term. So, this gives you the volume of that elemental section multiplied with the rate of reaction in this case. So, if you, you know the steps now, just go forward quickly here.

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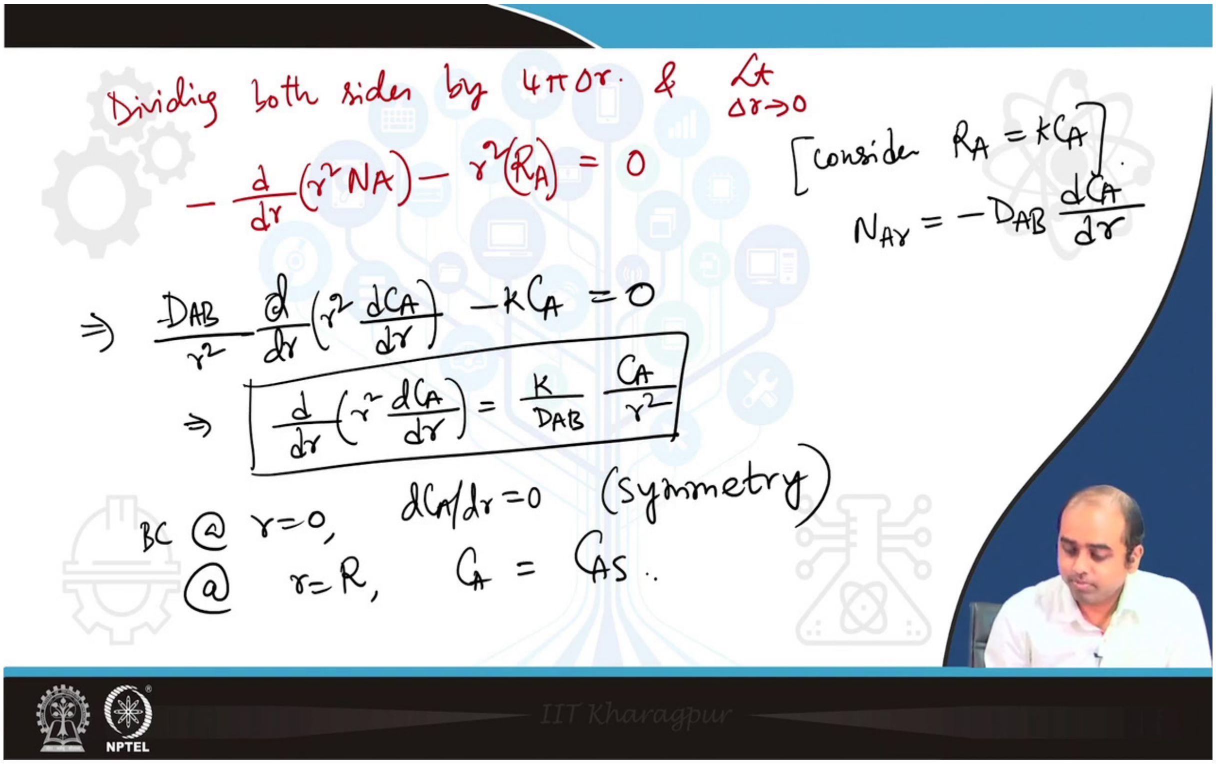

Dividing both sides by $4\pi\Delta r$. & $\underset{\Delta r \to 0}{Lt}$

$$-\frac{d}{dr}(r^2 N_A) - r^2(R_A) = 0$$

[consider $R_A = kC_A$].

$$N_{Ar} = -D_{AB}\frac{dC_A}{dr}$$

$$\Rightarrow \frac{D_{AB}}{r^2}\frac{d}{dr}\left(r^2\frac{dC_A}{dr}\right) - kC_A = 0$$

$$\Rightarrow \boxed{\frac{d}{dr}\left(r^2\frac{dC_A}{dr}\right) = \frac{k}{D_{AB}}\frac{C_A}{r^2}}$$

BC @ $r=0$, $dC_A/dr = 0$ (symmetry)

@ $r=R$, $C_A = C_{AS}$..

That dividing both sides by 4 pi delta r and then taking the limits of delta r and limit of delta r tending to 0, if we do these steps, then we are going to get something like this. Now, if you consider that we are, there is a first order reaction, so please note when I write this C A here, this means that it is the reaction, the concentration of the species inside the particles.

So, I am saying this because in the last class we have considered C A as the concentration in the, in the, in the packed bed reactor. So, the best option would be to consider this to be like C A p or something like that to distinguish between the concentration inside the particle and in the packed bed. And I can also consider that N A r is equal to minus, that is the Fick’s law of diffusion.

So, we get, is not it? So, this is the equation we are getting. I can do some rearrangement here, something like this. It is just to, for the ease of calculations. What about the boundary condition? It needs two boundary conditions in r. So, at r is equal to 0, of course, d C A d r has to be equal to 0 because that is the symmetry boundary condition.

And at r is equal to capital R, we can write C A is equal to something like C A S which is the surface concentration, that is something can be equated from the, the packed bed reactor condition, either you can consider continuity of the concentration or you can also consider flux continuity at the surface. So, this is something which is determined or which is coupled to the packed bed reactor calculations.

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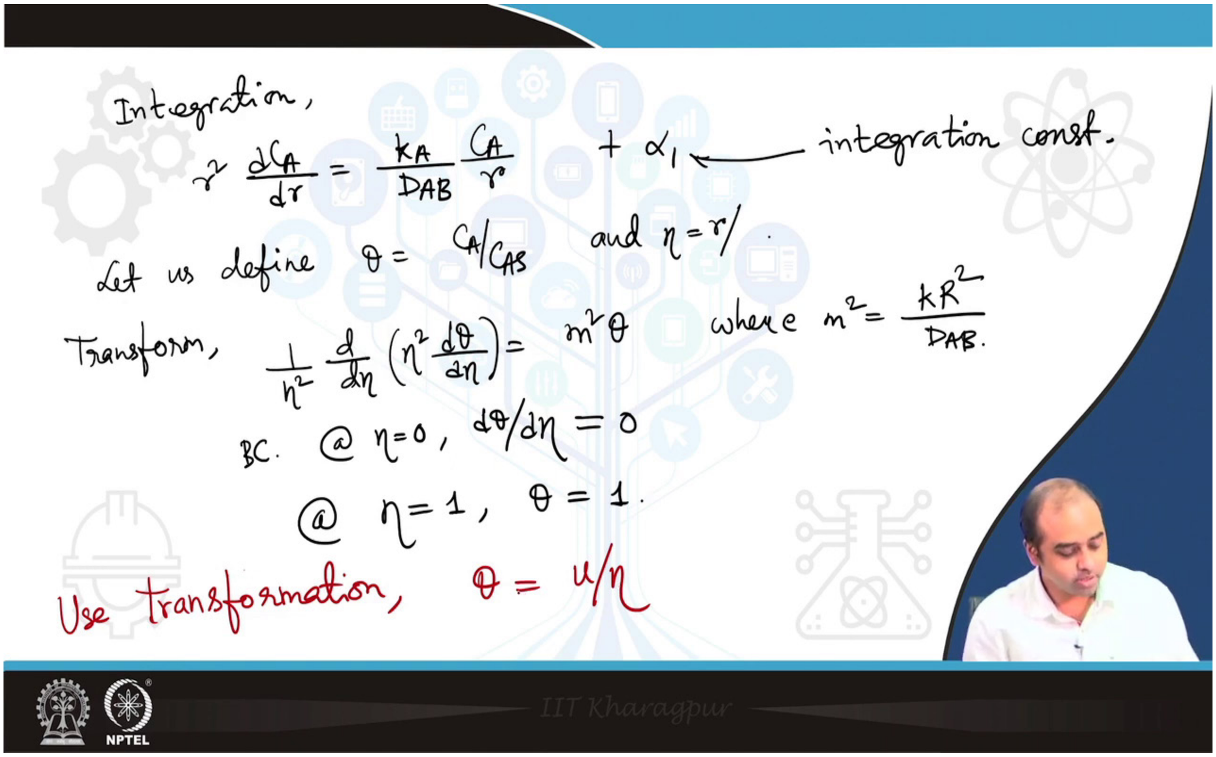

Integration,

$$r^2 \frac{dC_A}{dr} = \frac{k_A}{D_{AB}} \frac{C_A}{r} + \alpha_1 \longleftarrow \text{integration const.}$$

Let us define $\theta = C_A/C_{AS}$ and $\eta = r/$.

Transform, $$\frac{1}{\eta^2}\frac{d}{d\eta}\left(\eta^2 \frac{d\theta}{d\eta}\right) = m^2\theta$$ where $m^2 = \frac{kR^2}{D_{AB}}$.

BC. @ $\eta = 0$, $d\theta/d\eta = 0$

@ $\eta = 1$, $\theta = 1$.

Use transformation, $\theta = u/\eta$

So, this equation that we have here, we can do integration once, and try to get the solution. So, we can proceed like this. But there is also easier way. This will end up in trouble because at r is equal to 0 on the right hand side what you get is this one of these terms actually becomes, sorry there is no minus sign here. One of these, this, the first term on the right hand side becomes undefined. So you will end up in some sort of making the problem bounded.

So, an easier way, let us say we define, to resolve this issue is, let us define theta is equal to something like C A by C A S, ratio of the concentration, and define this eta is equal to r by capital R. So, I can transform the equation with this, this non-dimensionalization. So if you work out the transformation, you will be getting 1 by eta square d d eta eta square d theta by d eta. I, let me write this as m square theta where I define m square is equal to K R square by D A B.

Similarly, the boundary condition also needs to be defined. So as theta, eta is equal to 0 you have d theta d eta equal to 0. At eta is equal to 1, you have theta is equal to 1. Now, to this equation, let us use, this is just like non-dimensionalizing. So now let us use the transformation, something like this. Let us say theta is equal to u by eta. This is something which we have also studied in one of the problems before. So, if you do this transformation, if you do this transformation what you are going to get is this.

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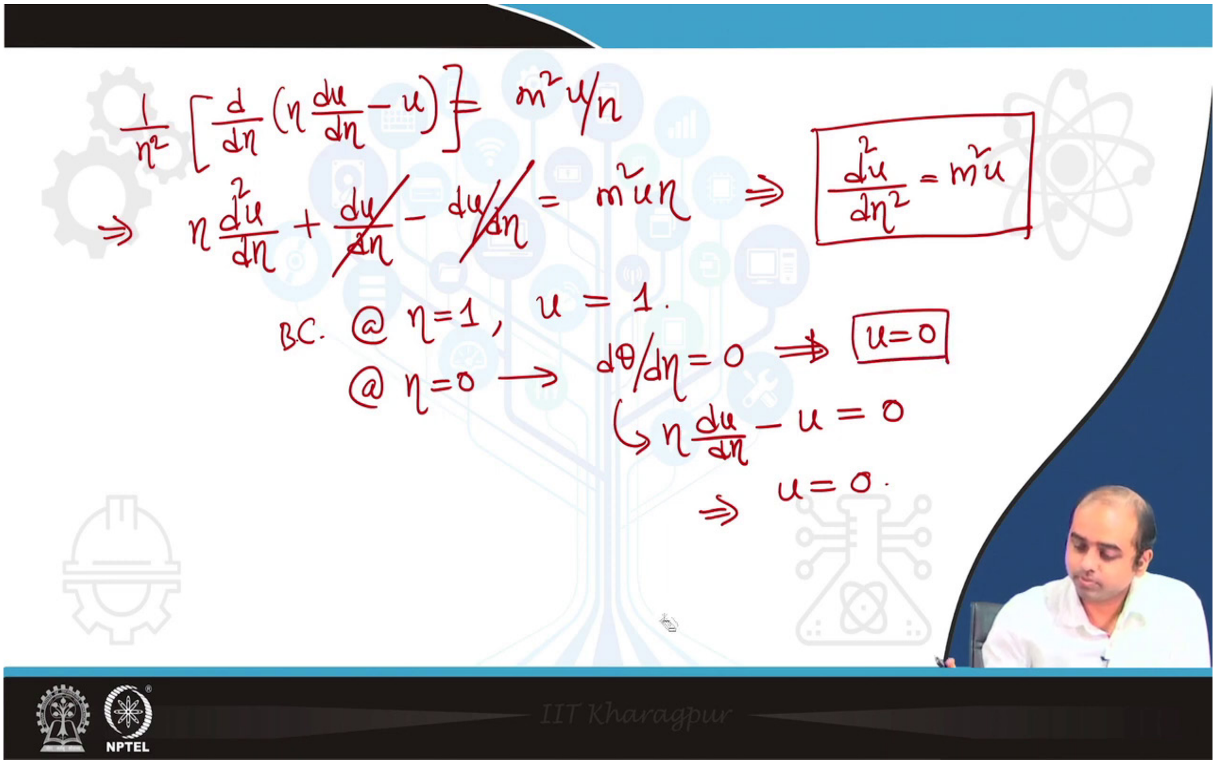


$$\frac{1}{\eta^2}\left[\frac{d}{d\eta}\left(\eta\frac{du}{d\eta}-u\right)\right] = m^2 u/\eta$$

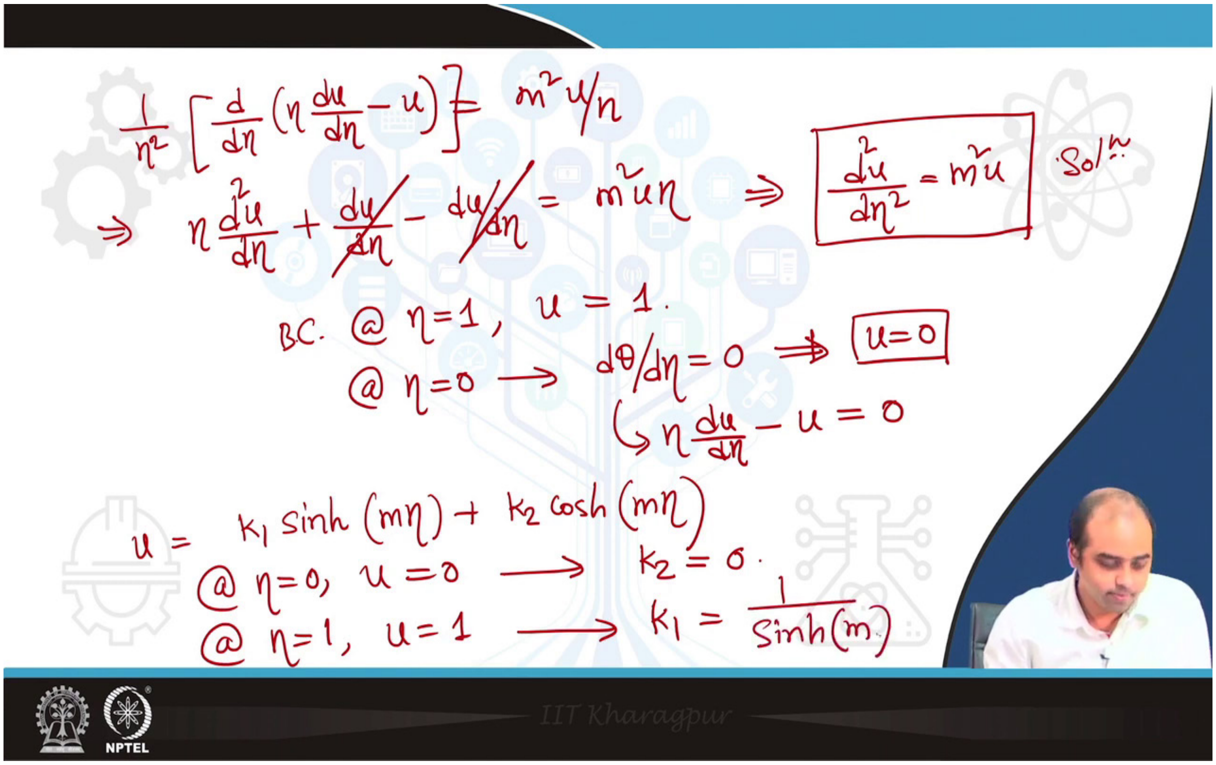
$$\Rightarrow \eta\frac{d^2u}{d\eta} + \cancel{\frac{du}{d\eta}} - \cancel{\frac{du}{d\eta}} = m^2 u\eta \Rightarrow \boxed{\frac{d^2u}{d\eta^2} = m^2u}$$

BC. @ $\eta=1$, $u = 1$.

@ $\eta=0 \longrightarrow d\theta/d\eta = 0 \Rightarrow \boxed{u=0}$

$\hookrightarrow \eta\frac{du}{d\eta} - u = 0$

$\Rightarrow u = 0.$



$$\frac{1}{\eta^2}\left[\frac{d}{d\eta}\left(\eta\frac{du}{d\eta}-u\right)\right] = m^2 u/\eta$$

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BC. @ $\eta=1$, $u = 1$.

@ $\eta=0 \longrightarrow d\theta/d\eta = 0 \Rightarrow \boxed{u=0}$

$\hookrightarrow \eta\frac{du}{d\eta} - u = 0$

$u = k_1 \sinh(m\eta) + k_2 \cosh(m\eta)$

@ $\eta=0$, $u=0 \longrightarrow k_2 = 0.$

@ $\eta=1$, $u=1 \longrightarrow k_1 = \frac{1}{\sinh(m)}$

Let me help you to write the transformed equation, you will be getting, you can also work out the steps yourself, there is nothing big mathematics involved, just like some few algebraic steps. So, I can further break this down into. So, this and this will cancel out and ultimately you will be getting, right?

Of course, the boundary condition needs to be modified. So, at theta is equal to, at eta is equal to 1, you will be having u is equal to 1. And interestingly, at theta is equal to 0, the condition was d theta, d theta d eta is equal to 0, now which is getting converted now to eta d u by d eta minus u to be equal to 0, which essentially means that for eta is equal to 0 you have u is equal to 0. So, this condition leads to the fact that u is equal to 0.

So, these are the boundary conditions. And you very well know the solution of this equation. The solution to this equation is something given by u is equal to, it is based on 2 cos, the sin h and cosine h are exponential functions, sin h m eta plus K 2 cos h m eta. So if you use the boundary condition that for eta is equal to 0 you have u is equal to 0 which leads to the condition that K 2 is equal to 0, and for eta is equal to 1 you have u is equal to 1 which gives you the condition that K 1 is equal to 1 minus sin h m.

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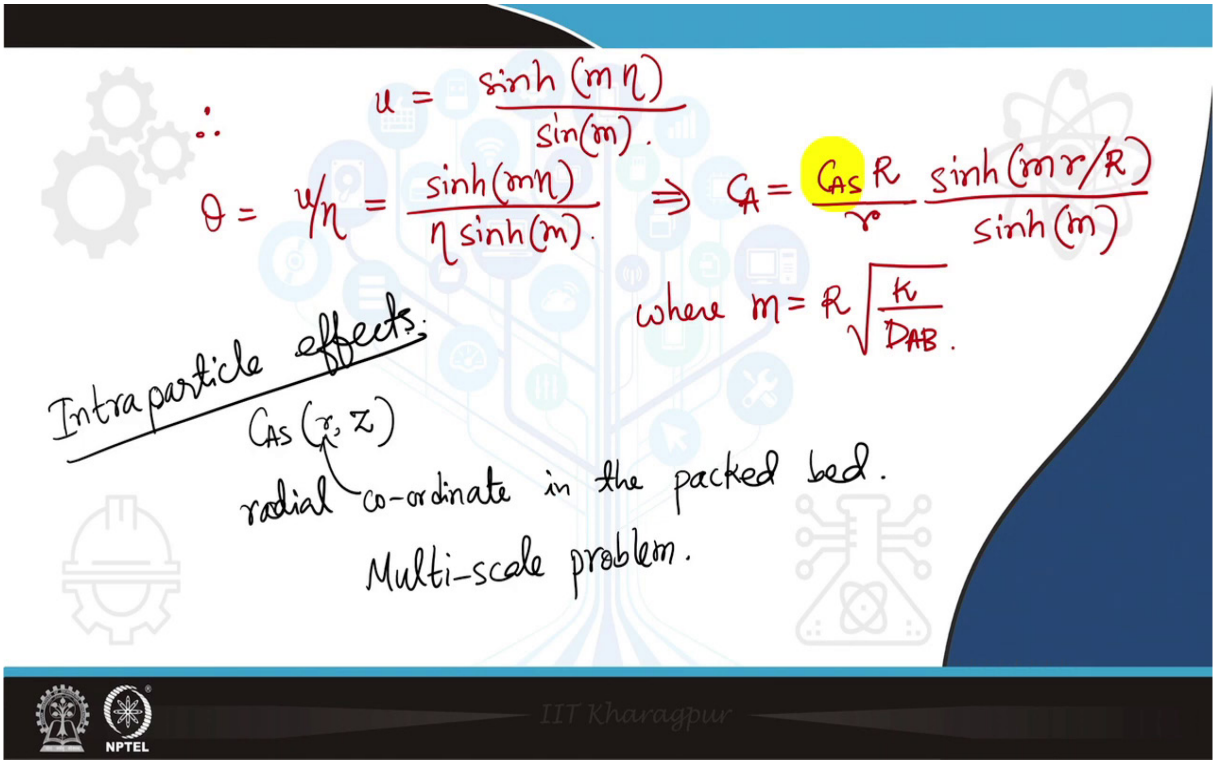


$$\therefore \quad u = \frac{\sinh(m\eta)}{\sin(m)}.$$

$$\theta = u/\eta = \frac{\sinh(m\eta)}{\eta \sinh(m)}. \Rightarrow C_A = \frac{C_{AS} R}{r} \frac{\sinh(mr/R)}{\sinh(m)}$$

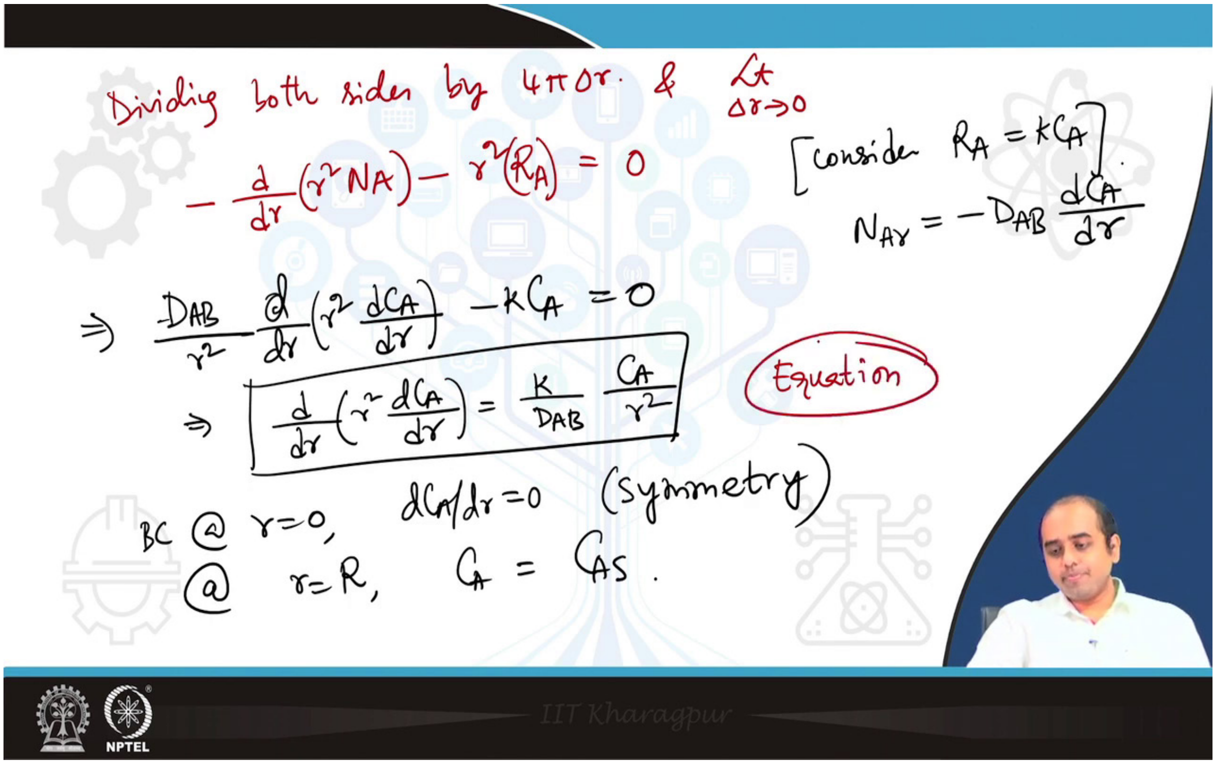
$$\text{where } m = R\sqrt{\frac{k}{D_{AB}}}.$$

Intraparticle effects:

$C_{AS}(r, z)$

radial co-ordinate in the packed bed.

Multi-scale problem.



Dividing both sides by $4\pi\Delta r$. & $\lim_{\Delta r\to 0}$

$$-\frac{d}{dr}(r^2 N_A) - r^2(R_A) = 0$$

[consider $R_A = kC_A$].

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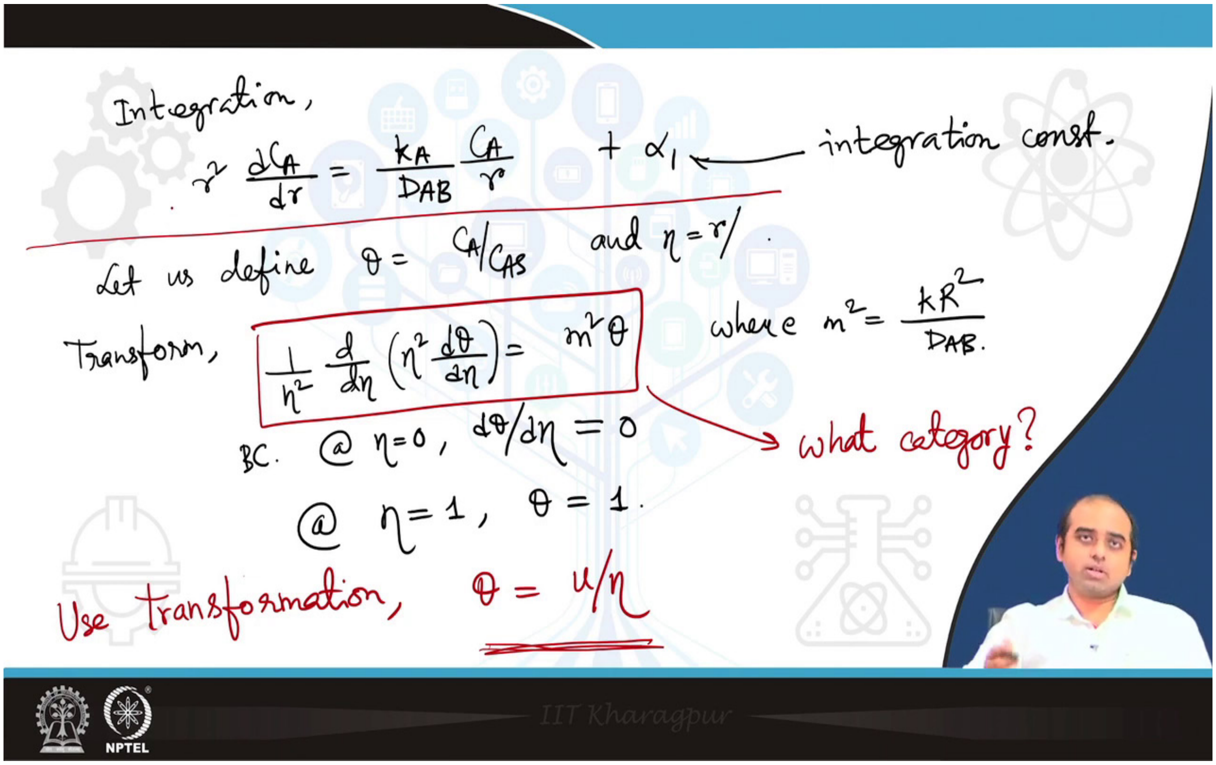
$$\Rightarrow \frac{D_{AB}}{r^2}\frac{d}{dr}\left(r^2\frac{dC_A}{dr}\right) - kC_A = 0$$

$$\Rightarrow \boxed{\frac{d}{dr}\left(r^2\frac{dC_A}{dr}\right) = \frac{k}{D_{AB}}\frac{C_A}{r^2}}$$

Equation

BC @ $r=0$, $dC_A/dr = 0$ (symmetry)

@ $r=R$, $C_A = C_{AS}$.



Integration,

$$r^2\frac{dC_A}{dr} = \frac{k_A}{D_{AB}}\frac{C_A}{r} + \alpha_1 \longleftarrow \text{integration const.}$$

Let us define $\theta = C_A/C_{AS}$ and $\eta = r/$.

Transform, $\boxed{\frac{1}{\eta^2}\frac{d}{d\eta}\left(\eta^2\frac{d\theta}{d\eta}\right) = m^2\theta}$ where $m^2 = \frac{kR^2}{D_{AB}}$. → what category?

BC. @ $\eta=0$, $d\theta/d\eta = 0$

@ $\eta = 1$, $\theta = 1$.

Use transformation, $\theta = u/\eta$

So, u is equal to, therefore u is equal to sin h m eta divided by sin m. Now, this u is equal to theta by eta, sorry this, I can write my theta is equal to u by eta. So, this means I have sin h, same thing, divided by eta. And subsequently, I can write my C A, theta is nothing but C A by C A S. So, I can write this is as C A S capital R small r sin h m r by capital R, where m is this quantity.

So, I am sure all of you have studied this in your reaction engineering class, the significance of this m, m is something, a very known quantity to you. I am sure and I am not going to describe more on what does physically m represent, and how changing m, changing m can be changed by the diffusivity or the, this reaction constant K for the first order reaction as well as the size of the particles. And what is the corresponding implication in the final solution.

I also like to draw your attention to one of the facts that this equation here, this equation, I want also you to think deeply about what is the type of this equation that or, what is the class of this equation, this belongs to. This, sorry, this equation, or even this equation also. It is just non-dimensionalized form of this equation. What category does this equation belongs to, and what is the general solution of this equation that you are aware of.

This is something for you to think. Like, you can directly get the solution of this equation without using the transformation here. So, without the need of this transformation, of course, if you do the transformation, life becomes more easy, but even without this transformation, there is a direct possibility of the solution of this equation, something that we try to do by integration but then we realize that this leads to undefined values, and it does not satisfy the boundary conditions.

So here, whatever we try to write is, is not feasible. Mathematically, it is not feasible because it is not able to satisfy, or the problem, or this conditions become unbounded at the boundary r is equal to 0, it becomes undefined. So, integrating straight away, this equation may not help you to find the appropriate solution. There is a direct solution to this problem.

And if you recall, probably in one of the lectures in the second week, I think, on special functions, if you look back, you can realize that this has a special type of solution, and you can directly get the solutions in those forms or in, using those functions. And, but here we try to do an alternate approach by using this transformation u by eta, which of course helps you to get a solution in terms of sin h and the cos, cos h functions. And as you know, sin h and cos h functions can also be represented alternatively as a form of exponential functions.

So, the idea that we try to work here or the final solution that we get here C A is equal to C A S r by R, this helps us in evaluating the concentration profile inside the particles. So, in the packed bed reactor, when the particle or the intraparticle effects are important and we need to solve out, we need to solve out what is happening at the inside of the particles, so the particle level calculation needs to be done.

And this is the case mostly when diffusion inside the particles plays a dominant role. So, you need to work out the calculations there. And here, the coupling parameter, this is something I really want to stress or draw your attention to the fact, that the, this value of the C A S, so this value of the C A S, which is the particle surface concentration, is something linked to the packed bed (concentration), the packed bed simulation. So the C A S, essentially, this C A S, so this C A S is a function of both r and z.

And this r is the, this coordinate or the radial coordinate in the packed bed. This is not inside the reactor. So, this is the radial dimension in the packed bed. And at different location or different cross-sectional location as well as vertical positions or axial positions, this C A S will be different. That is something we are actually solving out that is actually linked to the, the, the, the reaction term, if you recall.

This C A S is actually linked to the particle surface concentration, where we of course, made an assumption if you recall that the reactions or, the, the reaction contribution to the packed bed reactor is given by the particle surface concentration minus C A which is the particle, which is the bed concentration. And then we assume that C A S can be considered to be negligibly small. But if that is not the case, then this is how C A S is linked to this problem.

So, C A S is unknown in that packed bed reaction, C A S is also an unknown in this equation, and these two are coupled through the surface concentration of the particle. So, this becomes, this, so, so simulating the packed bed reactor, along with the particle level effects becomes a multi-scale problem, where at the bulk scale you solve the packed bed equations, but at the micro-scale, you solve the, this particle, intraparticle effects of the intraparticle concentration. And this is how these two are hooked up.

So, at every, so for all different locations or points in the packed bed, there has to be a coupling equation solving that from which the information has to pass on from the intraparticle diffusion and mass transfer. So, this is a multi-scale problem. And of course, this multi-scale problem reduces to either the micro-scale or the macro-scale depending on in which case the dynamics is, which, which is more dominant or which limits the overall transport phenomena. But essentially, this is a multi-scale problem, and this is also very similar to packed bed adsorption column also.

So, I hope I could give you a nice flavor on this very important packed bed reactor, and how the intraparticle effects are actually coupled in this problem. So, the transport inside the particles needs to be computed and can be hooked up to the bulk or the macroscopic calculations of the packed bed. So, I hope all of you found this lecture to be useful.

In the next class, we are trying to dig more deep into this catalyst particles and we will see that how the reactions at the pore level or how the transfer, mass transfer or diffusion, whatever is happening inside the pores, can be computed, and we can model them as a form of surface reaction. So, I think we will continue this in the next class. I hope all of you like the lecture on, on this problem today. See you in the next class. Thank you.