Chemical Reaction Engineering - II
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Module - 5
Lecture - 22
Internal Effectiveness Factor II

In the last lecture we derived the relationship between the internal effectiveness factor and the thiele modulus for a first order reaction occurring in a spherical catalyst pellet. We also observed that such a relationship can actually be obtained for any order of a reaction that is happening in the catalyst pellet. Now, we also noted that the catalyst pellet can be of different shapes.

For instance, it can be a cylindrical pellet or it can have a cartesian coordinates, where it is a slab geometry. So, in today's lecture, we will look at how to find out the relationship between the effectiveness factor and thiele modulus, for a slab geometry, for a first order reaction.

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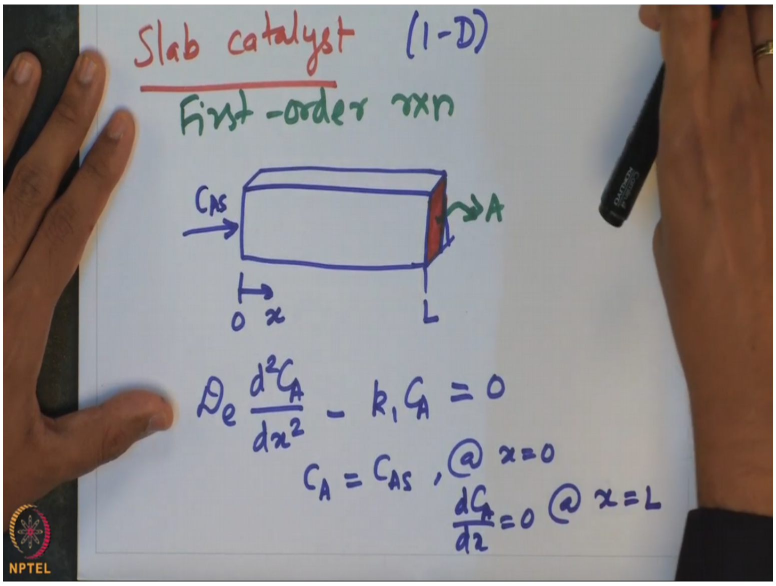

So, suppose we have a slab. And let us say that I define my positive direction x. And let us say that the slab goes from 0 to L. Length of the slab is L. And the species is actually diffusing from this direction. And suppose, let us say I seal the other end of the catalyst, so that nothing is actually leaving this surface. And if I assume that in all the other dimensions, the concentration is actually uniform.

Let us look at a one-dimensional case. So, let us look at a 1 D slab. And if I assume that the cross-sectional area through which the species is diffusing is actually = A. So, that is the cross-sectional area. So, the mass balance for this system is essentially given by; one can actually write the shell balances. And you can find that the balance is essentially given by diffusivity into d square C A by d x square, – k 1 into C A is = 0.

What are the boundary conditions? So, concentration of the species will be = the surface concentration @ x = 0. Essentially, the species at this location is at the surface concentration. And because nothing is leaving this, from this end at L, so the next boundary conditional will be d C A by d x, essentially is = 0, @ x = L. So, we can solve this model in exactly the same way we did for a spherical catalyst by first non-dimensionalizing the model equation. So, let us do that exercise. So now, we introduce the dimensionless quantities.

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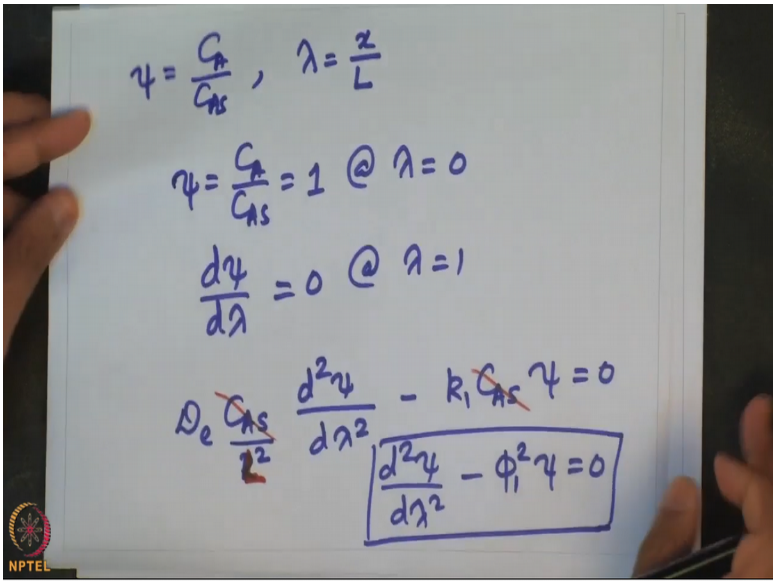

Is = C A by C A S. And lambda is = x by L. So clearly, lambda goes between 0 and 1. And so now, the boundary conditions will be, psi = C A by C A S, is = 1 @ lambda = 0. And d psi by d lambda is essentially = 0 @ lambda = 1. Now, if we now substitute the dimensionless quantities in the model equation, we will see that diffusivity D e into C A S into d square psi, divided by R square into d lambda square, – k 1 into, C A S into psi is = 0.

Now, we can cancel out the like terms. And then, we can pull in the D e, we can basically take this D e by R square into the second term. And so, we will essentially, the model equation, dimensionless model equation will be d square psi by d lambda square, – phi 1 square, into psi = 0. So, that is the model equation, which will be subject to these 2 boundary conditions, where psi is = 1 and lambda = 0. And d psi by lambda = 0, at lambda is = 1. So, let us solve this model first. So, what is the general solution?

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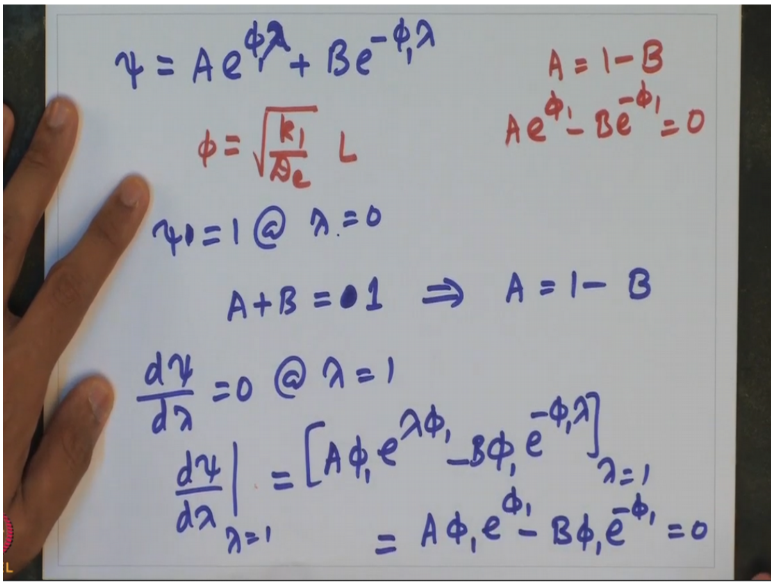

General solution is, psi is = A e power phi x + B e power – phi lambda. B e power – phi lambda. So now, now phi is essentially = square root of k 1 by D e into L. Note that this is not radius. This is L which is the length of the slab. It is L square. So, phi is = square root of k 1 by D e into L. And so now, we can substitute the boundary condition. The first boundary condition is psi = 1 @ lambda = 0.

So, substituting that, we will see that A + B is essentially = 1; which means that A is = 1 – B. So, when I substitute lambda = 0, e power 0 is 1. And this is 1. So, therefore A + B is = 1. And A = 1 – B. Now, I substitute the second boundary condition. d psi by d lambda equal 0 @ lambda = 1. And so, d psi by d lambda is essentially =; that is = A into phi into e power lambda.

So, if I now put subscript 1 to represent the first order reaction. So, A phi 1, e power lambda into phi 1 – B phi 1 e power – phi 1 lambda, evaluated at lambda = 1. So now, if I put lambda is = 1; this is essentially becomes A into phi 1, A into phi 1 e power phi 1 – B phi 1 e power – phi 1. And that is essentially = 0. So, from here, we get 2 conditions on A and B.

One is that A = 1 – B. And the other one is, A into e power phi 1 – B into e power – phi 1 is = 0. Because this is thiele modulus. And thiele modulus clearly cannot be 0. So therefore, it is the other product which is actually = 0. So, from this we can actually find out the constants A and B. Let us do that. So, the solution of these 2 equations will essentially be A is = e power – phi 1 divided by e power phi 1 + e power – phi 1.

And B is equal e power phi 1 divided by e power phi 1 + e power – phi 1. So, substituting this back into the solution, you will find that psi is = e power – phi 1 into e power phi 1 lambda, + e power phi 1 into e power – phi 1 lambda divided by e power phi1 + e power – phi 1. And so, rewriting this by taking this into, by joining these 2 exponentials, we will see essentially that this is = e to the power of phi 1 into 1 – lambda, + e to the power of phi 1 – phi 1 into 1 – lambda, divided by e to the power of phi 1 + e to the power of – phi 1.

And this is, if I now multiply and divide by a factor 2. This is nothing but, this is = cos hyperbolic of phi 1, 1 – lambda, divided by cos hyperbolic of phi 1. So, the solution psi which is the dimensionless concentration as a function of position, is essentially given by this ratio, cos hyperbolic phi 1, 1 – lambda, divided by cos hyperbolic of phi 1. So, once again we can find out the internal effectiveness factor. How do we do that? We do the same exercise as we did for spherical catalyst;

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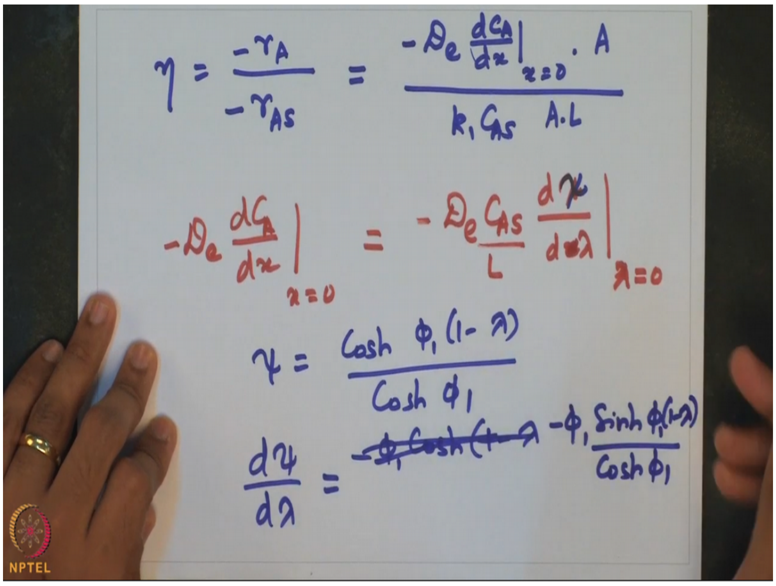

Where we say that eta is essentially – r A which is the actual rate at which the reaction is happening, divided by the rate as though the conditions everywhere inside the slab is that of the surface conditions or the concentration at x = 0. That is, C A S which is the concentration at x = 0. And this is nothing but – D e into d C A by d x at x = 0 multiplied by the cross-sectional area through which the diffusion is happening, divided by k1 into C A S, which is the intrinsic kinetics, multiplied by the volume of the slab which is area into the length, cross section area into length.

So, we need to estimate this d C A by d x at x = 0. How do we do that? We know the solution. So, from the solution, we can actually find out what this one is. So, – D e, d C A by d x at x = 0. By introducing the dimensionless quantities, we will see that this is = – D e C A S into d psi, divided by L into d x. And that should be, d psi by d lambda. That should be evaluated at lambda = 0. So, this is d psi. d psi by d lambda. And that should be evaluated at lambda = 0.

But we know what is the relationship between psi and lambda. So, psi is essentially = cos hyperbolic of phi 1, 1 – lambda, divided by cos hyperbolic of phi 1. So, from this we can find out what is the first derivative. So, the first derivative d psi by d lambda is essentially given by – phi 1 cos hyperbolic 1 –, – phi 1 sin hyperbolic phi 1 into 1 – lambda, divided by cos hyperbolic of phi 1. Now, we need to evaluate this at lambda = 0. So, let us do that.

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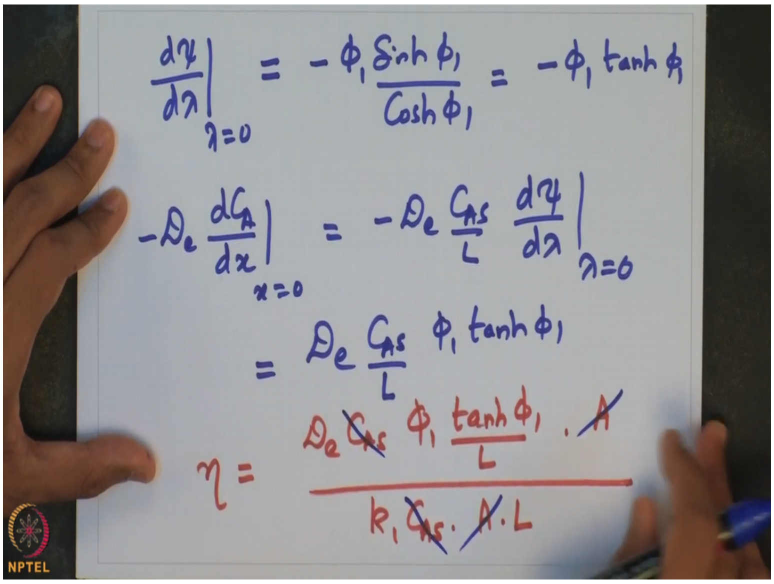

So, d psi by d lambda, at lambda = 0 is essentially given by – phi 1 into sin hyperbolic of phi 1 divided by cos hyperbolic of phi 1. Now, this is = – phi 1 tan hyperbolic of phi 1. So, this we can substitute back into the effectiveness factor equation which we just solved. We can substitute it back here. And so, that we will essentially be, so – D e into d C A by d x at x = 0 is =, – D e C A S by L into d psi by d lambda at lambda = 0.

And we have found out what is d psi by d lambda. So, this is essentially D e C A S by L into phi 1 tan hyperbolic of phi 1. And this we can substitute back and we can find out that, eta which is the effectiveness factor is essentially given by D e C A S divided, into phi 1 tan hyperbolic of phi 1, divided by L multiplied by the area. The whole divided by k 1 C A S into area into L.

So, we can now cancel out the like terms. We can cancel the cross-sectional area, the surface concentration. And so, what we are left with is essentially D e, phi 1 and k 1 and L square. So, let us write this.

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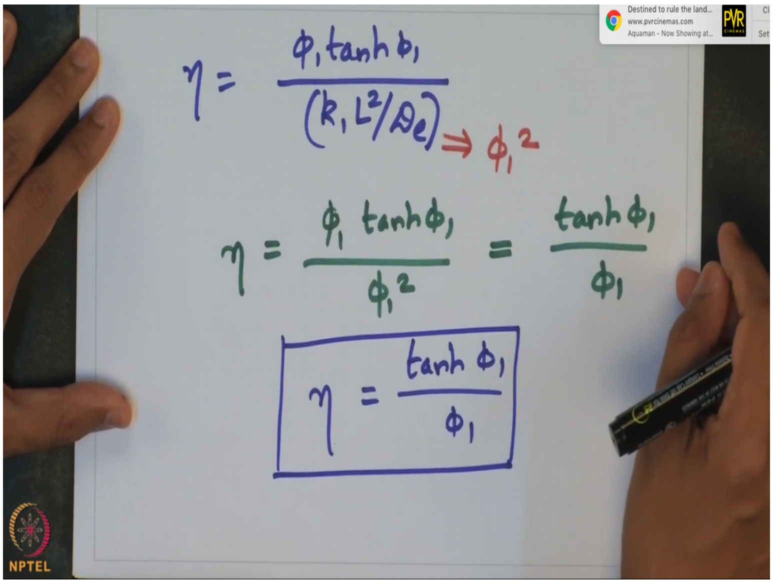

So, eta is essentially given by phi 1 tan hyperbolic of phi 1, divided by k 1 L square by D e. Now, we know that k 1 L square by D e is nothing but phi 1 square. This is nothing but phi 1 square. So, substituting that we find that eta is essentially = phi 1 tan hyperbolic of phi 1, divided by phi 1 square. Or that is = tan hyperbolic of phi 1 by phi 1. So, for a slab geometry, we find that eta is essentially = tan hyperbolic of phi 1 divided by phi 1.

That is the relationship between the internal effectiveness factor and the thiele modulus for a, a slab geometry. Now we can plot this, once again we can plot this eta versus phi. And we will see that the profile that we get is very similar to what was observed for a spherical catalyst pellet.

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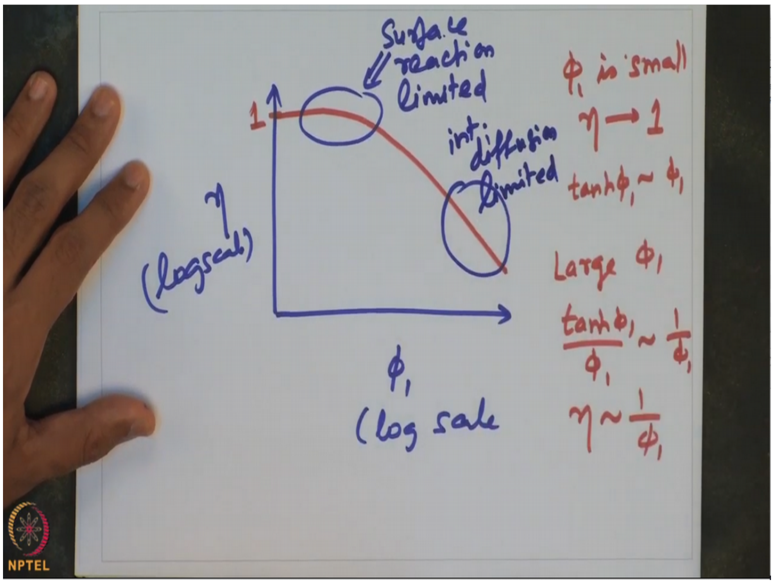

So, if I now plot phi 1 versus eta, once again log scale. I use log scale here. And clearly, when phi is very small, eta essentially goes to 1, because tan hyperbolic of, when phi is small, tan hyperbolic of phi 1 essentially goes as phi. So, when phi 1 is small, so tan hyperbolic of phi 1 essentially goes as phi 1. And so, eta essentially tends to 1. And for large values of phi 1, for large phi 1, tan hyperbolic of phi 1 by phi 1, essentially scales as 1 by phi 1.

So therefore, eta goes as 1 by phi 1 for large values of phi 1. So clearly, we can draw this eta versus phi, eta versus phi. And recall that, for surface limited case, for small phi eta goes to 1, similar to what we saw in the spherical catalyst pellet. And also for large phi, where it is diffusion limited conditions, eta scales as 1 over phi, which is the similar for, similar to what we saw in a spherical catalyst pellet.

Except that that0 we had a 3 by phi. So, the scaling factor or the slope of the line, for large values of phi is only different. So, now we can draw the sketch the thiele modulus versus effectiveness factor graph. So, this is, starts from 1. And so, this is the, this region is now the surface reaction limited. And this region is now the internal diffusion limited. So, anywhere in between, it could be both surface reaction and internal diffusion that actually contributes to the overall rate at which the reaction can happen.

The same procedure can actually be followed for finding out the eta versus phi relationship for a cylindrical catalyst pellet. And in fact, you will see that the relationship between eta and phi for a cylindrical catalyst pellet is also very similar to what we saw for a slab or what we saw for a spherical catalyst pellet. So, what is remarkable is that the, irrespective of the shape of the catalyst pellet, the by and large, the functional relationship or the dependency of eta versus phi is actually very similar.

And in fact, for large values of phi, irrespective of the geometry that we consider, the effectiveness factor essentially scales as 1 over thiele modulus. And that actually is quite an interesting observation. Now, so far what we considered is the case where the density of the system is constant.

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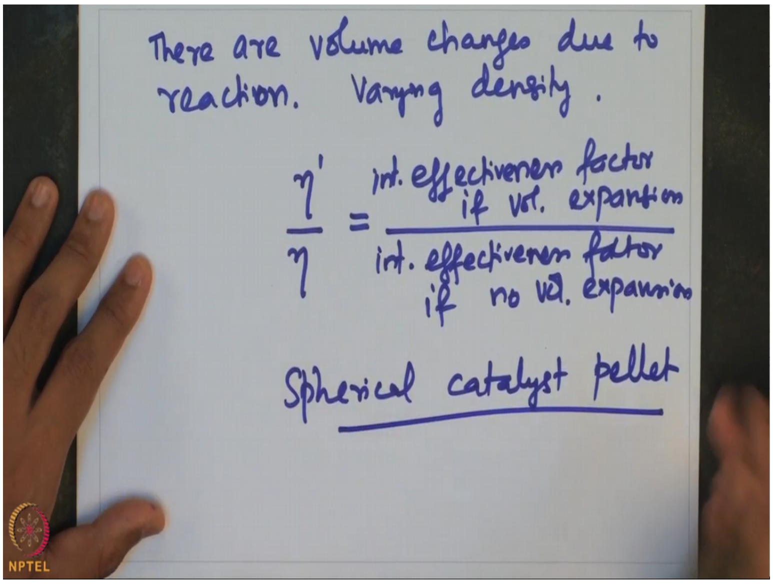

Suppose, let us say that there are volume changes due to reaction. Let us say that there are volume changes due to reaction. And if, let us say that, which basically means that we are looking at varying density systems. So now, if you want to understand how the eta versus phi actually behaves when the density is changing. So, we can actually try to relate it to what is called as the ratio of the effectiveness factor, if there is volume changes, divided by eta if there is no volume changes.

So, we can try to find the ratio of this, which is basically the effectiveness, internal effectiveness factor, if volume expansion, divided by the corresponding internal effectiveness factor if there is no, if no volume expansion. So, let us consider the case for a spherical catalyst pellet. Now in fact, for a spherical catalyst pellet, this has been worked out and it is essentially captured by this graph here.

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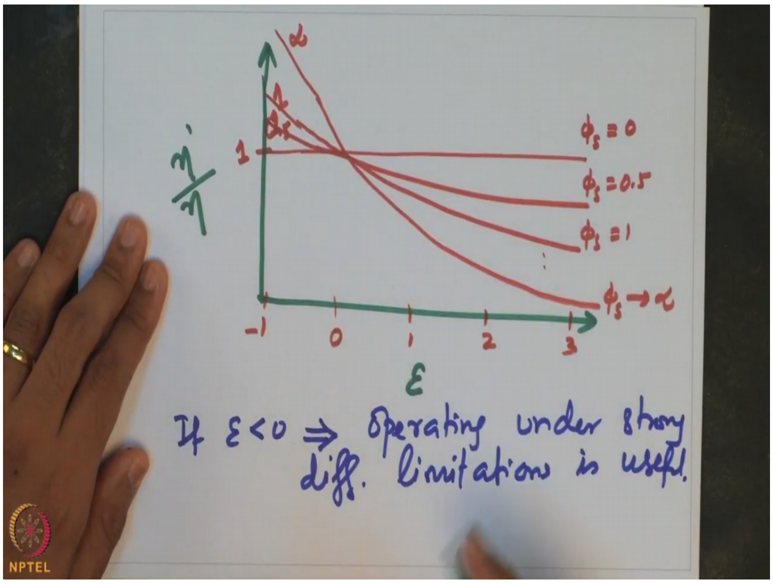

Where we can plot, eta prime by eta, divided by the expansion coefficient epsilon. And let us say that there is no volume change or 0 expansion that corresponds to this location. And let us say – 1 is here, + 1 is here, 2 is here and 3. So, this essentially says what is the extent to which the molar changes happen because of the reaction. And if, let us say that, if there are no volume change effects, then eta prime by eta is essentially same, which means, 1 corresponds to eta prime being = eta.

So, suppose let us say this is the, this is the location where the diffusional, where this essentially says that eta is = eta prime, for all values of this. And suppose, let us say this corresponds to the thiele modulus. Let us say the thiele modulus of approximately 0. That is, no diffusional limitations. Which means that very small or 0 thiele modulus, where every, for every case it is essentially the surface reaction which is controlling.

In that case eta prime is essentially = eta. And now, if I plot this curve for different values of thiele modulus. We will see that, for phi; so, this is for phi s = 0.5. And then, so this is for a different value of phi s. We will say phi s is = 1. And so on and so forth. And typically for infinite, very large phi s, this is the kind of profile. So, this is phi s corresponding to 1. And this is let us say this is 0.5. And let us say this is 1.

And this corresponds to tending to infinity. Now, this graph actually provides a useful insight in terms of design. That, if epsilon is less than 0, then operating under strong diffusional limitation is useful. So, classically for the cases that we have seen before, we saw that the effectiveness factor is maximum when the reaction is actually conducted at a surface reaction conditions. And not the diffusional limitations.

Because effectiveness factor is approximately = 1 when the surface reaction is controlling and which is the maximum that can be obtained for all these cases. On the other hand, if there are density or volume changes, then we will see that when the, when there is negative volume change, that is the epsilon is –1, then if you operated the strong diffusional limitations, then we are able to get a much higher effectiveness factor.

Eta prime is actually much larger than eta if there was no volume expansion. So clearly, that if there is volume shrinking because of the reaction, then one would actually want to conduct the reaction under strong diffusional limitations. And that would actually help in increasing the overall rate at which the reaction can happen, which actually strongly affects the productivity. So, let us take an example. Let us look at some numbers.

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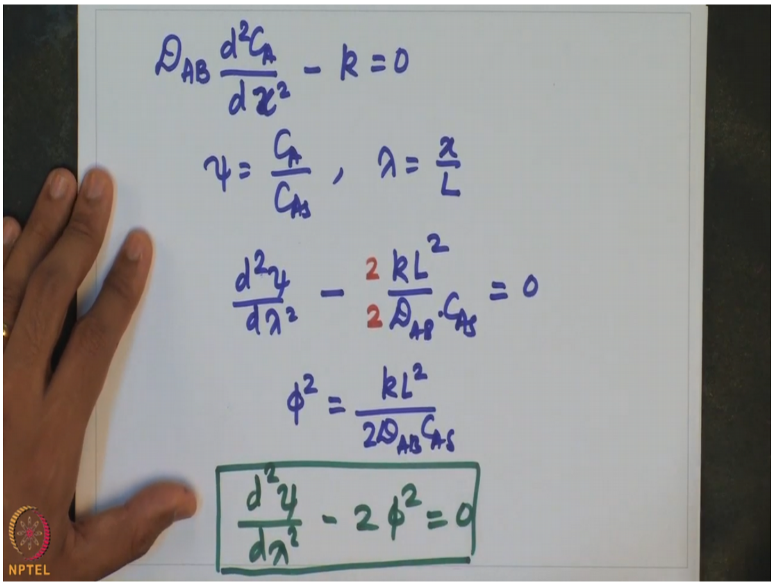

Suppose we have, so this problem has been taken from Fogler, 4th edition, page number 824. So, suppose there are hydrogels which are present, which contains hydrogel containing cells. And in fact, these days it is being considered as an alternative for tissue replacement; where you have cells of the host species, is actually embedded in the hydrogels and can we see if that can actually replace the cartilages for instance.

So, if these cells have to survive in normal post conditions. They do not have blood vessels. And, but the oxygen has to penetrate for cells to survive. So, one can actually post this as a diffusion reaction problem and see how diffusional limitations could play a role here. So, suppose I consider that there is a hydrogel which is present here. And I pass oxygen from both sides. And if we assume that there is a midpoint that is present here.

If I called this as, let us say x = 0; where is a, there is a symmetric point that is present here. And now, I can write my, and let us say that the length is x = L here and x = – L. And I can now write the model equations to find out what should be the length that would actually that would actually support the, you know, diffusion, support the diffusion of oxygen all the way to the end of the, or to midpoint of the hydrogen; in such a way that sufficient quantity of oxygen is always present at that location.

Now, suppose if we assume that the oxygen consumption is a 0 order reaction, we assume that oxygen consumption is actually occurring through a 0 order reaction. We can now write a mass balance between 0 and L, assuming that it is symmetric. So, if we write a balance between 0 and L; it is as good as writing a model between 0 and – L. So, let us write the model for this half section. So, if D A B is equimolar counter diffusion of oxygen.

That multiplied by d square C A by d x square, – k = 0. Because we assume it is a 0 order reaction. Once again, we can introduce the dimensionless quantity. Psi is = C A by C A S. If we assume that the concentration of oxygen at the location where it enters the gel is actually C A S, the concentration here is C A S. Then we can actually rewrite the model in terms of the dimensionless quantities, where lambda is = x by L.

And we can rewrite the model as d square psi by d lambda square, – k L square by D A B into C A S = 0. Now, let us introduce a factor of 2 which actually will help in solving the model equation. So, we will introduce a, multiply and divide the second term by a factor of 2. And so, we can now define phi square as k into L square by 2 times D A B into C A S. And so, the model equation now boils down to d square psi by d lambda square.

That is, – 2 times phi square = 0. Now, what is the solution of this equation? It is very easy to find the solution of this equation.

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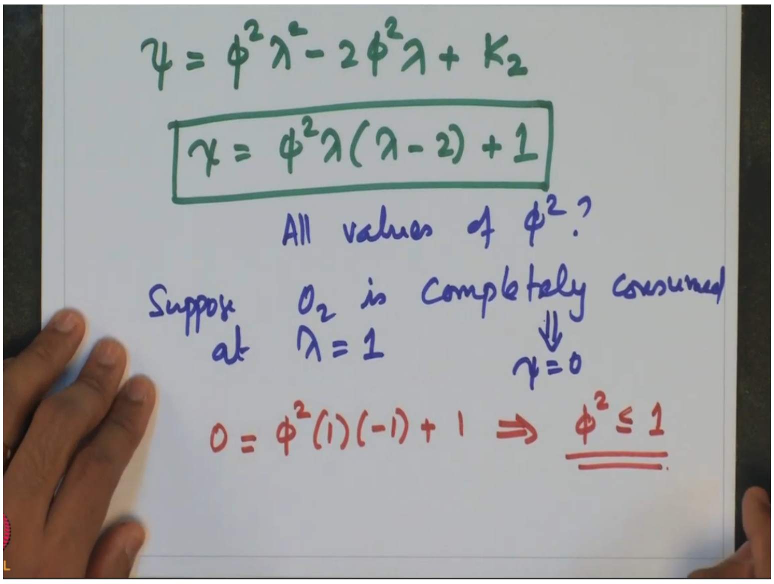

The solution is essentially given by, psi is = phi square lambda square, – 2 phi square lambda + sum constant K 2. And so, from using the boundary conditions we can find out what is this constant K 2. And so, essentially the solution is given by phi square lambda into lambda – 2 + 1. So, this is the relationship between concentration of oxygen at any location inside the gel, as a function of position lambda.

Now, is this valid under all situations? Is it valid for all values of phi? Is it valid for all values of phi square? So, it turns out that the solution, in fact the model itself is not valid for all values of phi square. So, because the oxygen is being consumed through a 0 order reaction; somewhere, let us say that the oxygen concentration becomes 0 or oxygen is completely exhausted.

So, let us find out what is this phi square which will actually permit that what is this location lambda and corresponding phi square, which actually permits complete consumption of the oxygen species. Suppose O 2 is completely consumed at lambda = 1, which is the domain of the hydrogel which we have considered. We can substitute this. So, that is, completely consumed, that is psi is = 0.

So, we can substitute that and see at 0 is = phi square into 1 into – 1 + 1, which means that the solution is valid only when phi square is actually less than or = 1. So, the model is not valid at every location. The solution is not valid at, for all values of phi square. It is valid only when phi square is actually less than or = 1. So, let us summarise what we have done now.

We have actually looked at the thiele modulus and effectiveness factor relationship for a slab geometry. We also looked at, what is the effect of having volume changes, where the effectiveness factor can actually be much larger than 1, depending upon the thiele modulus and if the volume is actually shrinking because of the reaction. We looked at an example problem where we looked at oxygen diffusion through hydrogels containing cells.

And we looked at the solution and found out that the solution is not valid for all values of phi square. And what we will see in the next class is, we will put some numbers to these and see what should be the size of the, what should be the thickness of the gel or what should be the value of L that actually is mimicking the realistic situation. Thank you.