Chemical Reaction Engineering - II
Prof. Ganesh A Viswanathan
Department of Chemical Engineering
Indian Institute of Technology - Bombay

Module - 4
Lecture - 19
Non-dimensionalization: Thiele Modulus

In the last lecture we derived the mole balance for internal diffusion with surface reaction simultaneously happening. We will build up on that today and solve the equation. And we will look at how the concentration profile actually is a function of the position and what insights we can derive from the concentration profile.

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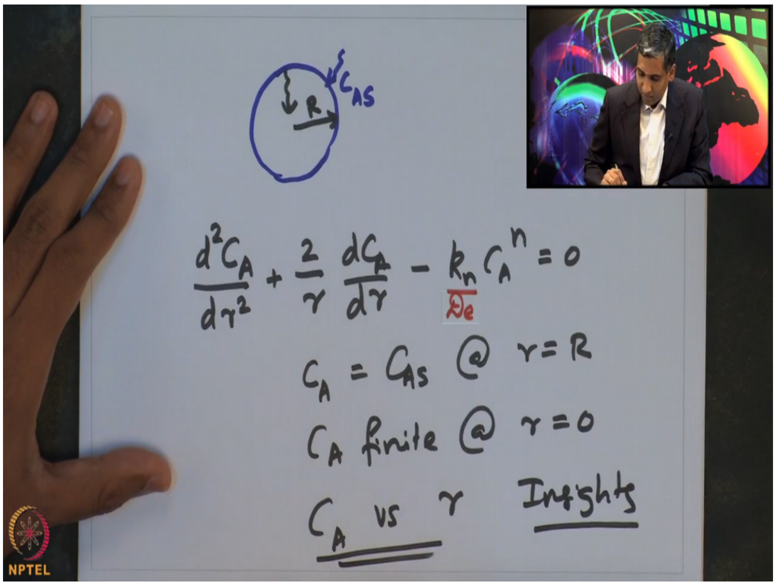

So, if we take a catalyst pellet, where we have species A which is diffusing from bulk; if the concentration of the species at the surface is C A S and there is internal diffusion that is happening of the species. We derived the mole balance in the last class, where we said that the mole balance is d square C A by d r square + 2 by r into d C A by d r – k n into C A to the power of n, divided by D e = 0 for a nth order reaction; where k n takes care of the surface area which is available for the reaction, density of catalyst, so on and so forth.

And the boundary conditions being C A = C A S @ r = capital R; where capital R is the radius of the pellet that we considered. And C A is finite @ r = 0. So, what we will do now is, we will solve this equation and then we will find out what is C A versus r and what kind of insights we can get about the diffusion process by looking at the profile of concentration vs position inside the pellet.

So, as a first step what we will do is, we will actually non-dimensionalize the model equation. And it is often useful to actually non-dimensionalize the equation so that the solution and the insights we get can actually be independent of the size of the pellet that we consider. So, let us first non-dimensionalize the equation and it also helps in solving the model equation.

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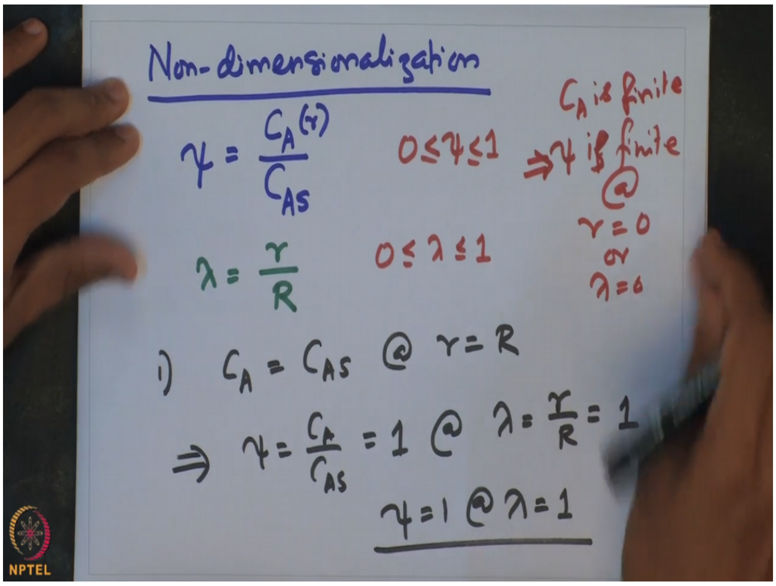

Let us assume that psi is C A which is the local concentration at any position r, divided by the surface concentration C A S. So, what will be the range for this value psi? Because C A S is the concentration of the species that comes from the surface into the catalyst pellet; therefore, the maximum possible concentration anywhere inside the palate can at best be the surface concentration itself. So therefore, psi is essentially going to be between 0 and 1.

So clearly, psi can, is always in the range of between 0 and 1. 0 when the concentration is 0 at any location, when, 1 when the concentration is equal to that of the surface concentration. Let us also define the, a non-dimensional quantity for position, because the model equation has both concentration and position. Let us define this as r by capital R. What will be the range for the lambda which is the dimensionless position?

Once again clearly lambda is always between 0 and 1. So, let us first look at the boundary conditions in this non-dimensional form. So, the first boundary condition is C A = C A S @ r is = capital R. So, this means that in the non-dimensional form, will see that psi = C A by C A S, which should be = 1 @ lambda = r by R = 1. So, the boundary condition is that psi = 1 @ lambda = 1. This is the boundary condition, one of the boundary conditions in the non-dimensional variables that we have just defined.

And what will be the second boundary condition? The second boundary condition will essentially be psi is finite @ r = 0 or lambda = 0. So, concentration C A is finite, which implies that psi is finite @ r = 0 or lambda which is the dimensionless position, that = 0. Now, let us look at the model equations. Let us try to find the dimensionless form of the model equation.

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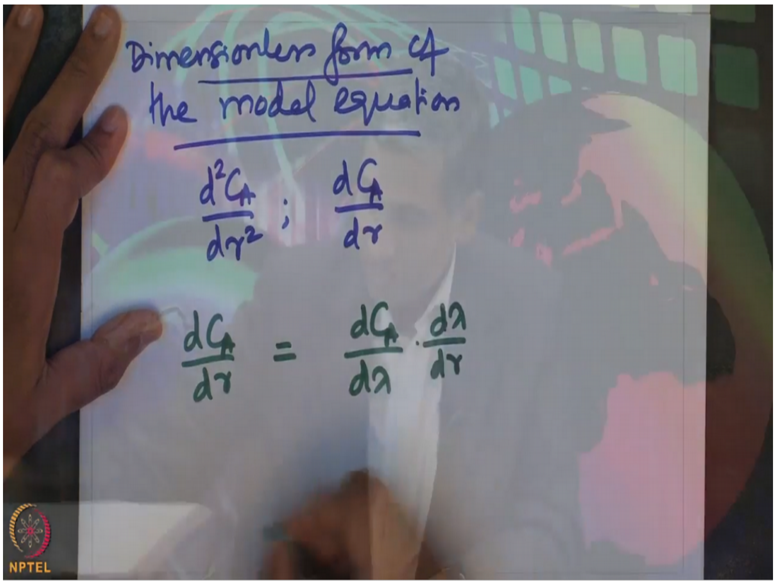

So, the model equation has the second derivative of concentration with position. It has first derivative of concentration with position. So, let us try to find out what is the first derivative d C A by d r, in terms of the dimensionless quantities. Now, simply by chain rule, we can write this as d C A by d lambda into d lambda by d r.

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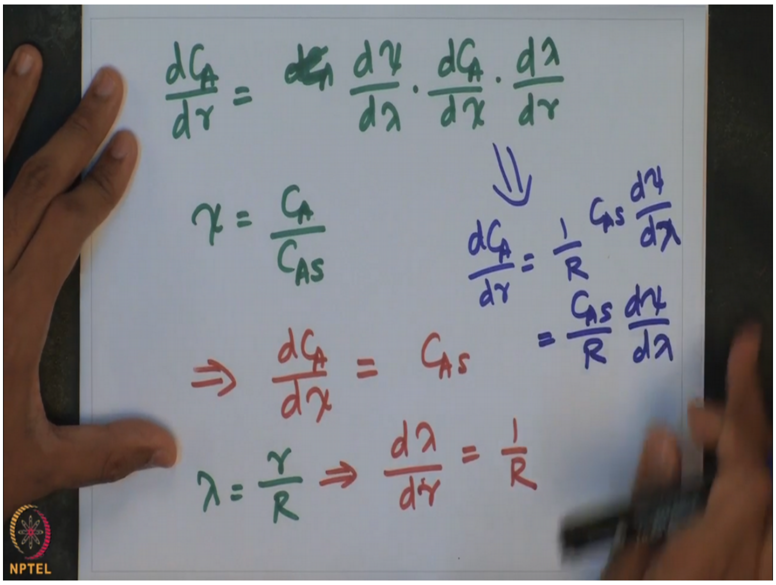

And from here we can rewrite this as, by d r is essentially = d psi by d lambda, multiplied by d C A by d psi into d lambda by d r. Now, we know that psi is = C A by C A S. So, from here d C A by d psi is essentially = C A S. And we know that lambda is = r by capital R. So, from here, d lambda by d r is essentially = 1 by R. So, substituting these, we will find that d C A by d r is = 1 by r into C A S into d psi by d lambda. Okay. So, that is = C A S by R into d psi by d lambda. So now, if we now look at the dimensionless form for the second derivative or second derivative in the new variables;

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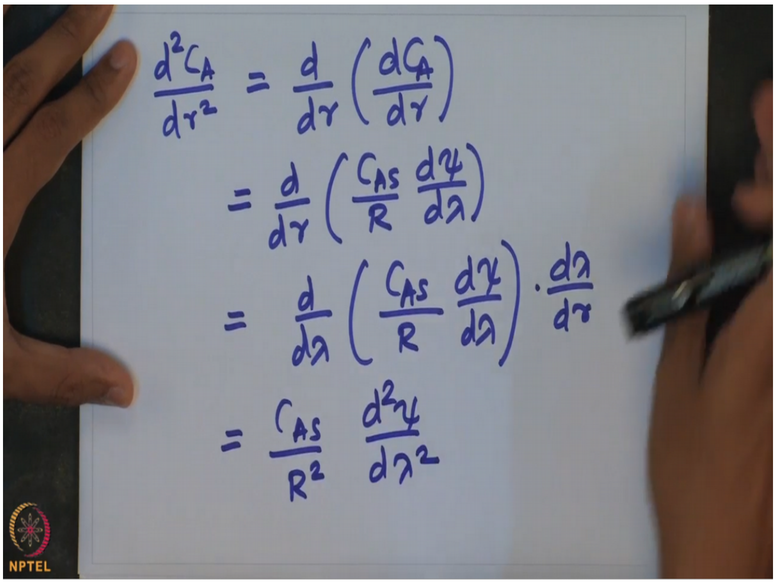

d square C A by d r square. That is nothing but d by d r into d C A by d r. But we just found out what is d C A by d r. So, that should be = d by d r into C A S by r into d psi by d lambda. And this we can write by chain rule as d by d lambda into C A S by r, d psi by d lambda into d lambda by d r, which is = C A S by R square into d square psi by d lambda square. So, now we can plug in the first derivative and second derivative in terms of the new variables.

Whatever new variables we have just defined, that we can substitute into the model equation and we can find out the model equation in the new variables. So, what is the model equation?

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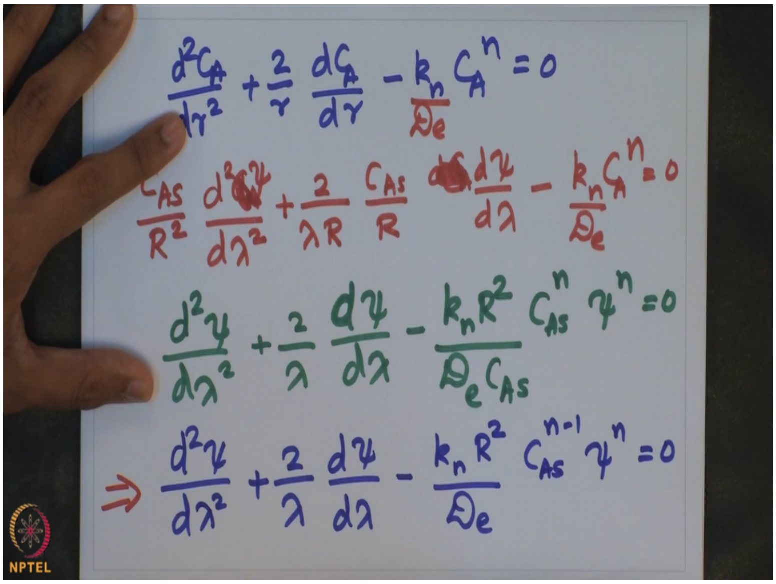

The model equation is d square C A by d r square + 2 by r, d C A by d r – k n, C A to the power of n divided by D e = 0. So, we know that d square C A by d r square is nothing but C A S by R square into d square C A by d lambda square + we have 2 by, we can write r in terms of lambda, which is r, lambda into capital R is small r. And that multiplied by C A S by R into d psi A. This should be psi A. d psi by d lambda – k n into C A to the power of n = 0. That divided by D e.

So therefore, so we can rewrite this expression as, d square psi by d lambda square + 2 by lambda into d psi by d lambda – k n R square divided by D e into C A S. And we can also now write C A n in terms of the new variable. So, that will be C A S to the power of n into psi to the power of n = 0. So, this we can rewrite as d square psi by d lambda square – 2 by lambda, d psi by d lambda. That should be +. – k n R square by D e into C A S to the power of n – 1 into psi to the power of n = 0.

So, this is the model equation in the dimensionless form which incorporates the dimensionless quantities we just defined. So now, if you stare at this expression here in the model equation, the dimensionless from where we have k n R square by D e and C A S to the power of n – 1. So now, let us see what this coefficient actually means. So, the coefficient in front of psi in term, which is the rate term here is essentially called as the thiele modulus, square of the thiele modulus.

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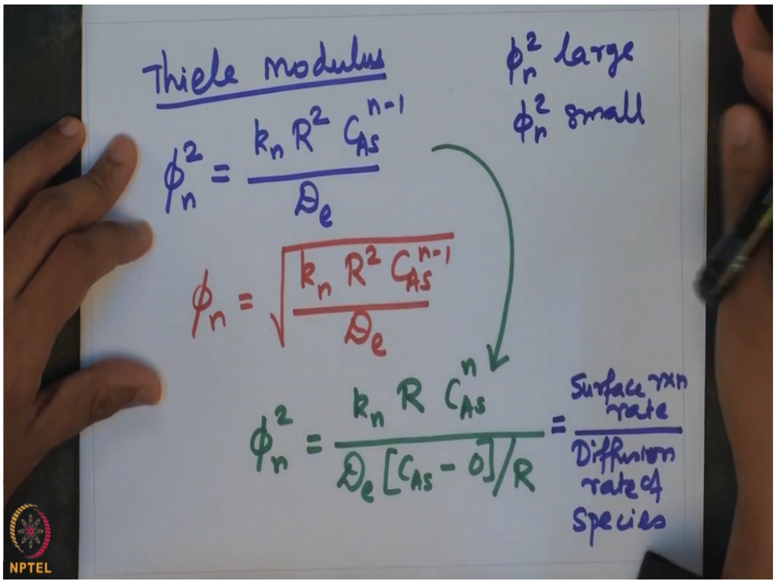

So, we can define phi n square as k n R square, C A S to the power of n – 1 divided by D e. So now, this expression here is what is called, is famously called as the square of the thiele modulus, where the thiele modulus phi n is given by square root of k n R square, C A S to the power of n – 1 divided by D e. So, if we stare at this expression here, what we see is that in the numerator we have the rate constant or which signifies the rate at which the reaction happens and at the denominator we have effective diffusivity.

So now, we can, we usually use this notation of phi subscript n, because we use phi typically for porosity. So, we use phi subscript n to actually refer to thiele modulus for catalytic systems. We can now rewrite the phi square expression here in a slightly different manner. We can write it, rewrite this expression as, phi n square is = k n into r, multiplied by C A S to the power of n, divided by D e into C A S – 0 divided by R.

So, this quantity here in the numerator, this quantity in the numerator refers to the surface reaction rate and the quantity in the denominator actually refers to the diffusion rate of the species. So, one can actually look at thiele modulus as a ratio of the surface reaction rate to the diffusion rate of the species. Now, what happens if phi square is very large? So, if phi square is very large, it means that the diffusion of the species is very small.

So, if diffusion of species is very small, then one can actually think of the possibility that the overall reaction rate is essentially controlled by the diffusion of the species or diffusion rate may be the slowest step in the whole process. So now, let us consider the 2 cases where phi square is, phi n square is large and phi n square is actually small. So, if phi n square is large, then it means that the diffusion rate of the species is very very small.

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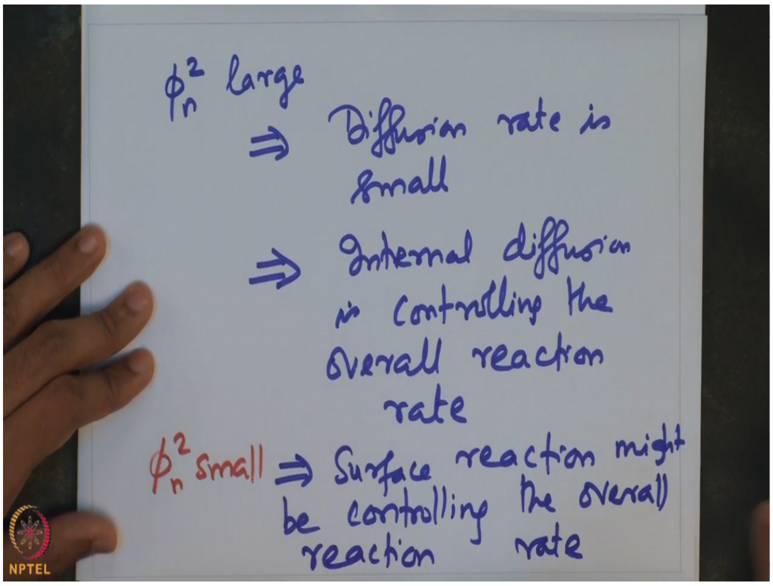

And therefore, if phi n square is large, it means that the diffusion rate is small; which implies that the internal diffusion is controlling the overall reaction rate. Suppose if phi n square is small, then it means that the surface reaction might be controlling the overall rate. So, if one knows what is the thiele modulus for a given system that we are looking at, given catalytic reaction and the reaction that is happening, then based on thiele modulus, value of thiele modulus, one can actually find out whether the reaction is likely to be internal diffusion controlled or it is likely to be the surface reaction control. Suppose we take a first order case, first order reaction case, let us consider the;

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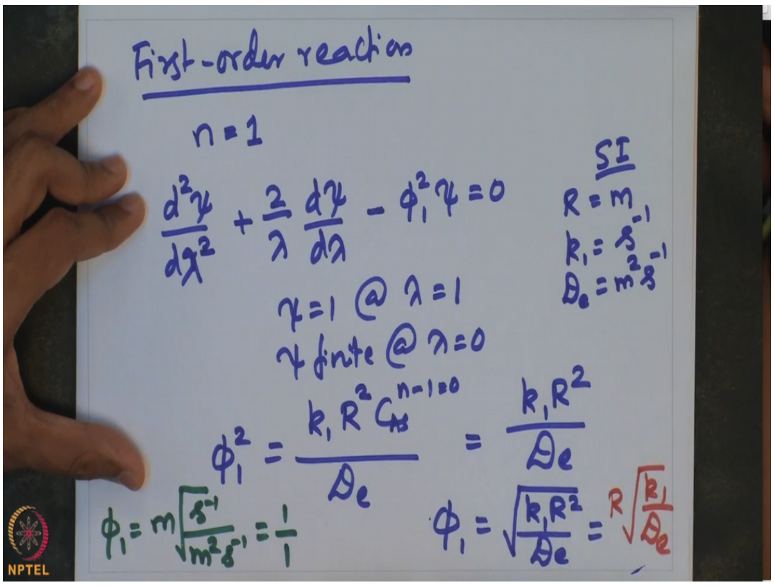

Suppose, let us consider first order reaction here. Where now, order of the reaction n is essentially = 1. And the model equation in the dimensionless form is essentially d square psi by d r square, d lambda square + 2 by lambda, d psi by d lambda – phi 1 square into psi = 0. And the boundary conditions are essentially psi = 1 @ lambda = 1. And psi is finite @ lambda = 0. So, what will be the expression for phi 1 square?

So, phi 1 square will be k 1, which is be the rate constant for the first order reaction, multiplied by R square into C A S to the power of n – 1, but n is 1. So therefore, C A S to the power of n – 1, that is essentially = 0, divided by the effective diffusivity which is essentially = k 1 R square by D e. So now, thiele modulus now is essentially square root of this expression. So, phi 1 is essentially = k 1 r square by D e, which can be read, so I can now pull out r from here.

So, that is R into square root of k 1 by D e. So, what are the units of phi 1? So, let us look at the units of phi 1. Units of R is, let us say meter. If I use SI units. Units of R is meter. What will be the units of rate constant k 1 for a first order reaction? It is second inverse. And what are the units of effective diffusivity? Is metre square second inverse. So, if I now substitute this into the expression for thiele modulus, I can see that the units of phi 1 is, radius is given by metre and square root of the units for rate constant is second – 1.

And the units for diffusivity is metre square second – 1. So essentially you will see that the dimensions of thiele modulus is actually no dimension. It is a dimensionless quantity. So, it is a dimensionless quantity which actually looks at the ratio of surface reaction to the diffusion rate or it actually captures the relative effects of surface reaction and the surface reaction rate and the diffusion rate. It is a quantitative number which helps in identifying whether the surface reaction rate is dominating or the diffusion rate is actually dominating.

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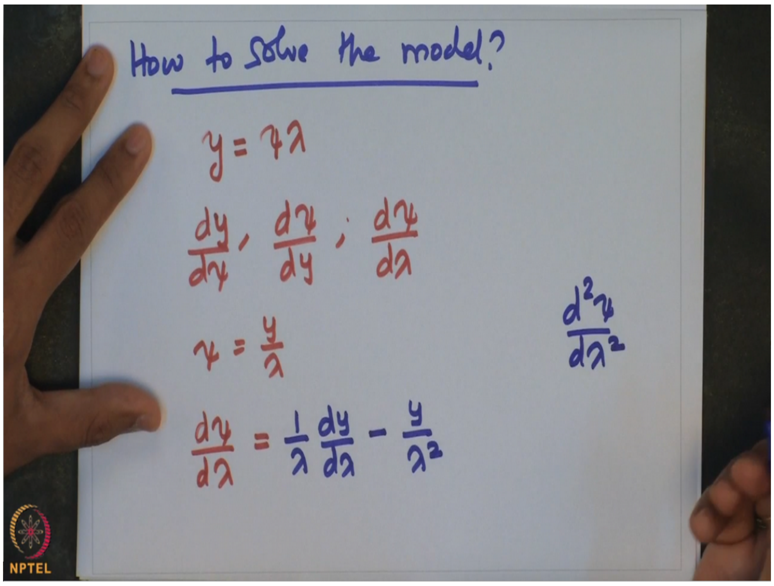

So, how to solve this equation? So, how do we solve this model? So, in order to solve the model, we need to make a simple substitution. So, let us introduce a substitution where we define a quantity called y, which is essentially = psi times lambda. So, from here, we can see that d y; we can find out d y. d y by d psi. We can also, of course we can find out d psi by d y. We, but what we require is actually d psi by d lambda.

So, how do we find d psi by d lambda. So, let us rewrite this expression as, psi is = y by lambda. And so now, d psi by d lambda is essentially given by 1 by lambda into d y by d lambda – y by lambda square. What is next? We need to find out what is d square psi by d lambda square. So, let us find out what that is.

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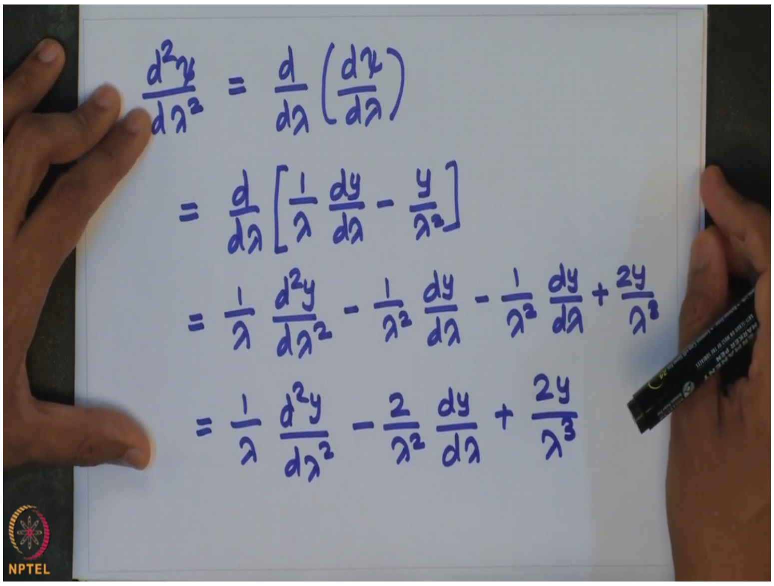

So, d square psi by d lambda square is essentially given by, d by d lambda of d psi by d lambda. And that is = d by d lambda, of; We already know what is d psi by d lambda. We just found out what is d psi by d lambda. So, we substitute that here. So, that will be 1 by lambda, d y by d lambda – y by lambda square. That is = 1 by lambda, d square y by d lambda square – 1 by lambda square, d y by d lambda – 1 by lambda square into d y by d lambda + y, 2y by lambda q.

So now, we can, so this is = 1 by lambda, d square y by d lambda square, – 2 by lambda square, lambda + 2y by lambda cube. So, we know what is the second derivative. We also know what is the first derivative. And we can now substitute that into the model equation. Let us do that. So, what is the model equation.

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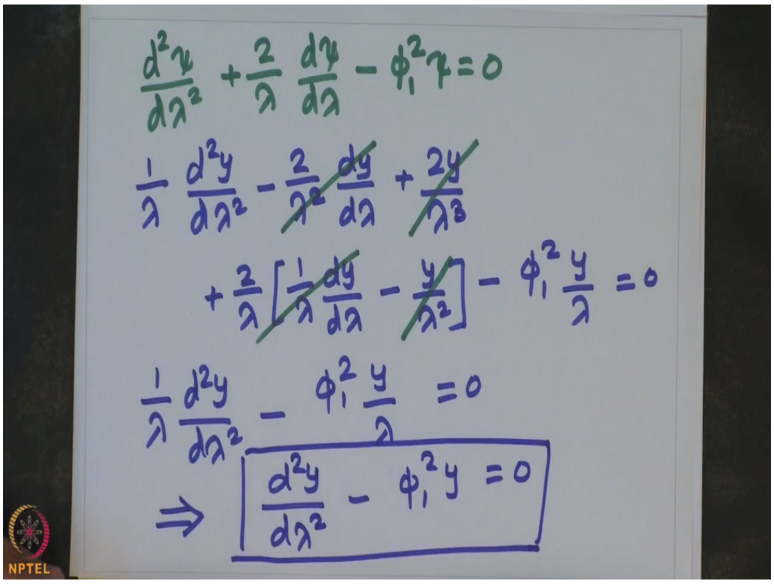

The model equation is d square psi by d lambda square + 2 by lambda, d psi by d lambda – phi 1 square into psi = 0. So, from this expression, we can substitute d square psi by d lambda square. And so, that is essentially = 1 by lambda, d square y by d lambda square – 2 by lambda square, d y by d lambda + 2y by lambda cube. And now we need to substitute for the first derivative.

So that will be 2 by lambda into 1 by lambda d y by d lambda – y by lambda square and – phi 1 square. Psi is essentially given by y divided by lambda. So, that is = 0. So, from here, we can see that this term cancels out this term. And this term cancels out with this term. And so essentially the model equation is 1 by lambda, d square y by d lambda square – phi 1 square into y by lambda = 0.

Which essentially means that the model equation is reduced to d square y by d lambda square – phi 1 square y = 0. So, what we have seen in today's lecture is we started from the model equation that we derived in the previous lecture. And then we non-dimentionalized the equation. We found out what is the thiele modulus, the dimensionless quantity which characterises the ratio of or captures the ratio of surface reaction rate to diffusion rate.

And then we introduced the transformation of y = psi lambda which is required to solve the model that we are looking at. In the next lecture we will actually solve the model. And we will see what the profile of concentration with respect to position and what is the kind of insights that we can obtain from the solution of the model equation. Thank you.