# Chemical Reaction Engineering - II
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## Module - 5
## Lecture - 25
## External Mass Transport Limitations: Mass Transfer Coefficient

So far, till the last lecture, we have completed looking at the resistance that may be offered due to internal diffusion and how that would affect the overall rate at which the reaction could happen. Besides that, we also looked at how to estimate the overall rate of reaction, if the internal diffusion is actually limiting the overall rate. So, starting today's lecture, the next few lectures we will look at what happens if the external diffusion is actually limiting the overall rate at which the reaction can happen.

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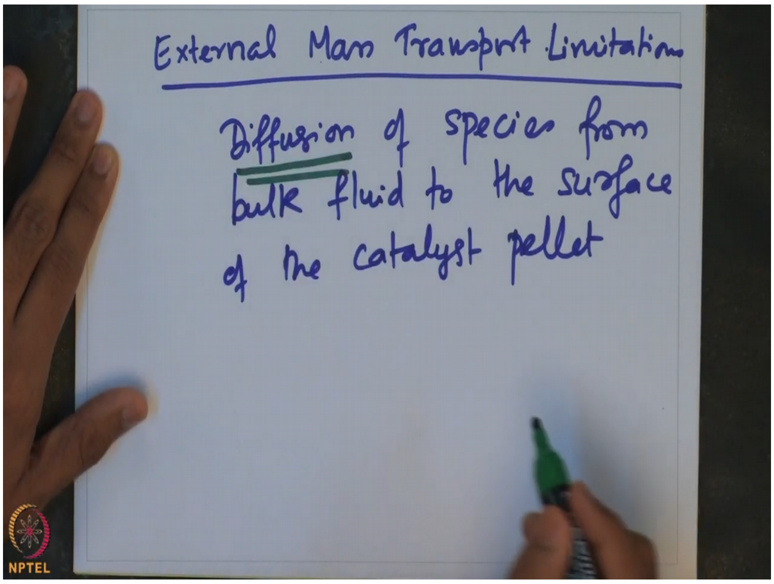

External Mass Transport Limitation

Diffusion of species from bulk fluid to the surface of the catalyst pellet

So, we look at what is classically called as external mass transport limitations. The external mass transport typically refers to the diffusion of species, mass transport due to diffusion of species from bulk fluid to the surface of the catalyst pellet. So, when we say mass transport limitations, what we really refer to is the diffusion of species from bulk to the surface of the catalyst pellet.

And if diffusion of the species is slow, then it is clearly that, it is slower than the other rate processes such as the internal diffusion or the surface reaction. Then it is clearly the external diffusion or the external mass transport which actually will control the overall rate at which the reaction can happen. So, how is the reaction typically conducted? It is typically conducted, let us say in a reactor. Let us say, a packed bed reactor. How does it look like?

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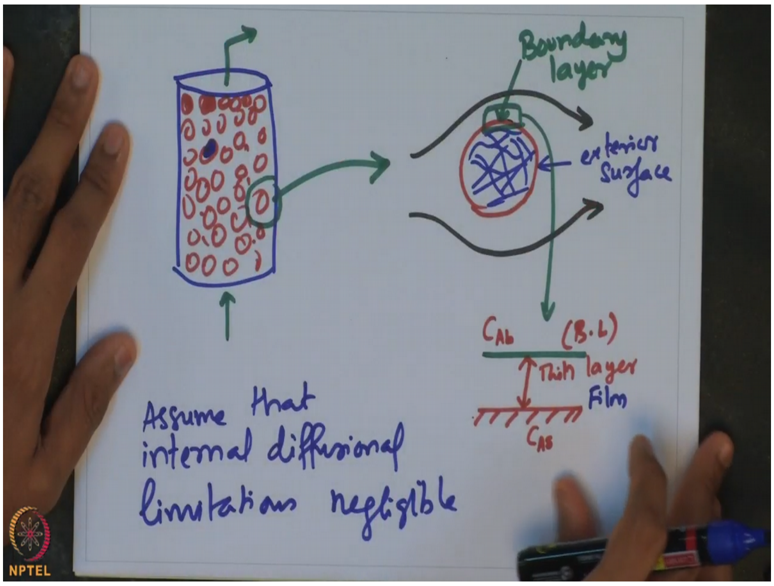

So, suppose we have a tank, which is a reactor. And let us say that the, is filled with catalyst. And so on and so forth. Catalyst, it is packed with catalyst everywhere. And let us say that the fluid is actually flowing from bottom to the top of the reactor. And the reaction is happening in the catalyst, in the active surface of the catalyst. So, let us say that this is a catalyst. Let us now zoom and see what happens close to a catalyst pellet.

Let us say that we zoom this. We zoom this and look at what happens very close to the catalyst pellet. So, let us say that we have a catalyst pellet here, which has lot of pores inside. And the reaction is happening in the active surface available close the pores. Now, when the fluid is actually flowing through the reactor, very close to the catalyst pellet; what happens is that the fluid is actually flowing past the object.

So, the fluid is actually flowing past the catalyst pellet. Now, when the fluid comes in contact with the surface, with the exterior surface of the catalyst pellet. So, this is the exterior surface of the catalyst pellet. When the fluid comes in contact with the exterior surface of the catalyst pellet, then what happens is that, there is a boundary layer that is actually formed. So, there is a boundary layer that is actually formed.

So, let us try to look at what happens very close to the boundary layer. Suppose, let us say we zoom this region. Let us look at what happens close to the boundary. So, there is a catalyst surface. There is a surface of the catalyst. And then, there is a region which is very close to the fluid, very close to the surface of the catalyst pellet, where all the concentration changes are happening.

So, in this small thin layer, which is basically the boundary layer; all concentration changes are actually happening in this thin layer. Now, everywhere outside the boundary layer, the concentration is, let us say the bulk concentration of the species. And if the concentration of the species which is actually undergoing reaction is actually surface concentration is, let us say C A S at the surface of the catalyst.

So, if it is infinitesimally small boundary layer that we can assume, that we can actually ignore the curvature which is present. And we can assume that it is actually a flat boundary layer which is present very close to the surface in an infinitesimally small region. Now, because it is very small, what, and, all the concentration changes are happening in this thin layer. We can actually assume that this is a, we can assume that this is a hypothetical film which is present close to the surface of the catalyst pellet.

Now, all the concentration changes that is actually observed, or all the concentration that is actually happening, would actually essentially happen in this film. So, if you understand and if you model or characterise the concentration changes in this film, then we would, actually we should, we could actually understand what is the nature of the resistance that is actually offered because of the transport at this, in this small thin film layer.

Now, if we assume that, let us assume that the, assume that internal diffusional limitations are negligible, let us assume that the internal diffusional limitations inside the pellet, that is the diffusional resistance that is offered for transport of the species in the catalyst pores is negligible. So, how do we characterise the concentration changes in thin layer. So, much of the next few lectures, we are going to look at, how to actually correlate this when the, when there is reaction, when there is no reaction.

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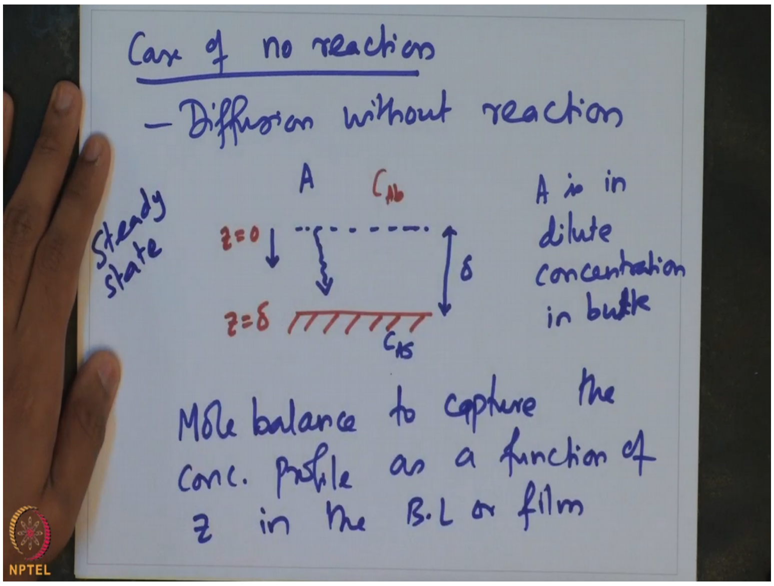

Case of no reaction

- Diffusion without reaction

A is in dilute concentration in bulk

Mole balance to capture the conc. profile as a function of z in the B.L or film

So, let us take the case of no reaction first. So, that is diffusion without reaction. So, let us now zoom the interfacial location, which we assumed as hypothetical thin film. So, let us say that this is the catalyst surface where the concentration is C A S. And let us say that this is the interface. And let us say that the interface thickness is, let us say delta. And if you assume that the concentration of the species A is actually, A is in dilute concentration.

Dilute concentration in bulk. And the species A which is present in bulk, they would actually diffuse in, through this film and reach the catalyst surface, for the reaction to happen inside the catalyst pellet. Now, suppose if I assume that my positive direction is this direction. If I assume that Z = 0 is here. And if the concentration of the species in bulk is, let us say C A b. And let us say that the thickness of the boundary layer is delta.

So therefore, this location is Z = delta. And the concentration of the species at that location is C A S. We can now write a mole balance to capture the concentration profile as a function of position in the boundary layer or the film that we have considered, hypothetical film that we have considered. Suppose we assume that the, that the diffusion is actually happening under steady-state conditions.

Let us assume that there is a steady-state condition. So, let us see how to write the mole balance. So, in order to write the mole balance, we need to first write a, we need to define what is the control volume.

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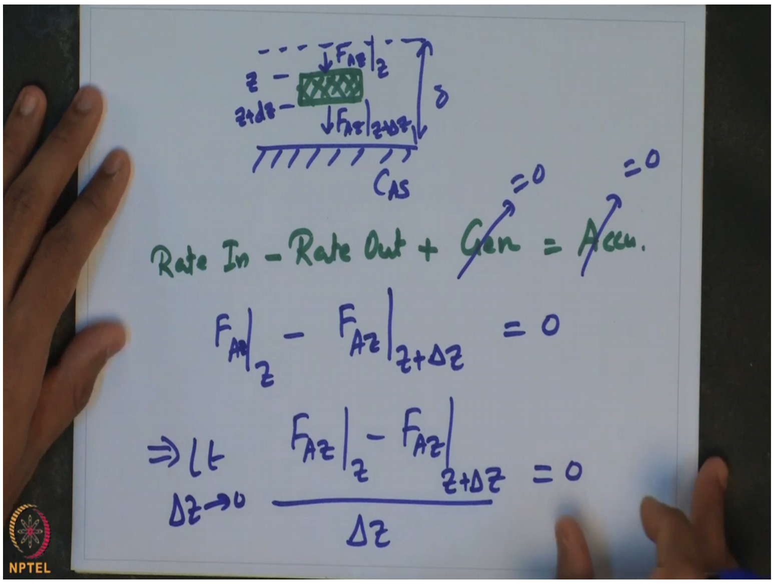

Rate In − Rate Out + $\overset{=0}{\cancel{\text{Gen}}}$ = $\overset{=0}{\cancel{\text{Accu.}}}$

$$F_{Az}\big|_z - F_{Az}\big|_{z+\Delta z} = 0$$

$$\Rightarrow \lim_{\Delta z \to 0} \frac{F_{Az}\big|_z - F_{Az}\big|_{z+\Delta z}}{\Delta z} = 0$$

So, suppose this is the surface of the catalyst pellet. And this is the boundary layer. We can define a small control volume here. And we can actually say that, the rate at which the species diffuses, into the element. Let us say that the element starts at some Z location. And the rate at which the species diffuses is F A Z. And let us say that this location is Z + d Z, as tiny element. And the rate at which the species diffuses out is F A Z at Z + delta Z.

We can now write a mole balance. How to write the mole balance? So, the rate at which the balance is, rate at which the species comes into the element, – the rate at which the species leaves the element, + whatever is generated in the element; that should be = accumulation of the species in the element. But we have assumed steady-state. So therefore, the accumulation is = 0. And there is no reaction that is happening in the fluid phase.

All reaction is happening only in the catalyst phase. So, the generation term also is = 0. So, plugging in the rates at which species is entering the element and leaving the element; we can actually complete the mole balance. So, that is, F A entering at Z – F A, F A Z, which is the rate at which the species is entering the element in Z direction, delta Z = 0. Now, I can divide this by delta Z. So, that is essentially = divided by delta Z = 0.

And I can now take limit delta Z going to 0. Because if the element is very small, I can take the limits. And once I take the limits, what I essentially get is that, d F A Z by d Z is = 0. So, this is the mole balance that captures the species, dependance of the species concentration on the position. Now, what is the rate at which the species would come in at any location? So, F

A Z is essentially = the flux with which; so, this is the molar flux with which the species actually diffuses into that location, multiplied by the cross sectional area A C.

Whatever is the area at which the species is actually diffusing. So now, if I substitute that into the mole balance, I will see that the mole balance is essentially, reduces to A C, area being constant. So, that is essentially, or that is d W A Z by d Z = 0. Now, how do we find out the flux. What is the relationship between flux and the concentration at any location?

We know from Fick's law, that if it is equimolar counter diffusion or if it is dilute concentrations, then the flux at any location is essentially given by – equimolar counter diffusivity into d C A by d Z is basically the gradient of concentration, with respect to position at that location. So, the flux at any location is given by – D A B into d C A by d Z. Basically we have written, what is called the Fick's law. And so, plugging Fick's law into the mole balance;

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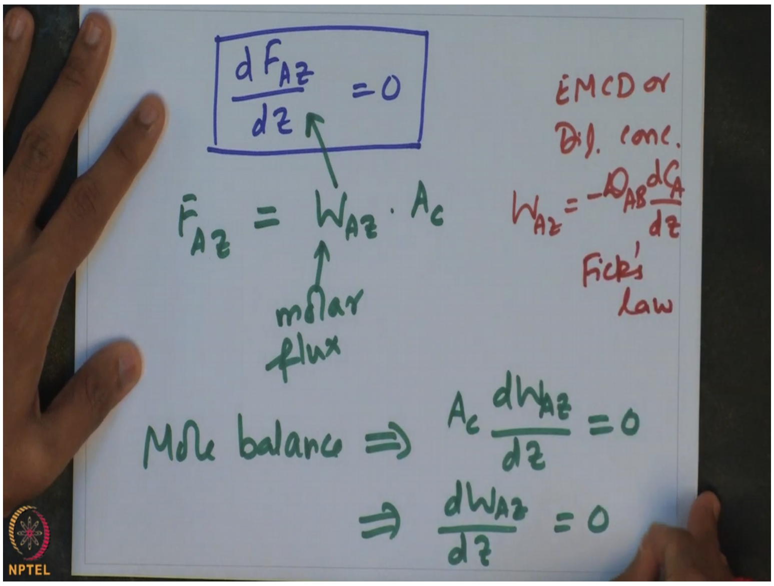

$$\boxed{\frac{dF_{Az}}{dz} = 0}$$

EMCD or
Dil. conc.

$$F_{Az} = W_{Az} \cdot A_c$$

molar
flux

$$W_{Az} = -D_{AB}\frac{dC_A}{dz}$$

Fick's
law

Mole balance $\Rightarrow A_c \frac{dW_{Az}}{dz} = 0$

$$\Rightarrow \frac{dW_{Az}}{dz} = 0$$

We will see that the balance essentially reduces to d by d Z of – D A B, into d Z is = 0. And that can be rewritten as, into d square C A by d Z square = 0. And we know that the diffusivity is actually a positive quantity. It is never 0. So therefore, the balance reduces to d square C A by d Z square is = 0. What are the boundary conditions?

What are the boundary conditions for this problem? So, the boundary conditions are, at the concentration of the species is = the bulk concentration at Z = 0. Recall that we said that the boundary layer, the location of the boundary layer or where it ends into the bulk fluid, that is what we defined as Z = 0. And this is delta. And this is, the concentration here is the surface concentration and this concentration here is the bulk concentration.

Therefore, the boundary conditions are C A concentration of A at Z = 0, which is the bulk concentration is = C A B. And concentration of the species at the catalyst surface that is Z Z = delta, is essentially = the concentration of the species at the surface which is C A S. So, we now have the model equation and we also have the boundary conditions. We can now solve the model equation to find out the concentration profile as a function of position.

So, the solution of this equation is, C A is essentially = some constant K 1 into Z + another constant K 2. So, that is the solution of this equation d square C A by; that is the solution. And now, we can substitute the boundary condition. What is the first boundary condition? The first boundary condition is at Z = 0, C A is = C A bulk. So, substituting that, we find 0 is =, that term goes away, 0, this is C A bulk. CA bulk is = 0 + K 2.

So, from here we find that K 2 is = C A bulk. And now, we can substitute that back into the equation. So, the current form of the solution is C A is = K 1 Z + C A bulk. Now, we have second boundary condition. We can actually substitute the second boundary condition to find another constant K 1. The other boundary condition is Z = delta, which is the boundary layer thickness. C A = the surface concentration.

So, substituting that, we find that C A S is = K 1 into delta, + C A b. From here, we find K 1 is = C A S – C A b divided by delta. So, I can now substitute K 1 and K 2 back into my model equation. And I will find that, C A is = C A S – C A b by delta into Z + C A b. So, this is the solution of the model equation. In fact, it tells me how concentration is changing as a function or position in the boundary layer.

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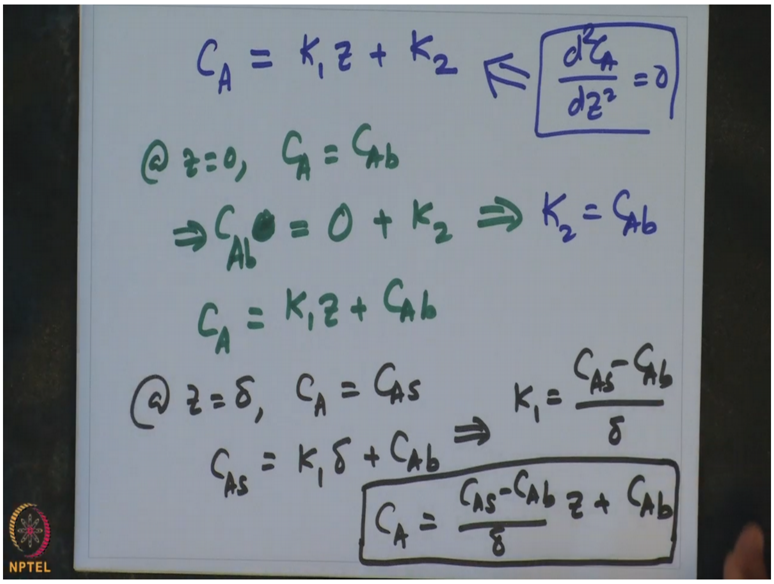

$$C_A = K_1 z + K_2 \Leftarrow \boxed{\frac{d^2C_A}{dz^2} = 0}$$

$$@\ z = 0,\ C_A = C_{Ab}$$

$$\Rightarrow C_{Ab} = 0 + K_2 \Rightarrow K_2 = C_{Ab}$$

$$C_A = K_1 z + C_{Ab}$$

$$@\ z = \delta,\ C_A = C_{AS} \qquad K_1 = \frac{C_{AS} - C_{Ab}}{\delta}$$

$$C_{AS} = K_1 \delta + C_{Ab} \Rightarrow$$

$$\boxed{C_A = \frac{C_{AS} - C_{Ab}}{\delta} z + C_{Ab}}$$

I can now rewrite the solution as C A – C A b divided by C A S – C A b is = Z by delta. So, if I now plot the concentration profile as a function or position. Let us say that this is Z by delta and going from 0 to 1. And let us say that this is my concentration going from, let us say surface concentration C A S, all the way up to the bulk concentration. And so, essentially it will have, what is a straight line behaviour.

So, this location as my Z by delta is = 1. Now, what are we interested in? We actually want to understand what is the nature of the resistance that is actually offered by the diffusion. Now, in order to understand the resistance, we need to define or we need to find out what is the actual rate at which the species is diffusing. And given that the cross-sectional area is constant, it would be sufficient to estimate what is the flux with which the species is actually diffusing at any location; particularly at the surface.

So, let us now try to estimate what is the diffusion. What is the flux with which the species is diffusing? So, which is given by W A Z, which is = – D A B equimolar counter diffusion of species A, into d C A by d Z. We know C A versus Z. So, we can calculate what is d C A by d Z. So, that is = D A B, – D A B by delta into C A S – C A b.

Now clearly, we have actually assumed that the bulk concentration is actually greater than the surface concentration. And that is not a surprise. The species is actually diffusing from the bulk, all the way to the catalyst surface for the reaction to happen inside the catalyst pellet. So, therefore clearly the bulk concentration must actually be greater than the surface concentration. So therefore, this, therefore the flux can be written as D A B divided by delta, into C A b – C A S.

So, that is the flux with which the species is actually diffusing from the bulk to the surface. In fact, this flux that we have estimated as a function of the bulk concentration, is actually valid for both dilute concentrations and for equimolar counter diffusion. Because the Fick's law that we have used, the form of the Fick's law that we have used, is valid for both these cases. Which means that this Fick's law that we have used is essentially for the case where the concentration, the total concentration is actually is constant.

And by assuming equimolar counter diffusion, we can actually assume that the total concentration is constant. Now, how do we understand whether equimolar counter diffusion is possible in the case that have looked at. We have assumed that the species A is actually diffusing through the film, from the bulk to the surface of the catalyst. Now, in fact, we could assume that the film essentially consists of, let us say, some other species B.

And therefore, there is this 2 species A and B which is present. And so, it is fine to assume what is called as an equimolar counter diffusion of species A in, through the film. And therefore, the Fick's law that we have used, the form of the Fick's law that we have used is actually valid. So, once we understand what is the flux;

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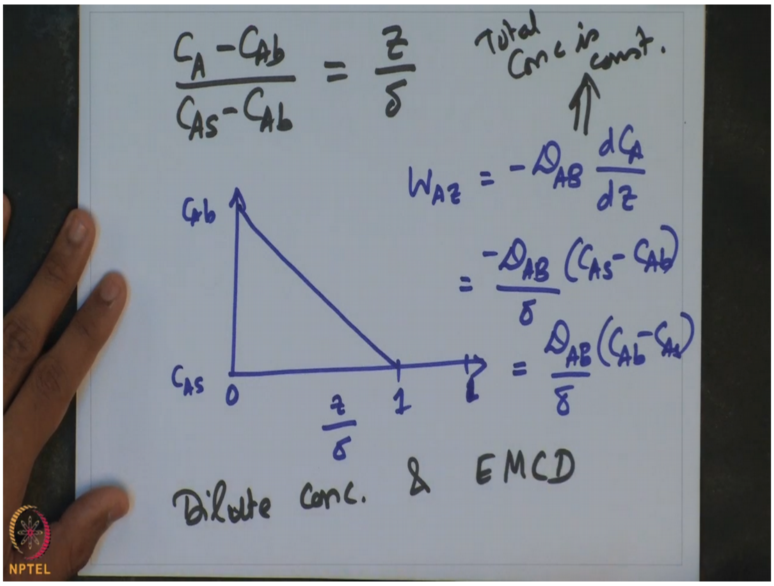

We can actually define an important concept called mass transport coefficient. So, what we are actually interested in, is to find out what is the nature of the resistance offered by the external diffusion. Now, in order to understand the resistance, it is actually useful to define an important quantity called the mass transport coefficient. And in fact, the mass transport coefficient actually captures quantitatively the resistance offered.

And we are going to see how that is the case. How the mass transport coefficient actually quantitatively captures the resistance. Now we found that if there is no reaction the flux with which the species is actually diffusing, through the film is essentially given by D A B divided by delta; which is the boundary layer thickness. That multiplied by C A b – C A S. Now, we can sort of rewrite this expression in a slightly different manner. This is the boundary layer thickness. We can rewrite this as C A b – C A S divided by delta by D A B. We can sort of post this as a ratio of driving force to some resistance.

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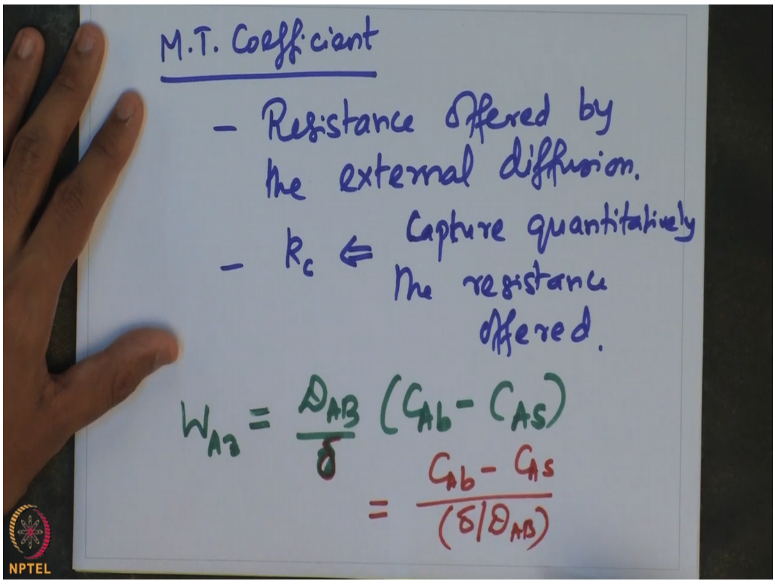

M.T. Coefficient

- Resistance offered by the external diffusion.
- $k_c \Leftarrow$ Capture quantitatively the resistance offered.

$$W_{Az} = \frac{D_{AB}}{\delta}(C_{Ab} - C_{AS}) = \frac{C_{Ab} - C_{As}}{(\delta/D_{AB})}$$

So, we can now write as ratio of some driving force, divided by resistance offered. And if we now say that the concentration of species at the bulk is a measurable quantity. And if you look at the driving force. What is the driving force here in this case? We can say that C A b – C A S is the driving force. The concentration difference between the bulk and surface. And so, we can sort of write the flux as the driving force C A b – C A S multiplied by a mass transport coefficient k c.

But we estimated that the, if there is no reaction, this is = the D A B equimolar counter diffusivity divided by delta into C A b – C A S. So, from this we can clearly read that the mass transport coefficient k c is essentially = D A B by delta for a film that we have used which essentially lumps all the transport that is actually happening from the bulk to the surface of the catalyst. Now, suppose let us say, we look at this, we now express the flux in terms of the driving force resistance framework.

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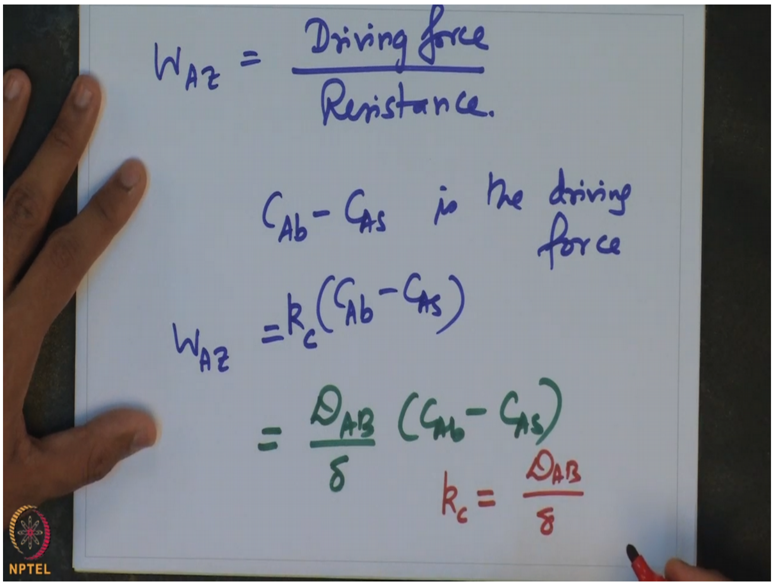

$$W_{Az} = \frac{\text{Driving force}}{\text{Resistance.}}$$

$C_{Ab} - C_{As}$ is the driving force

$$W_{Az} = k_c (C_{Ab} - C_{As})$$

$$= \frac{D_{AB}}{\delta} (C_{Ab} - C_{As})$$

$$k_c = \frac{D_{AB}}{\delta}$$

We can rewrite this as the flux W A Z is = C A b – C A S divided by 1 by k c. Where k c is essentially = D A B by delta. So, somehow if we know what is this delta and what is the equimolar counter diffusivity of a species, which is a property of the species that is diffusing in a particular medium, then we can estimate what is the mass transport coefficient for that particular case.

Now, we can measure this bulk concentration. But measuring the surface concentration is actually very difficult. In fact, in most of the cases, it is not possible to measure the surface concentration. So, if we now sketch the concept of mass transport coefficient. What we essentially have is, we have a catalyst surface where the concentration is C A S. And then we have the bulk fluid where the concentration is C A b.

And the concentration essentially is changing linearly with respect to position, where the height of this location is delta. And mass transport coefficient essentially captures the resistance offered because of transport from that particular location, which is the bulk, all the way to the surface of the catalyst. So, the resistance offered if there is no reaction; if there is no reaction, then the resistance offered for the mass transport is essentially given by 1 by k c.

So, what we have seen. To summarise what we have seen in this lecture is, we have actually looked at, what is external mass transport diffusion. What we really mean is the resistance that is offered because of the diffusion of the species, from the bulk, all the way up to the surface of the catalyst. And we assume that there may be a hypothetical film which is present close to the catalyst surface.

And because it is very small and it is actually very small compared to the actual size of the catalyst pellet. We can assume that it is a planar surface by neglecting the curvature. And we have actually modelled the concentration changes in that film as a function of position, by assuming that there is no reaction. What we will see in the next class is, we will actually look at how to estimate the mass transport coefficient.

If we know the mass transport coefficient for a given system, then we would have a sense of what is the nature of the resistance that is offered for transport, from bulk to the surface of the catalyst. So, in the next lecture, we will look at how to estimate mass transport coefficient. And from there on, we will look at how to estimate the mass transport resistance when the reaction is also present simultaneously. Thank you.