Module - 4
Lecture - 18
Internal Diffusion Effects: Model Development

In the previous lecture we looked at the effective diffusivity. We defined what is an effective diffusivity and what effective diffusivity might depend upon. And we defined each of these factors. So, in this lecture we will start quantifying the internal diffusion process.

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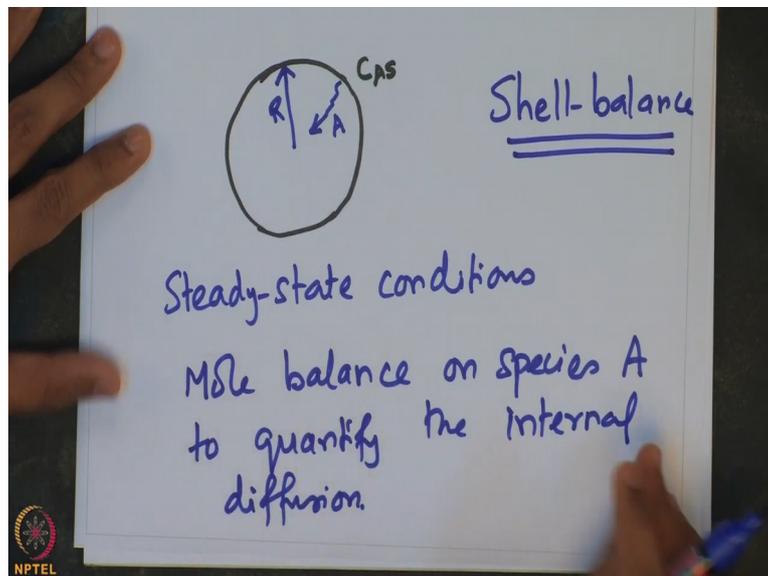
So, if I have a catalyst pellet, the species present at the surface; let us say that, the concentration of the species is C A S at the surface. We assume that the species is sufficiently available at the surface. And because of internal diffusion the species actually diffuses through the catalyst pellet. So now, if we assume that the radius of the pellet is capital R. And let us assume steady-state. We assume that the process is happening under steady-state conditions.

We can now write a mole balance on species A to quantify the internal diffusion process. Now, in order to do this, what we will do is, we will write shell-balance. A classical well-known method. We will write a shell balance to actually capture the mole balance or to write the mole balance on species A to capture the internal diffusion process. So, let us define a shell.

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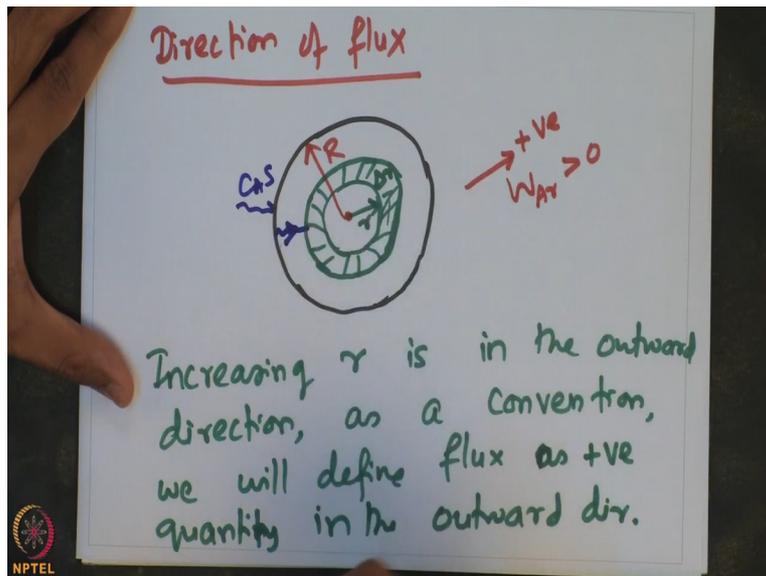
So, if we have a catalyst pellet and if the radius of the pellet, let us say is capital R; we can define a small shell. This is the centre of the pellet. We can define a small shell at a certain radius R. And let us say that the thickness of the pellet, thickness of the shell is, let us say delta R is the thickness of the shell. So, this is the shell that we are going to write our mole balance. So here is the shell. And we need to define the direction of flux.

What is the convention that we are going to use? So, given that the increasing radius is actually in the outward direction. The increasing r is in the outward direction. As a convention, we will define flux as a positive quantity in the outward direction. Okay. So, the flux that actually moves the positive direction of, is basically the direction in which we will assume that the flux is also positive.

So, we will assume that, as a convention, that the positive radial direction will be the direction in which the flux is actually greater than 0. And note that the species is actually diffusing. This is C A S, the concentration of the species at the surface. And the species is actually diffusing in the decreasing radial direction. So, because of that, the flux with which the species will defuse will actually be negative; indicating that the species is actually diffusing in the inward direction or the decreasing radial direction.

So, it is important to define what is the convention when the balances are written. And so, as a convention, I repeat, we will assume that the flux is positive in the direction of increasing radial direction. And as a result of which the flux with which the species is actually diffusing through the catalyst pellet, will actually be a negative quantity indicating that the species is

actually moving in the decreasing radial direction against the positive direction that we have actually considered as a sign convention in writing the mole balance. So, in order to write the mole balance;
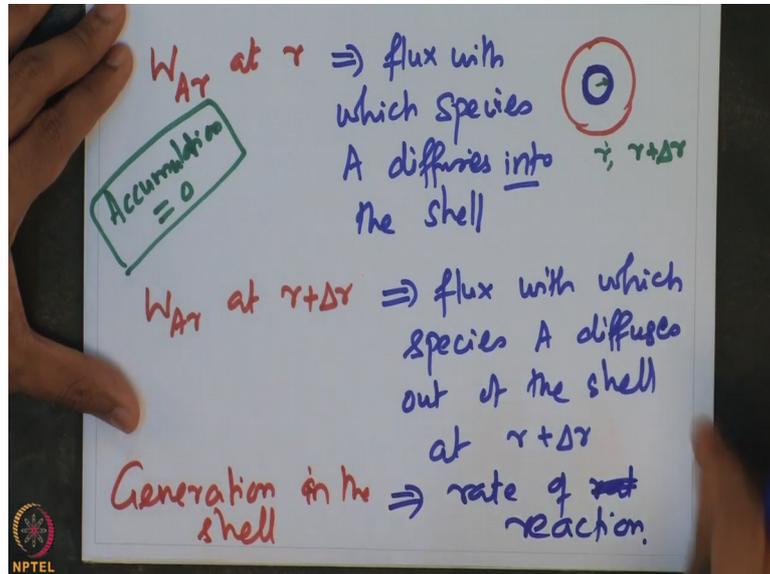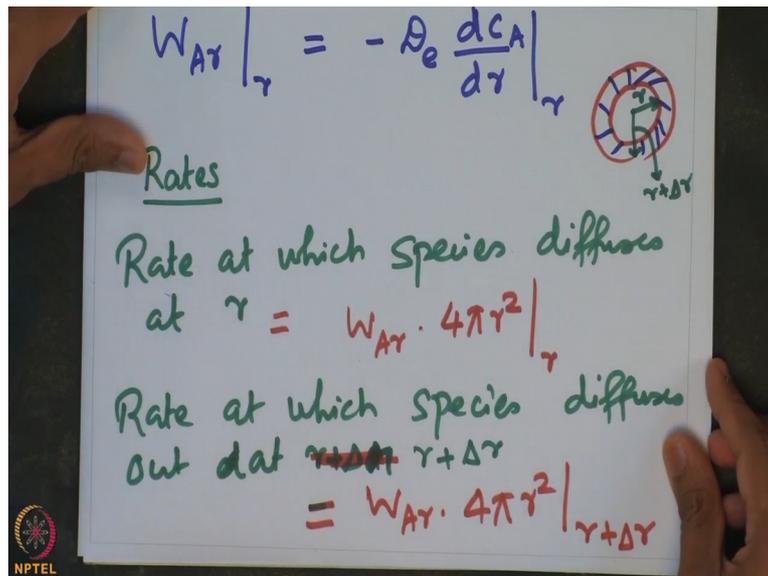
So, let us have a small sketch here. So, this is my shell. So, that is the shell in which I am going to write my mole balance. And let us say that the radius inside is r. And the outer radius is r + delta r, is the outer radius. So, this is the inner radius and r + delta r is the outer radius. So, what is the flux at radial position or what is the flux with which the species A is diffusing into the shell, at r which is basically the flux with which species A diffuses into the shell.

And we also need to find out what is the flux at r + delta r, which is essentially the flux with which species A diffuses out of the shell at r + delta r. Okay. We have assumed steady-state. So, therefore the accumulation is 0. Accumulation is essentially = 0 for this problem, because we assume steady-state. So, the other quantity we need to find out is, what is the generation in the shell; what is the generation term in the shell, which is essentially controlled by the rate of reaction.

Which can be found out from the rate of reaction. So, let us start with the first one. What is the flux at, what is the flux with which the species is actually diffusing into the shell that we are considering?

$$W_{Ar}\bigg|_r = -D_e \frac{dC_A}{dr}\bigg|_r$$

Rates

Rate at which species diffuses
at r = $W_{Ar} \cdot 4\pi r^2\big|_r$

Rate at which species diffuses
out dat ~~that~~ $r + \Delta r$
= $W_{Ar} \cdot 4\pi r^2\big|_{r+\Delta r}$

So, let us find out what is W A r at r. Now, this is important because we have said that the flux is actually positive in the increasing radial direction. And so, we need to take that into account. Besides, we have also defined when we discuss the effective diffusivity that the flux is essentially the happening through the entire cross-sectional area at that particular radius r, because the effective diffusivity takes, already takes into account, the voids and the solids that may be present in the, in that particular surface or that particular radius r at which the diffusion is actually happening.

So therefore, w a r, the flux, the flux essentially is given by the diffusivity – D e, into d c by, d c A by d c, d c A by d r at r. Now, when in order to write the mole balance, typically the mole balance is written in terms of the rates. So, we need to find out what is the rate at which species diffuses at r. And that should be essentially = the W A r which is the flux with which the species is diffusing at that particular location, multiplied by the area at that particular location, which is 4 pi into r square, at location r.

And the next thing is, what is the rate at which species diffuses out at r + delta r, which is essentially = W A r into 4 pi r square at r + delta r. Note that the radius at that location is different. It is not = r. It is the location from where the species is actually diffusing out. So, if I now look at the shell here. So, r is the inside radius and r + delta r is the outside radius of the shell; where the shell is essentially the volume that is present between r and r + delta r on which we are actually writing the balance. So, this volume between r and delta r and r + delta r radial location is what is called as a control volume.

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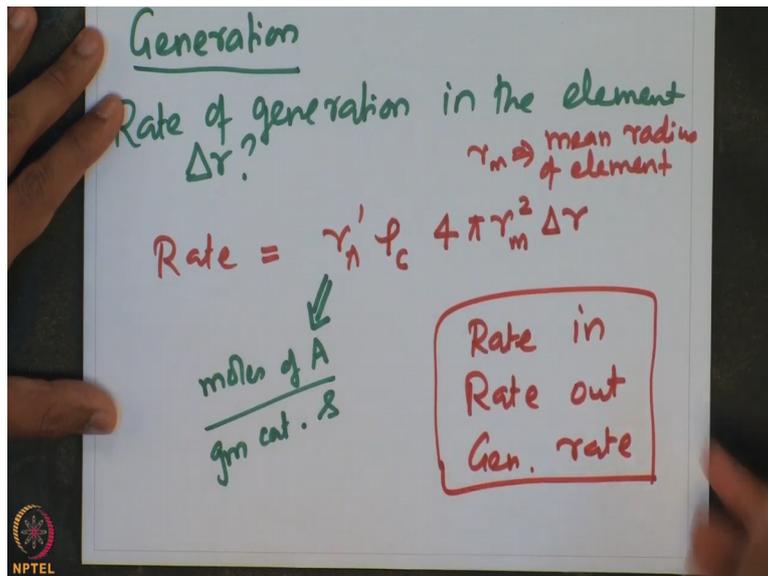
Next, let us look at what is the generation term. What is the rate of generation in the element, delta r? So, the rate can essentially be given by, so rate is given by the reaction rate r A prime, which is now, recall the convention, r A prime is the moles of species A that is formed per gram of catalyst into time. Okay. So, this is defined in terms of the weight of the catalyst. So, because it is defined in terms of the weight of the catalyst we actually need to multiply it with the density of the catalyst rho c.

And that multiplied by the volume of the element. So, suppose if we assume that there is a mean radius between r and delta r. So, r m is the mean radius of element, into r m square into delta r. So, the rate at which the species A is actually generated in the element is essentially given by r A prime, rho c into 4 pi r m square into delta r. So, we now have the rate at which species comes in. Rate in, we have the rate out and we also have the generation rate. So now we are all set for writing the balance. So, we will write the mole balance now.

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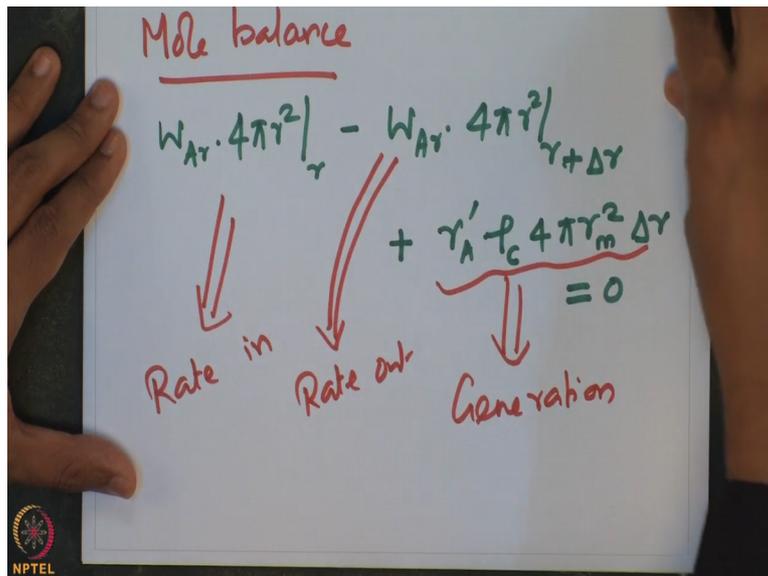
Let us write the mole balance. So, what comes in which is W A r into 4 pi r square at r. Note that the species as per the convention, the species is actually coming into the element at r and leaving out from the element at r + delta r. So, that − W A r into 4 pi r square at r + delta r + the rate at which it is generated. So, that should be = r A prime into the density of the catalyst. That multiplied by 4 pi r m square into delta r.

And that should be = 0, because we assume that the accumulation is 0. So, this term is rate in, this term is the rate out and this term is essentially the generation term. So, that completes the balance. And let us now do a little algebra here and modify this balance that we have written. So, you can modify this balance by dividing the expression with 4 pi delta r.

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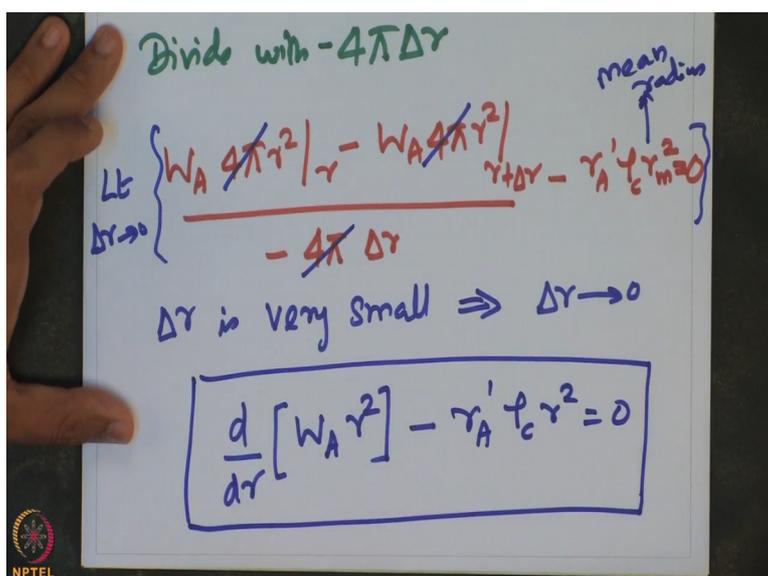
So, suppose let us say we divide with 4 pi delta r. And so, the expression becomes W A 4 pi r square. So, let us say we divide with – 4 pi delta r. And so that will be, – W A 4 pi r square, r + delta r divided by – 4 pi delta r – r A prime, rho c into r m square is = 0. So now, if we, if delta r is very small; if you assume that delta r is very small, that which basically means that delta r goes to 0. We can now take a limit; limit that delta r goes to 0.

We can now take a limit of this whole expression. And when we take a limit, the first term here essentially is, if I take the – sign into the numerator, it will be W A 4 pi r square r + delta r – W A 4 pi r square at r, divided by 4 pi. So, I can cancel out 4 pi from here. And so essentially it will be W A r square r + delta r – W A r square at r, divided by delta r. And that when we take limit r, delta r going to 0.

So, this is essentially d by d r into W A r square. In the second term, when I take delta r goes to 0, recall that r m is essentially the mean radius. This is the mean radius of the element. So, when delta r goes to 0, r m square essentially is = r square. So, that will be r A prime, rho c into r square = 0. So, this is the steady-state mole balance for species A, which is actually undergoing internal diffusion along with the reaction.

Recall that the reaction is also happening simultaneously at every location, every inside surface where the catalyst species is actually present; where the catalyst is present and the species actually is undergoing in each of these surfaces. So, we can now rewrite this expression as;

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$$W_{Ar}\Big|_r = -D_e \frac{dC_A}{dr}\Big|_r$$

$$\frac{d}{dr}\left[-D_e \, r^2 \frac{dC_A}{dr}\right] - r^2 \rho_c \, r_A' = 0$$

$$\Rightarrow D_e \, r^2 \frac{d^2 C_A}{dr^2} + D_e \, 2r \frac{dC_A}{dr} + r^2 \rho_c r_A' = 0$$

$$\Rightarrow D_e \frac{d^2 C_A}{dr^2} + D_e \frac{2}{r} \frac{dC_A}{dr} + \rho_c r_A' = 0$$

By substituting W A r; so W A r is essentially given by – D e into d C A by d r, if at r, it is given by r. So that, we can now rewrite this as, we can rewrite the mole balance as d by d r – D e into r square, d C A by d r – r square, rho c into r A prime = 0. Now, if I take this differential inside, I can rewrite this as, if D e is constant with respect to r, because it is essentially an effective diffusivity.

I can assume that it is constant with respect to the radial position. So, I can pull it out of the differential. So, that is essentially given as D e into r square, d square C A by d r square + D e into 2 r, d C A by d r – r square, rho c into r A prime = 0. So, if I now take this differential inside, the first term essentially corresponds to differential of this and the second term corresponds to differential of r square.

So, 2 r into d C A; all I have done is, we use the chain rule inside. So now, if I divide the whole expression by r square and recall, note that this is actually a + sign, because I have taken the – sign out. The – and – goes away. So, essentially if I divide the whole expression by r square, I will have D e into d square C A by d r square + D e into 2 by r, d C A by d r + rho c into r A prime = 0.

So, this is the mole balance. And now if I substitute or plugin for the actual kinetics which may be present; suppose let us say it is an nth order reaction which is happening at the surface of the catalyst.

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So, if we assume that it is nth order reaction; based on the rate, definition of the rates – r A prime which is the rate based on the weight of the catalyst, can be related to the rate based on the surface area which is available for the reaction to happen. So, that is essentially given by, say – r A double prime into the active surface area per unit weight of the catalyst. And if it is an nth order reaction, this is essentially given by – some k n double prime, which is the corresponding intrinsic rate constant, multiplied by C A to the power of n.

It is an nth order reaction. Multiplied by S a. So, therefore the, if I plug in this into the model, into the mole balance that we just derived; so, it will be D e into d square C A by d r square + D e into 2 by r into d C A by d r – k n double prime, S a, rho c into C A n = 0. So, that is the mole balance that we just derived. By plugging in the expression for the rates, we can see that it is nothing but k n double prime, S a, rho c.

So, if I now call this as some k, some rate constant k; so, I can now rewrite the whole expression as D e, d square C A by d r square + D e into 2 by r, d C A by d r – some k into C A to the power of n = 0. I can divide this whole expression by the diffusivity, effective diffusivity. And we can rewrite this expression as d square C A.

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We can rewrite this expression as d square C A by d r square + 2 by r into d C A by d r – some k divided by D e into C A to the power of n = 0. So, this is the mole balance that captures simultaneous reaction and the internal diffusion, in the case of the nth order reaction that happens at the catalyst surface. Now, when we write the mole balance, we need to also capture the boundary conditions.

Note that this is a second order differential equation. So, what will be the number of boundary conditions that will be there? There will essentially be 2 boundary conditions. What are these 2 boundary conditions? So, the first boundary condition is that, the species is at the, at some surface concentration, at r = capital R which is the exterior surface. So, we can assume that C A is = some C A S @ r = capital R. That is 1 boundary condition.

And the second boundary condition is that, it is because of axisymmetry at r = 0. We can assume that C A is = some finite value @ r = 0. So, in fact, when we derive this expression, when we assume that the flux is = – D e into d C A by d r. What we have actually inherently assumed that, we have assumed the equimolar counter diffusion; where species, if 1 mole of species A actually diffuses into form products, then equivalently a 1 mole of species be actually diffuses back into the bulk.

And thereby maintaining the total concentration. So, we have sort of inherently assumed, while driving this we have assumed what is called as the equimolar counter diffusion process. And we assume that the total concentration is essentially maintained constant. So, let us summarise what we have looked at in this lecture. We have said that the, we have said that, we have written the mole balance.

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And the mole balance which captures the internal diffusion is given by d square C A by d r square + 2 by r, d C A by d r – some k divided by D e into C A to the power of n = 0. In some literature, typically a subscript n is also used here to refer to the nth order reaction. So, we

may actually use this convention as well in the future lectures. And the boundary conditions are essentially C A = C A S @ r = capital R which is the outer surface.

And C A is finite @ r = 0. So, what we will do in the next lecturer is, we will take this expression and we will actually find the solution of this expression and actually look at how the concentration changes with respect to position. And what are the kind of insights that we can actually divide, by looking at the concentration profiles and what are the insights that we can derive about the actual diffusion process itself, that is happening inside the catalyst. Thank you.