Biochemical Engineering

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Lecture No. # 16

Interphase Mass Transfer and Reaction in Immobilized Enzymes (Contd.)

There in the last lecture of reaction and diffusion that occur simultaneously in rectangular slab is something that you found little hard. So, what I will do today before I go into the spherical coordinates and (( )) or immobilizing themselves sphere, I will try and recap once again what we did with a rectangular slab.

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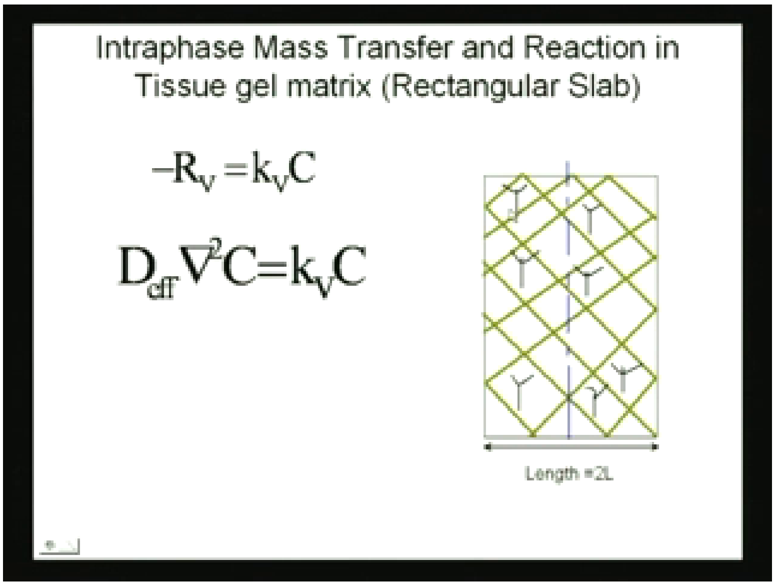

So, we are looking at this problem let us go through the to the transparency, and we will we are looking at this problem of the rectangular slab being here and the enzymes are immobilized inside that rectangular slab. So, these are infrared solvents encapsulated, and the length is the total length of in the direction in which the diffusion occur this 2L, and what we are suppose to do is, this is a heterogeneous system essentially right, but what we did (( )) we did a pseudo homogeneous approximation of it. So, once we do a pseudo homogeneous approximation, we assume that reaction and diffusion occur simultaneously. So, did just recapping what we did. So, it is just a quick question did any of you have any questions or doubts about what we did in the last class about the concept? What your problem was with the concept or your problem was with the calculations?

Sir concepts.

Concept. So, I will run through the concept one more time.

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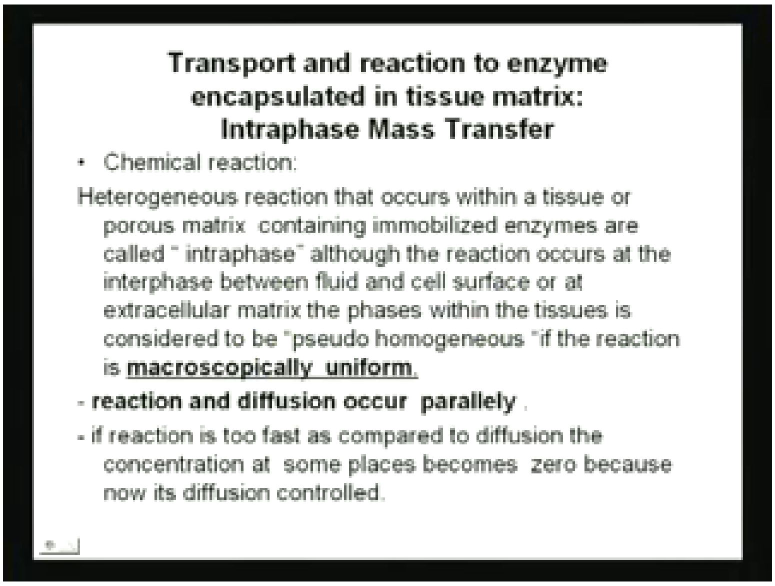

So, the idea was that you know here let us go back the idea was that when you have inter heterogeneous reactions and see a quick for example, reaction in a porous catalyst. So, reaction itself is heterogeneous, but when you look at it from microscopically from a large scale point of view. Then you can assume the reaction to be homogeneous. So, what are the criteria we discussed two criterions; one is that the length scale of heterogeneity over the microscopic length scale should be very, very small. So, in this case for example, if I am looking at a matrix like this, in which the enzyme is impregnated or encapsulated the length scale of the pore over the entire thickness of the solid core.

So, this is a core for example, or the encapsed total encapsulation (( )) if this length scale is L say or 2 L and that length scale of the pore is d the diameter of the pore, then d over

2 L should be very small that is my criteria number one to be very specific I said it will conceptual way. So, that is let me write it down also.

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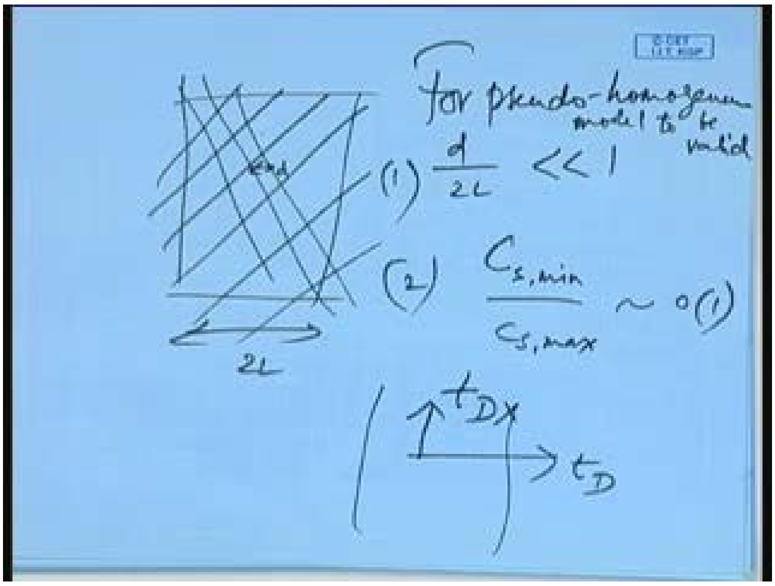

So, if this is my encapsulation in the whole thing and this length scale is L and the length scale the length scale of a pore for example, is say d then d over 2 L should be very smaller than one for the pseudo, for pseudo homogeneous model to be valid and what was the other condition we said.

(( )).

Yeah. So, concentration C s minimum over C s, maximum should be of the order one. So, it there should not be a large difference in variation between the maximum and the minimum concentration. Because see the whole idea is that averaging, what is you are doing here is averaging now? What is the average of any population signified? It means that somewhere you know you are trying to have a sense of the total population by looking at the average now, if that if you have three people over there and four people over there and. So, when you taking average of the four people out of which the ages have two of them are say 5 and 6 years old then, the other two ages are 60 and 70 or 65 and 70 then you will get an average of whatever 20 or whatever it is it makes no sense because it gives you no sense of the population.

So, that is the concept here is that the maximum over the minimum over maximum concentration should be of the of some order one should be very small number. So, once you are able to do that then we can substitute.

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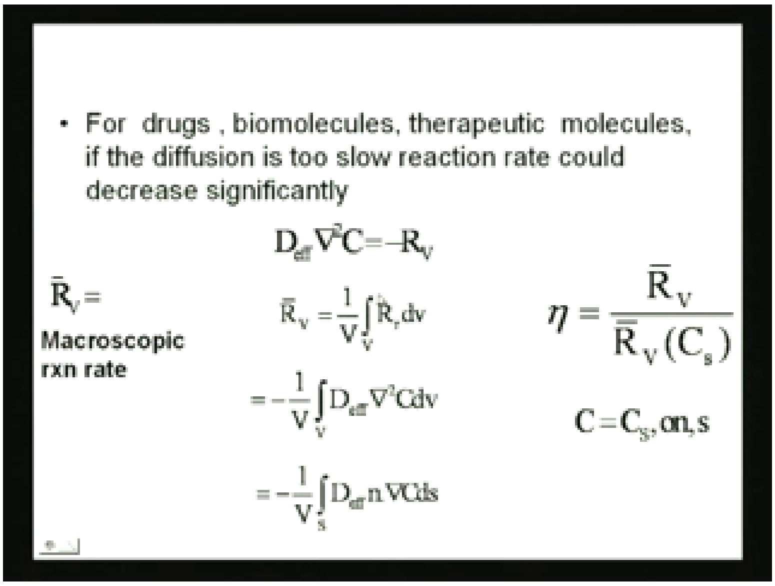

So, what we do is, we average out this thing. So, here we are we have the reaction let us go back to the reaction. So, the here we have the reaction. So, this is the R that you see over here is the reaction at the small scale at the scale of the pore. And if there is in uniformity model I think uniformity in the concentration and the minimum to the maximum pore scales minimum pore scale size over the macro scale size of the core scale is much smaller than one. Then only can do an averaging which means that we tend the reaction rate and integrated over the volume and divided by the total volume then you will get a average reaction rate which is given over here as R v bar.

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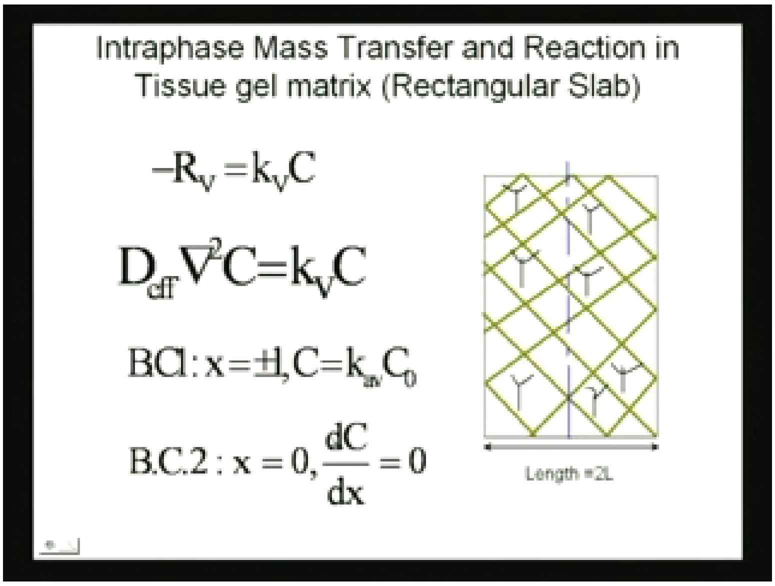

So, this is the basic concept there should it should be now. So, then we went over to this particular example. So, once we have been able to do that averaging, what we have been able to achieve? We have been able to convert a heterogeneous model which is much difficult to quite difficult to solve to a homogeneous model. We call it a pseudo homogeneous model because it is not really homogeneous we are just assuming to be homogeneous. So, once we have been able to write the pseudo homogeneous model. So, then we can write a reaction rate as time just like a homogeneous reaction rate which is first order homogeneous reaction rate k v times C. And again why you are doing first order? Because we are looking at the two asymptotes of first order and the 0 the order and the Michaels mention kinetics some or it going to be in between this. I am going to come and show you actually how the Michaels mention kinetics looks like may be if not in today's class the first mandate in the next class.

So, once we have been able to write our assume on pseudo homogenous model then you simply assume that. So, when once you assume a pseudo homogenous model, what does it come with the other assumption that diffusion and reaction can run parallely. So, in reality. So, what is a difference? The difference is this model that you are writing tries to mimic reality, but is not in a direct actual representation of the reality, it is a it is some solved form the representation of reality. So, in reality diffusion and reaction occur do not occur parallely they occur in series, but when you convert them into a pseudo homogeneous model, diffusion and reaction can be assumed to occur parallely.

So, when you assume them to occur parallely, then you can go back and write an equation of this sort that I have wrote over here. The effective length laplacian of C equals k v time C. So, k v time C being the reaction rate and the left hand side being the diffusion rate. What is that to note here is? The d a factor because we are using a pseudo homogeneous model the effective diffusivity is some total of the diffusivity through the solid pore solid part of the material and through the fluid in the pores. So, the because you have different diffusivities much different diffusivities actually through the solid and the and the fluid and.

So, if you had a simple fluid that gives you (( )) much higher where this effective diffusivity is going to be much lower than that because of the presence of solids fine. And then the solution was I do not know if you have the solution the solution we got by using the two boundary conditions one is that at this extremity x equals plus minus L actually it should not be 1 x equals plus minus L. So, this boundary and this boundary you assume that concentration equals k v k v time C naught fine. And the other condition was that at x equals 0, del C del x equals 0 that comes to a symmetry. We assume that it is because your it is exposed to the same boundary condition on both sides. We assume symmetry one thing I want you to understand at this point is that you can have this equation, but if I had two different boundary conditions on two sides.

For example, at x equals plus L I had k a v times C 1 or C naught 1 and then this x equals minus l k v time C naught 2, then you cannot use the symmetry boundary condition. For symmetry, you need symmetry of equation as well as symmetry of boundary condition the other boundary condition should be symmetric. So, if you have the same slab, and it is exposed to one kind of boundary condition, one kind of concentration on the left hand side; another kind of concentration on the right hand side. So, of course you cannot expect symmetry. So, in that case what how do you go and solve the equation? You do not have boundary condition tool. So, what did you do?

If a (( )) (( )).

Condition.

So, the only difference is here you are solving for half the slab, but there you are not going to solve it for half the slab. You are going to solve it for the full slab and the boundary conditions would be on both sides. So, you will use k naught C a k a v C naught one on one side and k a v C naught two on the other side. So, this is not going to be symmetry. So, these are assumption that you have to be careful about and should not get too complacent about these things because you know. So, I might give them (( )) details. For example, I might give you the same problem with just two different boundary conditions on two sides, and do not assume symmetry that will be very stupid of you to do. So, just you know be careful about what kind of boundary conditions have been used.

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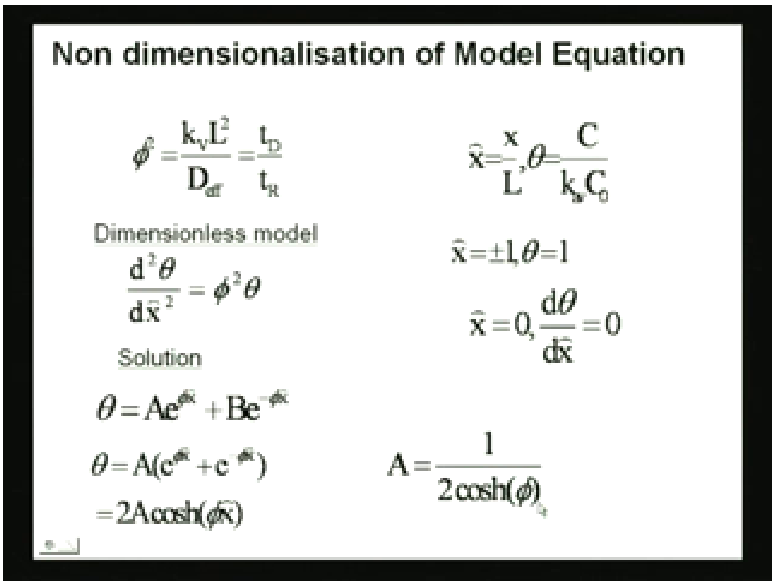

So, then the solution of this is a very standard solution which is a cos hyperbolic x and b cos hyperbolic y, but before we do that what we did was? We did the equations done the equations dimensionless because you know it is easier for scaling. And when we turned the equations dimensionless we got the dimensionless number Thiele modulus which is k v L square over d effective it is a ratio of the transverse diffusion time over reaction time. Why do you call it the transverse diffusion time? Because it is a diffusion time in the transverse direction; so, you have this is the transverse diffusion time t d and you can have a diffusion time in this direction as well which is typically you know as t d x which is the actual diffusion time.

So, anyhow, so because I. So, what would be that actual diffusion time it would be the length scale l over here, if I am to write the actual diffusion time the length scale l over here will be replaced by the actual diffusional length.

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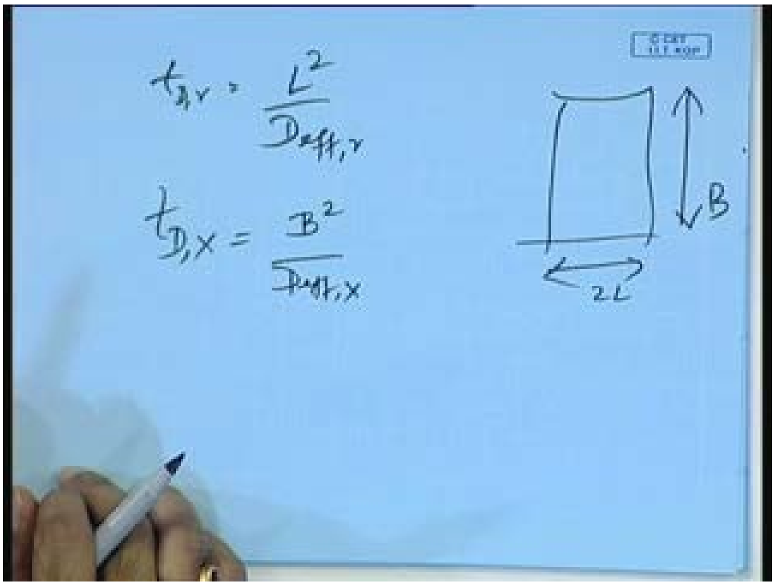

So, to repeat again. So, t D r if I call this is the transverse diffusion time say this is L square over D D effective, and if I have a actual diffusion time, then what would that be? So, if this is my 2 L and let us say this is my B then there would be.

B square.

B square.

By (( )).

Not necessarily this is d effective R and this is d effective x, because not necessarily if the diffusion coefficients are going to be the same in the radial and the actual coordinates. So, these are the things I want you to understand. because you know the for example, the mid seems are coming up and one of the things I would like you to do when. I give you a problem in the mid sem is not to just pounce under problem and solve it and get some numbers that is not what I am looking at, what I am frankly look at is that, how you approach a more you know these system that we are modeling over here there is some intuition there is some assumptions there is some understanding that come into the modeling. It is not just about writing pouncing on the on the system and writing an equation and solving it because at the end of the day you might get a solution which do not in any way they represent the system that you are trying to solve.

So, what is important is to understand the system? For example, I gave you this example of the boundary of the boundary condition being asymmetric one possibility, the other possibility is if you have to consider both actual and radial diffusions. Then there a diffusion times might be very different, and it is possible there are problems when your there could be encapsulations in matrices where the radial diffusivity could be very different from the actual diffusivity, or in other words the radial diffusion diffusivity itself is varying actually. Those kind of complications can come because these are matrices you make and you know you can make them in certain way.

So, you see do you see what I am trying to say? So, the radial you have a certain radial diffusivity with the radial diffusivity itself is varying actually, because how the pore structure is varying. The radial pore structures that you have might vary actually. So, anyhow. So, we did that and we used a exact used as x over l my dimensionless coordinate and theta as the dimensional variable C over k v C naught. And then my dimensionless equation became model became del two theta del x s square equals phi l square theta. And then the solution is this is what we wrote and we think we wrote it slightly differently. We wrote it cos hyperbolic and sin hyperbolic, and got rid of the sin hyperbolic we got just a cos hyperbolic, and then what did we do? We calculated eta the effectiveness factor.

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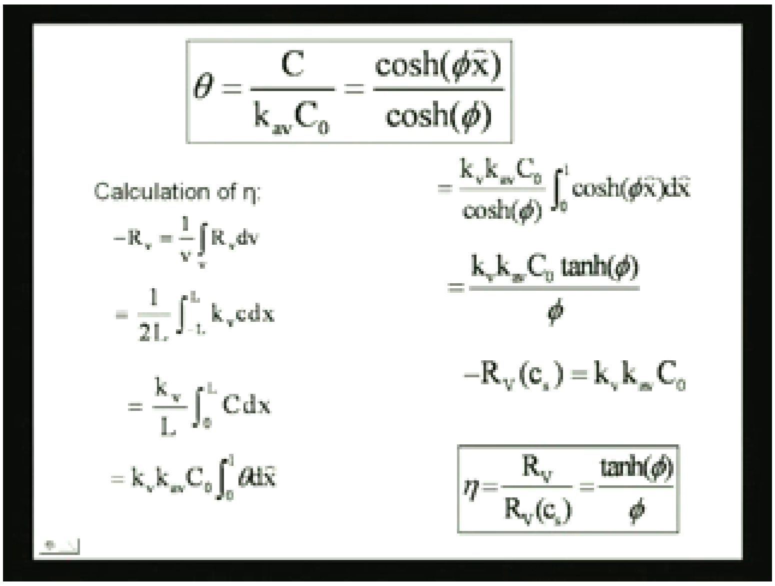

So, the effectiveness factor is the reaction rate as it happens inside the matrix itself which is a observed reaction rate, total reaction rate, actual reaction rate. Actually not the intrinsic reaction rate, over the reaction rate , intrinsic reaction rate evaluated the surface. That is how I have we have defined if you remember our eta. So, this is how we defined our eta? R v over R v value to that C s now R v, general R v is much lesser because the concentration inside is much lesser now. If there were this is something that you need to understand if there were no diffusional limitations in the system then your eta is going to be one. So, because of diffusional limitations that occur in the system ,what happens your R v? R v is decreased, because the concentration at any point inside the matrix is lower than that at the surface. So, because the concentration is lower and this is being a first order reaction it is different.

Now, what would you presume for a 0 the order reaction? This we had discussed it in the different context in the last week's class I believe.

Eta will always be one.

Eta will always be one, why is that? Because 0 the order reaction is independent of concentration a and you know, more than that this is the whole idea of 0 the order reaction as I told you is based on the fact that there is plenty of substrate. If there is plenty of substrate then the whole concept of mass transfer limitations do not come in at all. This is what we did in the in the previous scene that we did? So, eta is s and as I told you the tan had hyperbolic phi over phi is what comes out now, what happens one interesting thing that I asked you to do as, remember this formula eta s tan hyperbolic phi over phi the reason being that . This is a generalized formula this is something that you can use them and how do you use this is a and there's a method called shape normalization we heard of this shape normalization.

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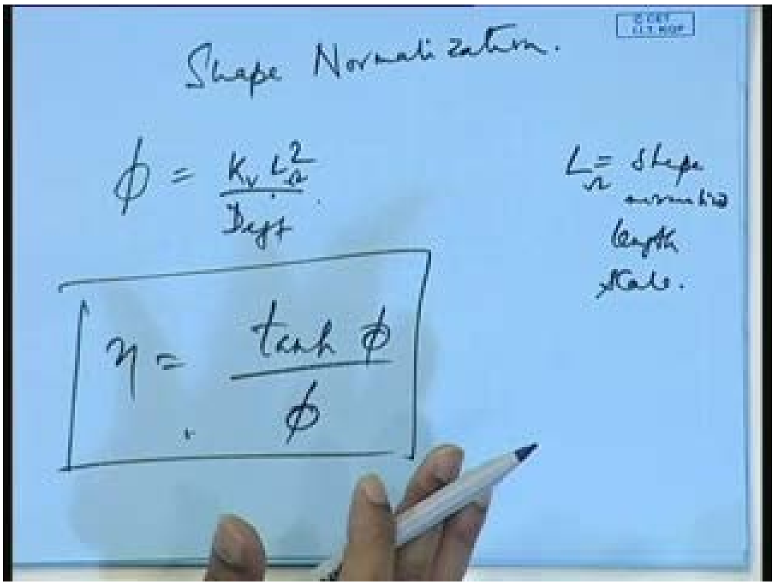

So, shape normalization is essentially that if you convert if you have any shape be spherical be it cylindrical be it is a very weird shape. You know the pentagon or cone some kind of weird shape pyramidal which you cannot capture. So, you cannot solve the equation in every shape all of these shapes. So, what you do is, you transform these shapes into standard shapes for example, a slab. And then you do all the calculations and when you transform them the only thing that is transformed is eta for phi square, for example, it is go this k v L square over d effective. So, there is that is your phi square. Now this L square over here, now your shape normalized length scale, do you see what I am saying. So, this L square now, so in your definition of phi square this is. Is it correct right you see?

So, in the definition of L square by a phi square the L that you have the length scale that you have is now a shape normalized length scale. So, which for example, I will give you in our next class itself I will show you what it is R over 2 and R over 3 per cylinder and sphere and. So, you can come up with what the shape normalized length scale even then you can. So, what is the idea is that irrespective of what from you have you can transform it into a slab. So, is that a perfect answer? No, it is not a perfect answer, but the advantage is this is very close to the perfect answer. So, if you say that your eta is, tan hyperbolic phi over phi and you define your phi this way in terms of the shape normalized value, and there is a mechanism for the that you know R over 2 R over 3 for different shapes there this how this l is going to vary is given.

So, what you can do? You can just use that value shape normalized value of radius and then use this formula this of this is not going to be a hundred percent perfect solution to your question, but you are 95 percent there you in terms of your eta. So, the advantage is that if you do not for example, if you want to use it as a form for a formula and something and you do not remember it. You can just remember this single formula and then we scale your phi based on that fine. So, this is I think where we stopped and then I gave you this example of these. Now two things I asked you to do one who has to be able to solve in a cylindrical coordinates. So, what is the solution of that in the cylindrical coordinate? I do not have I think I have these pages over here, I have got that pages.

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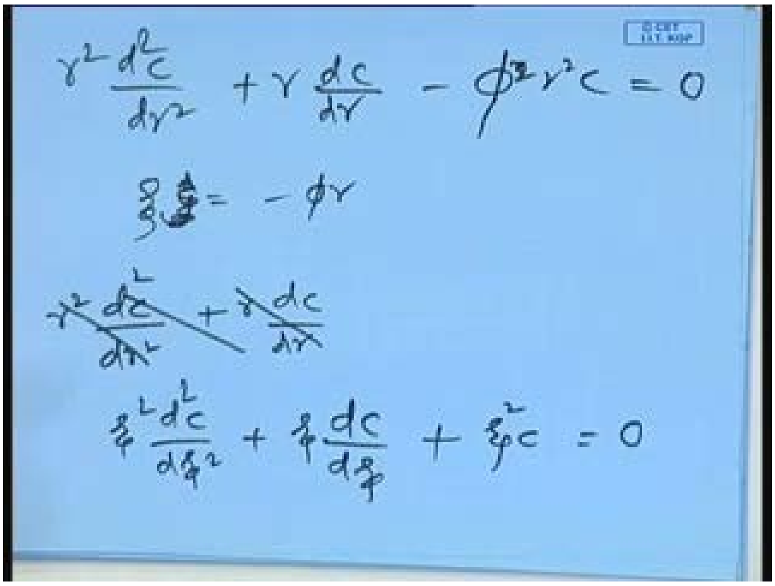

So, this is the Bessel function solution you have. So, this is this is one form if I remember this is one form, or another form you can do also if you have this r square del 2 C del r square plus r del C del r minus phi square r square C equal zero. So, I can call my say y hat equals minus phi times R, then you can convert this to another form let us call this not y hat, let us call this xi just for the sake of (( )). So, then your xi square del 2 C del xi square plus xi into fine plus xi square C equals 0. So, if I keep this and this over here next to each other, both is Bessel functions they are just two different Bessel functions of two different kinds. Why is that?

(( )).

One is Bessel one is modified Bessel. So, you can use either form. So, what will be the solution for the solution of this one? So, C equals.

a j naught.

Yeah j naught phi plus b.

(( )).

(( ))

No (( )) k k (( )) it is k.

Now.

(( )).

Y (( ))

Use a bold alphabets. So, this is the solution and then the solution for this one would be therefore, C equals some a hat, what it be?

I.

I and.

k.

(( )).

So, these two solutions are possible. So, either you write it in this form or that form. So, if it comes with a the negative sign, then you have the I and k and if it comes with the positive sign then fine then you have the j and y. It does not matter it is the same thing you will get now what after this you have to evaluate the constants. So, out of the two these two are Eigen functions I hope you know that out of these two Eigen functions these two here and these two here. What will happen?

Sir one is (( )).

Which one which one.

B second (( )).

The B right in both cases the B and the B hat would be 0 why is that.

We have finite value (( )).

Finite value at R equals 0 xi xi equal 0.

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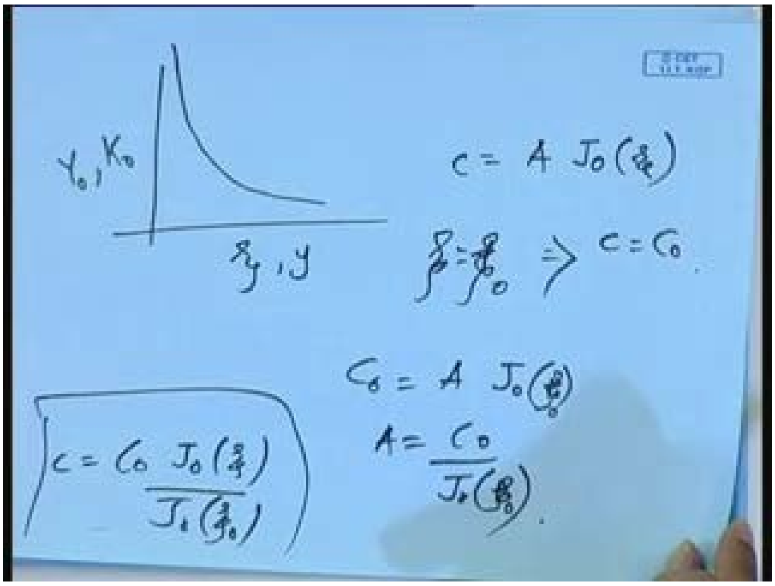

So, the problem is that you know both these say the y naught and k naught, they go to infinity as this is my xi or R xi or y say. So, as xi or y go to 0 they go to infinity. So, those two are not allowed. So, you will you can only have your solution in terms of J naught and I naught, and then it is simple because all you need to do. So, if you have your solution as C equal say a j naught xi. Then the other solution if I remember you have at xi equals one or something right xi equals one is the other concentration that is given let us look at the screen here.

No not this yeah. So, we are looking here. So, and. So, this is the same kind of thing. So, the concentration at xi equals, one say is some C naught C equal C naught fine. So, then you are pretty straight forward. So, a J naught 1 so you can just put it over there. And a would be equals to C naught over J naught something like this it may not be xi over here it may be xi may not be one over here say even if it is xi is at xi equals, any value you can put that value over here. So, if xi equals xi naught then you know you put xi equals xi naught over here. So, very straight forward then you essentially your final solution is C naught J naught xi over J naught xi naught. So, this is the cylindrical coordinate.

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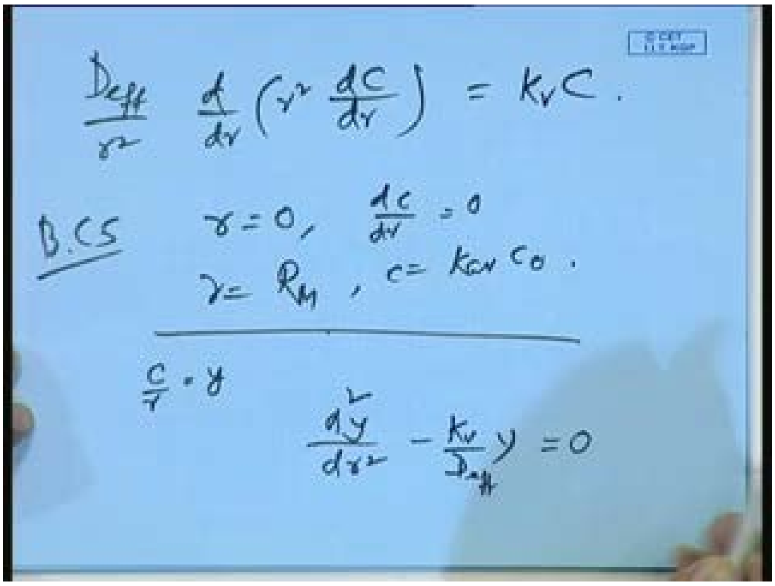

Now, then other question, we have whether the spherical coordinate what is it? This is the solution equation is. So, I asked you to solve it. So, what is the solution?

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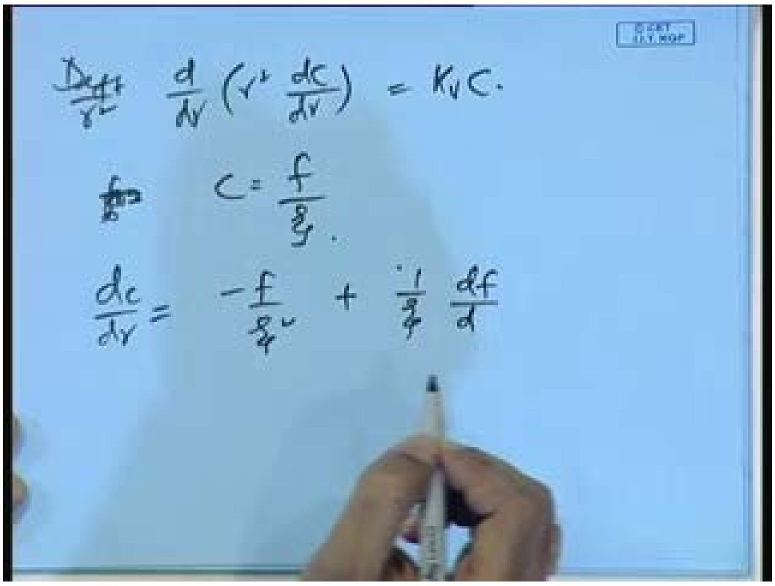

So, my equation is d effective r square d d r of r square Del C del r equals k v C, and my boundary condition are r equals 0 del C del r equals 0 fine. So, what do you do over now over here now?

(( )).

C.

(( )) r is (( )).

C times.

C by r (( )) C by r it is (( )).

C by R equals.

Y

Y it should be yeah fine. So, that. So, then what.

(( )) (( )) if changes then it will come.

What is the change two?

(( )).

You have done it or not done it.

(( )).

I asked you to do it yesterday and come with.

If you are by (( )) k a by d f y is equal to 0.

d 2.

Then.

d 2 y.

d 2 y by dr square.

dr square.

Minus k v by d effective y is equal to 0.

Right.

It can be solvable y is equal to three naught xi naught.

(( )) for some (( )) no it is not cos sir it is (( )).

No it is not cos

It is (( ))

But at least this form is correct so.

Hyperbolic.

(( )).

So, you know. So, while you know since none of you have done it and nobody has done it right you have done it, but nobody else has done it. So, I will do it here. So, this is my equation over here this deffective R square del R of R square del C del R equals k v. So, let us call it f equals C equals f over xi is it what you said something different is it What you assumed.

I assumed, but you said the other way round I think.

(( )).

You can also get it that way.

(( )).

C by r o equals some other variable.

(( )).

Anyway you check that now, but this is something that gives now. So, my del C del R equals now minus f over xi square plus one over xi del f del f del R or I mean I you have right very you will want to say xi over here. So, if I am correcting this or let us just let me just use another page.

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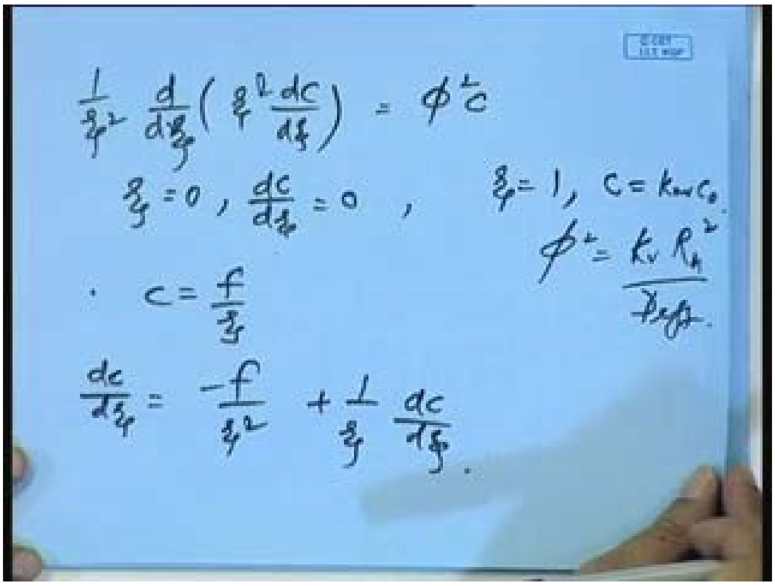

So, one over my equation that I am now trying to solve is one over xi square del xi of xi square del C del xi equals C square times C, that is what I am trying to say solve? And my boundary conditions are xi equals 0 del C del xi equals 0 and xi equals one C equals k v C naught Lisa what are these in these equations these are in dimensionless form. So, we started with a dimensional form and converted it with dimensionless form, and my phi square in this case is going to be what k v.

(( )).

K v times big R square over j affected. So, now my assumption is C equals f over xi. So, del C del xi equals minus f over xi square plus one over xi del C del xi correct then. So, I will go to the next one.

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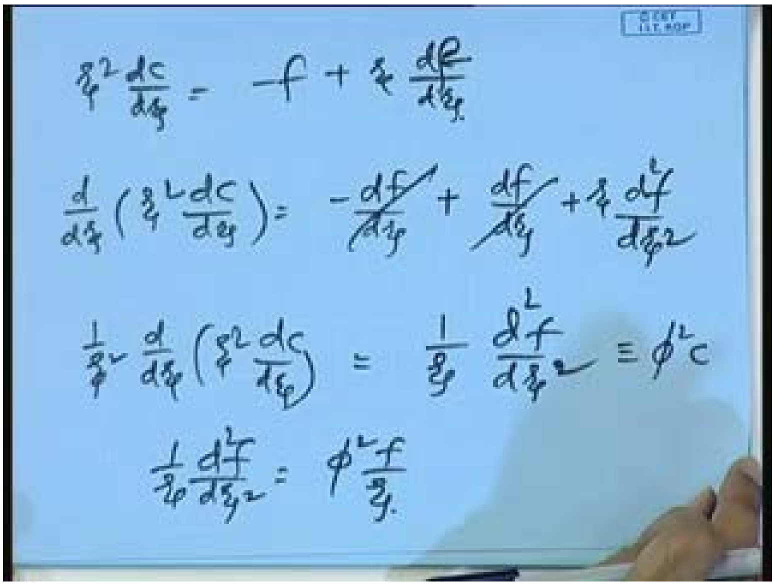

So, then my xi square del C del xi equals minus f plus xi into del C del xi, now del xi of this del xi of this is, this plus and cancels out. So, one of a xi square del xi of xi square del C del xi equals one over xi times del 2 f del xi square. So, my equation now. So, this equals this now this is equivalent to phi square of C phi square time C. So, what I get is? One over xi del 2 f del xi square equals phi square times C is now f over xi no.

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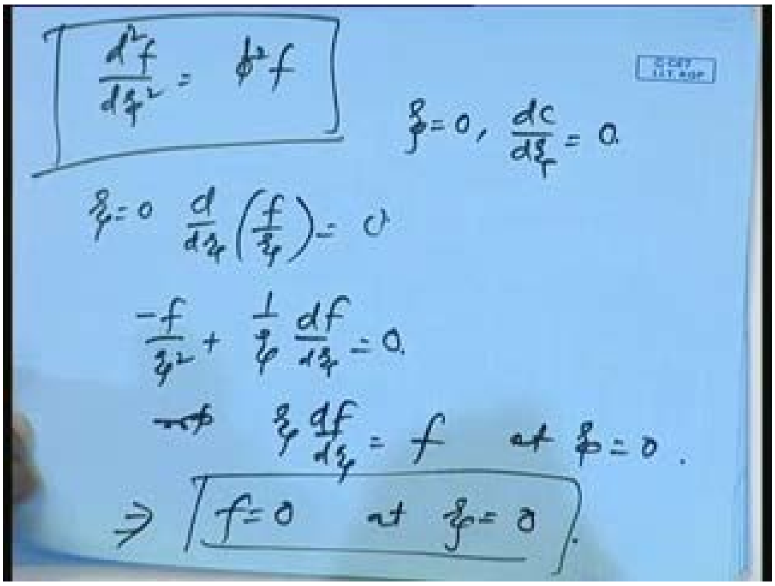

So, my equation becomes del 2 f del xi square equals phi square of f. So, this is a equation that you have solved before, and the solution you know is cos hyperbolic and sin hyperbolic. So, only thing that now left is a boundary condition. So, my boundary condition earlier was xi equals 0 del C del xi equals 0 now. So, which means that xi equals 0 del xi of f over xi equals 0. Which means that this is minus f over xi square plus 1 over xi del f del xi equals 0 want to play all through by xi square, you will get minus f for xi times del f del xi equals f this is your boundary condition at xi equals 0 which means that f equals 0 at xi equals 0 done.

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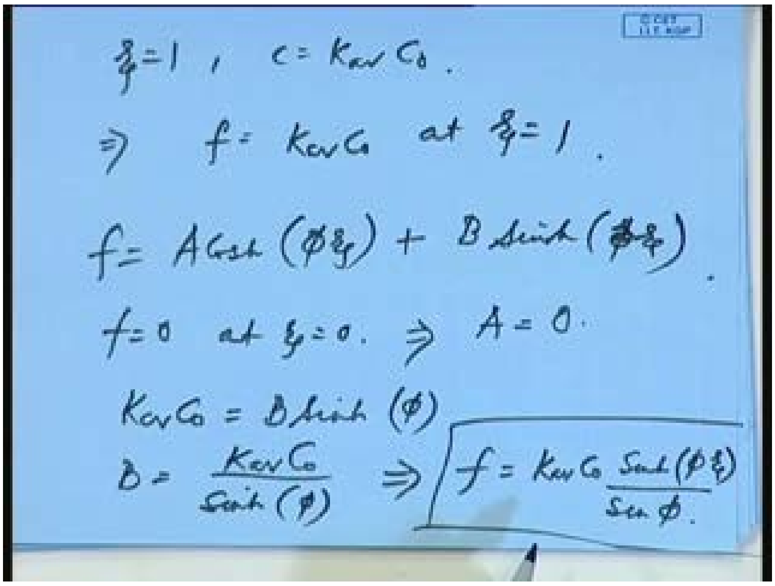

So, this you get your first boundary condition. The second boundary condition is what was that the xi equals is one here, xi equals one C equals k v C naught which means that f equals again same K v C naught at xi equals 1. Now your solution to your equation is f is Acos hyperbolic phi xi plus B sin hyperbolic phi xi. So, first boundary condition was f equals 0 at xi equals 0 implies that, A is 0, second boundary condition was this one. So, f equals k v C naught at xi cos 1. So, which means K v C naught equals b sin hyperbolic phi, if I remember last time it was my Eigen function that remained was the cosine hyberpolic.

This time there’s sin hyperbolic remain because of the boundary conditions. So, which means that B equals K a v C naught over sin hyperbolic phi; that means, mine f is K a v C naught sin hyperbolic. So, this is my final form for f that we get what is left now? We have to calculate what?

Convert it into C, converting into C is not a problem.

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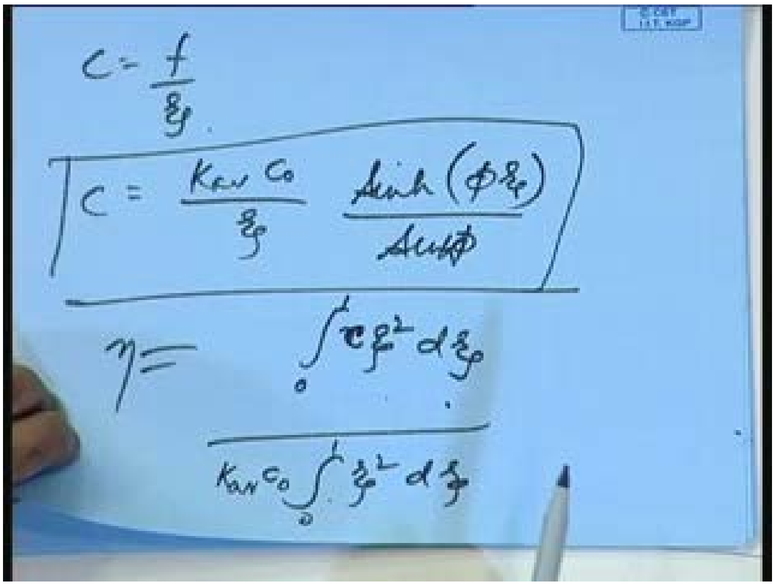

So, C is. So, C is f equals f over eta. So, which is K a v C naught over xi is this straight forward no, but what is left is we have to calculate our eta which was C, what is my definition of eta going to be now C times C?

(( )).

C times four pi r square or xi square whatever phi xi from 0 to 1 divided by xi going from C naught K a v, and K a v cancels out both places numerator and denominator the k a v will cancel out clear. Because eta is reaction rate devaluated overall divided by reaction rate devaluated surface. So, the K a v is in the numerator and cancels out this is, what remains now this is? So, this is very straight the denominator is straight forward, but the numerator is slightly tedious. So, what I will do is? I will just give you the solution to this.

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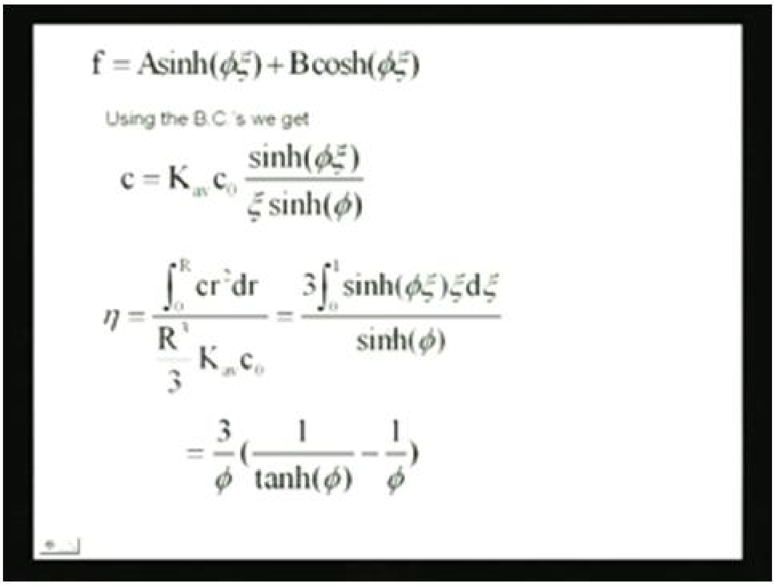

So, my eta after I do all these calculation comes out to be 3 over phi actually it is here. So, I do not need to write this. So, this is let us seeing up. So, eta comes out to be three over phi one over tan hyperbolic phi minus one over phi. So, what you see is that? It is a essentially goes a co tan hyperbolic the reason being that goes A co tan hyperbolic the reason being that the Eigen function is changed from cos to sin. So, we now finish we understand at least all the three, how you know three different geometries have to do it, and as I said you know so for you could be asked to do in any of these geometries using any of these boundary conditions. So, you should be prepared for that. So, as is a slab where the where the Eigen values are. So, what are the Eigen values for slab let us chart the Eigen values.

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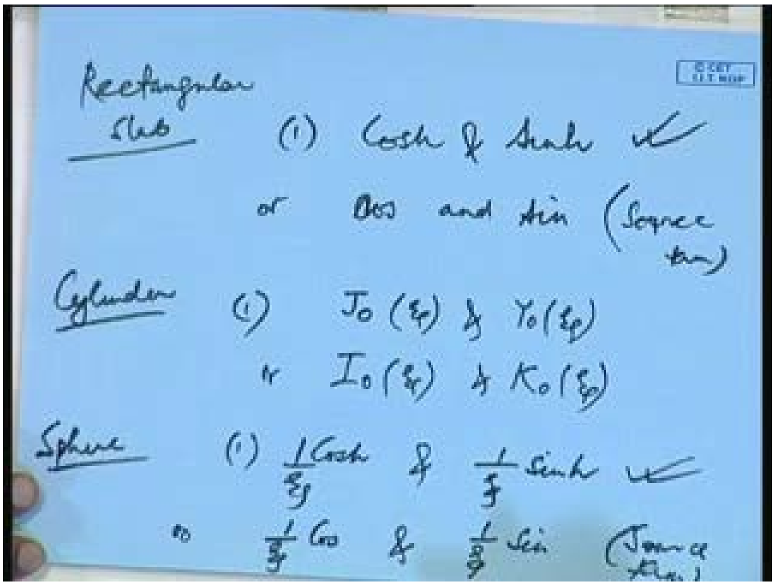

So, slab what are the Eigen values cos hyperbolic and sin hyperbolic or it could be cos and sin in which case.

(( )) source term.

Called the.

Source term.

Or in other words for the product of not necessarily for the product we have if it is A, if it is instead of taking part let us see how can it be, how can there be a source term for the substrate may be the substrate is produced from some other reactions. So, this is the freak case, but source term let us say, but I just want to chart that Eigen functions. So, this is the normal case and this is the special case if there is a source term I just want to write all the. So, then next one would be cylinder would be j naught fine and y naught or I naught, and k naught. If anyone source and sink is that clear and then whatever this sphere this sphere would be cos hyperbolic one over xi cos hyperbolic, and one over xi sin hyperbolic or it would be one over xi cos, and one over xi sin this is for a source term special case is that clear to all of you.

So, I am charting out all the three possibilities. So, rectangular slab is cos hyperbolic sin hyperbolic typically. If there is a source term for this substrate it could be instead of a sink it could be cos or sin, but this special case again. Cylinder is j naught y naught typically or you can write it as I naught k naught also, and sphere is cos hyperbolic over xi, and sin hyperbolic over xi it could be cos over xi and sin over xi for special case when there is a source term.

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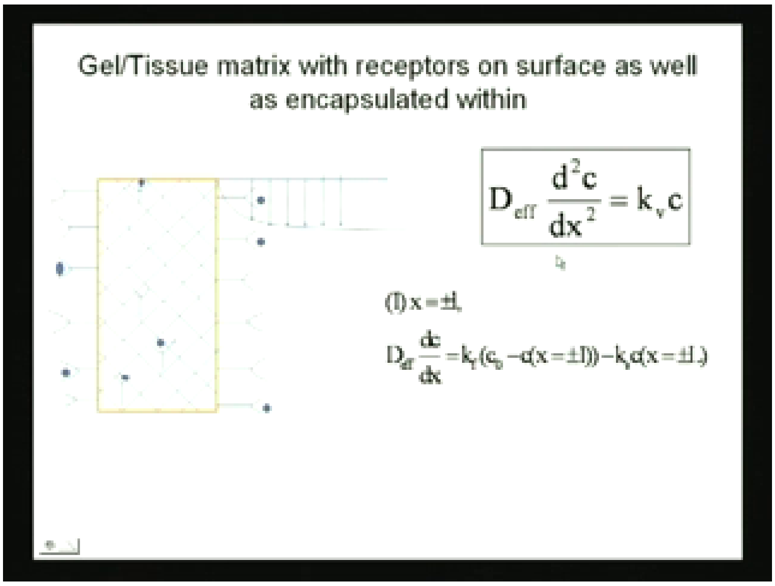

So, let us now go on to the next. So, is that clear is that clear to all of you. So, next now go on to the next issues that we are looking at and let us look at the screen here. So, till now what we did was in? And this is a slightly more complicated form a slightly advanced form of what we are doing? So, till now what we did was we looked at encapsulated matrices where the enzyme was entrapped only outside. And now it is we're looking at a more practical case where the entrapped enzyme is entrapped outside as well as well as inside the matrix. So, we looked at enzyme trapped outside or enzyme kind of attached outside, then we looked at the case where enzymes were trapped inside. And now we're looking at the case where both these things happen. So, enzyme is entrapped inside as well as it is covalently attached to the surface. So, this is a slightly more complicated case. So, what you think ? What you are suggestions on what should be the equation on the boundary conditions in this case?

We should not (( )).

Right equations will remain the same the reason being that, if you remember what we did before was that, this does not affect the you know then this only effects the boundary condition. The receptors on the surface only vector boundary condition it does not affect the equation right and the equation inside the matrix remains the same because reaction is occurring only inside the matrix. So, (( )) we are again back to the slab problem and what you get is d effective Del 2 C del x square equals k v times C? And what do you have boundary conditions now?

That boundary is C s.

It will be.

Something C s (( )) they have (( )) we have to solve them Bessel equation with the boundary layer solve it (( )).

So, there is a boundary layer. That is the thing that you have to what you said is not correct, but the equation is not correct that you said, but the concept is correct that there is a boundary layer. So, we have to account for that boundary layer and try and get the concentration across the boundary layer, and what was a mechanism that we followed in the last previously? We use the concept of mass transfer coefficient, we use the concept of mass transfer coefficient to calculate what would be my difference across the boundary layer. So, you do not essentially know what is your concentration exactly at the surface? But what you know is a concentration far outside the boundary layer far from the surface you know.

And you also know if you know the mass transfer coefficient you would know how much is the total driving force, and total transfer that is be the mass transfer coefficient times the outside concentrations C naught minus C at the surface. So, that would be my boundary condition let me show you and then it will be clear up to you. So, this step is that you see over here on the right hand side k f C naught minus C s forget this term over here do not do not worry about this term right now. So, let us look at this term alone C naught minus C this is you're the total driving force. C naught minus C is the total driving force times the k f which is the mass transfer coefficient that should be equal to the amount of flux that is coming in fine now what is this term doing over here because your receptors on the surface see if the surface had no receptors and you just had a boundary layer then this is what you have, but because there are receptors on the surface and there is a first order reaction going on the surface, you add that as well because that is your consumption and the surface.

So, whatever is coming in substrate or in other words whatever is coming in equals what reacts on the surface plus what goes in. So, if you bring this to this side for example, so there is (( )) whatever is coming in is? What reacts plus what goes in fine. Is it clear?

Not clear.

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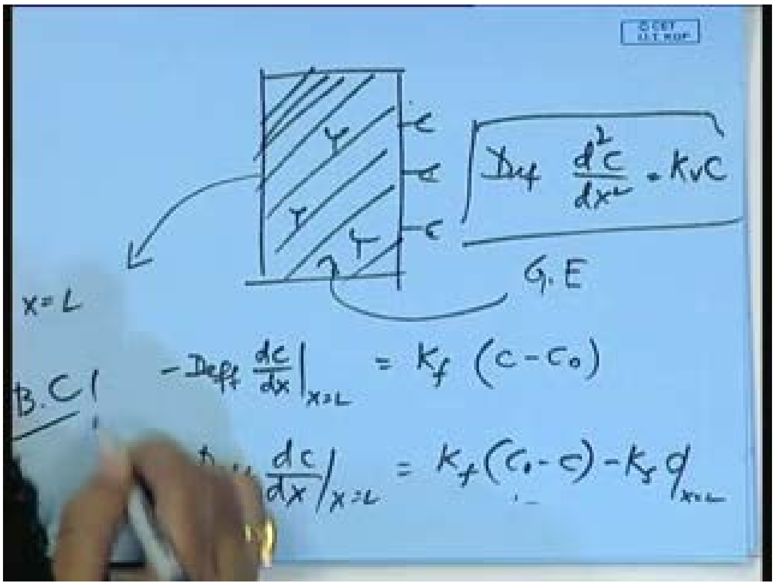

Not clear. So, draw a picture and try and show. So, this is my matrix now the receptors are on the surface and the receptors are inside as well fine. So, if the receptors are inside then I straight forward write, d effective del 2 C del x s square equals k v c. So, this is for the inside. So, governing equation for inside, the matrix is that clear till that point now the boundary conditions. So, first boundary condition is at this point x equals l let us said. So, what is happening over here is that if you are. So, d effective times Del C del x at x equals l should be equal to k f C minus C naught. So, this is nothing is happening or in other words you can just write it like this d effective times del C del x equals l equals k f C naught minus C that is how people write it because you know C naught is typically larger than c.

So, this is what you have of is? There any problem with this? No, absolutely not know what happens, because the reaction occurs on the surface. So, what is coming in does not all of it go all of it does not go in, a part of it is actually reacting on the surface, and how do you in incorporate that? So, take that out what is reacting on the surface which is the k s surface reaction rate times C at x equals l is it clear now. So, this is without what is happening on the surface. So, this part let us put it is over here. So, what is coming in what is coming in here through mass transfer is, what is going out? But that is not the reality in this case there are receptors on the surface.

And a part of it part of what is coming in is actually reacting with the with what is there on the surface. So, you have to take that out. So, what is coming in minus what reacts on the surface is what is allowed to go into the matrix.

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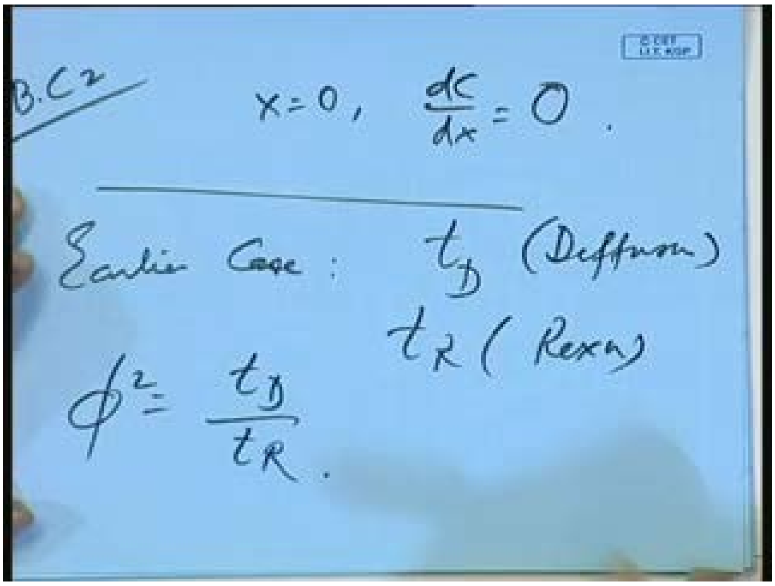

So, that is my b C one and B C 2 is again the same the straight forward B C which is x equals 0 the del C del x is 0 the reason being that again there is symmetry. So, all are all around you assume the same boundary condition. So, all you need to do is go ahead and solve it. But before we do that we will be going to make this equation dimensionless. So, we have to write the equation in dimensionless forms and we have to define some dimensionless variables. And can you tell me that, last time we had one dimensionless number, two dimensionless variables which were x and theta, and one dimensionless number which was the Thiele modulus. In addition do we have another dimensionless number this time yes we have and why do we have another dimensionless number.

(( )).

Because of k L, because see the dimensionless numbers are always quantitative of the physical phenomena that is happening; that is the way you have to look at it not in terms of coefficients and so on. So, earlier what were the physical phenomena that were there earlier case. What were the physical phenomena that were there the diffusion and reaction?

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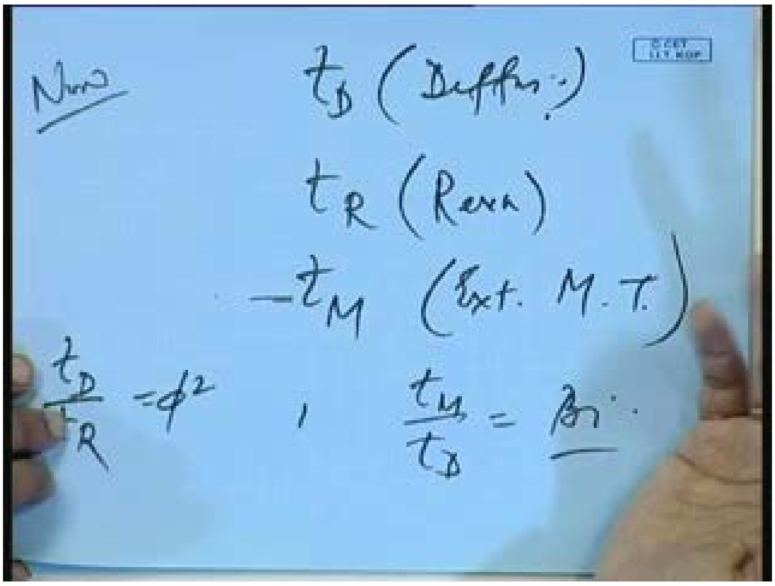

So, you had phi square, which was a ratio of diffusion time over reaction time. Now what you have diffusion, reaction and let us call this t M external mass transfer. So, these three phenomena occur simultaneously. So, you will have therefore, two dimensionless numbers, one would be say ratio of. So, out of these three you can get any two independent dimensionless numbers. Say it could be t D over t R is 1, and then you can have say t M over t D, which is you know? I will come to that.

So, typically these are the two numbers that are used one is the ratio of the diffusion time to reaction time phi square and the other one is the ratio of mass transfers. So, here for example, what you have is? This is a external mass transfer, and diffusion is internal mass transfer. So, what you have is another number which is the ratio of external to internal mass transfer, in addition you can form another number actually. Because you have surface reaction and the rate for surface reaction is going to be different for the rates for from reaction inside the matrix. Why is that? Because in inside the matrix it is a volume average rate wherein surface reaction rate is the intrinsic rate based on the surface reaction rate. So, you can form another number there we are not going there, but there’s a possibility.

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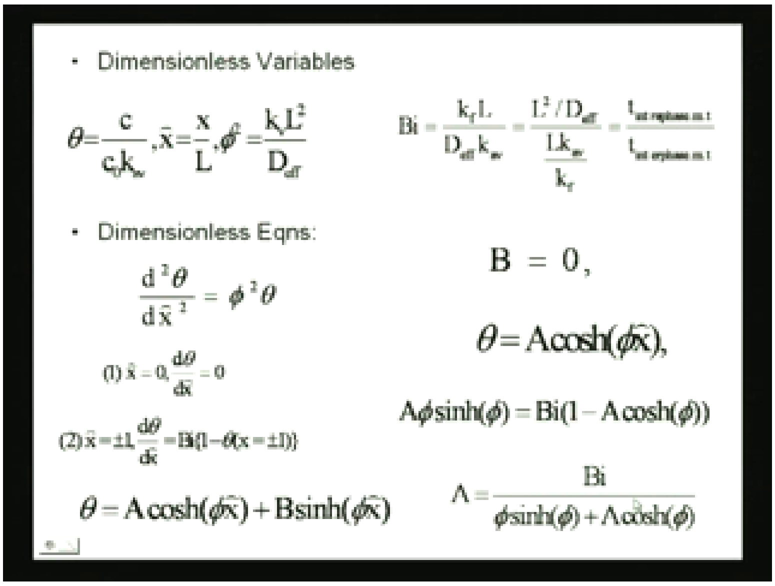

So, let us look at what we have over here. So, we have theta which is C over C naught k a v x hat which is x over l we have phi square which is k k v times l square over the D effective. And then we have this quantity by biot number which is a ratio of inter phase mass transfer or in other words internal mass transfer time ,over inter phase mass transfer in other words external mass transfer time. So, this is a new numbers that we have and you have studied this number elsewhere, but we just get back to it here. So, phi square is your ratio of transverse diffusion to reaction or inters phase mass transfer to reaction, if you want and biot number is a ratio of intra phase mass transfer to inter phase mass transfer in other words internal mass transfer time over external mass transfer time.

So, if your internal mass transfer is very slow then as compared to external mass transfer which is typically the case actually then, what will happen biot number is much greater than one ? And if your external mass transfer is very slow, as compared to internal mass transfer does not happen typically then your biot number is much smaller than one and. So, you have three different competing phenomena that are occurring over here. And the surface reaction we are not considering here because its only few receptors are engaged in the surface and the major reaction is occurring at the inside.

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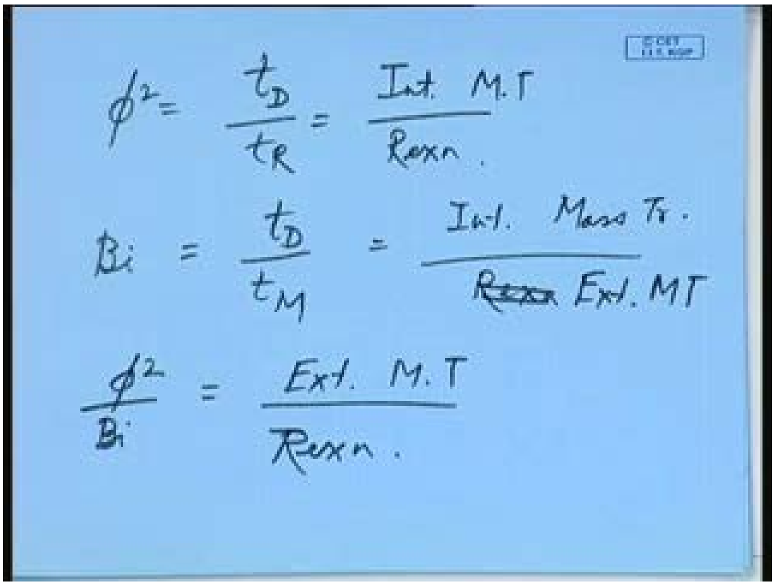

So, you have the ratios of these three numbers. So, you know for let me simplify it for you phi square equals t D over t R which is internal mass transfer over reaction. And biot number is t d over t m which is internal mass transfer over reaction. So, which means that phi square over biot number would give you the ratio of response reaction this is external mass transfer. I will give you the ratio of external mass transfer over reaction clear it is clear to everyone. I am not we are again running short of time today. So, one. So, I will go through this quickly a little bit and then you know one of the things I want you to do is actually go and look up your notes.

So, if there are problems. So, I will explain at the beginning of the next class like I did today, but I do want you to go back to your notes and have a look at it. So, when I write in terms of these two dimensionless variables, and these two dimensionless numbers my equation that i had, before comes out to be the same del two theta del x hat square equals phi square times theta. Boundary condition is except equal 0 del theta del x 0, and this boundary condition over here is x equals plus minus one del theta del x hat equals biot number one biot number times one minus theta. Who will tell me?

Krishna pratap you tell me, that is this boundary condition second boundary condition completely correct.

(( )).

Right.

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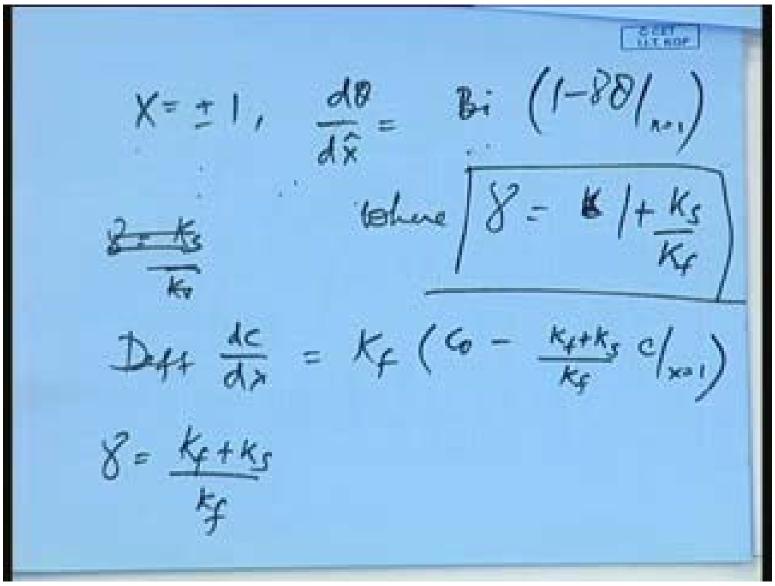

So, this boundary condition had been written without the reaction into consideration. So, you get del theta del x hat equals biot number into one minus theta at x equals one you had a if you have a reaction determined does not make much of a difference what happens is you. Just put a gamma out here because the reaction term if you remember also has a external boundary condition which is that x at x equals one. So, basically what you have is this? So, you can add your gamma over there and then gamma will you know have the k s over k v and so on. So, just a factor over there is that clear let me let me go back and show you then it will be clearer again here do you look at this equation this is k f C naught minus x at plus minus one minus k s times x at plus minus one.

So, you can club what I am trying to say is this and these are two same variables and you can club these two same variables. So, what you will have is d effective Del C del x equals k f C naught minus k f plus k s over k f C at x equals one right fine. So, this number is your gamma that is all I am saying. So, gamma equals k f plus k s over k f fine. So, in the same you know I have this boundary. So, so in dimensionless coordinates x equals plus at x equals plus minus one Del theta Del x hat is biot number times 1 minus gamma where gamma it is k f 1 plus k s over k s.

So, does that would not change your solution or any of these things just the boundary condition would be slightly altered, as a result your constant would be slightly altered, but otherwise it would not change anything else. So, as we know we do not have a lot of time today. So, let us quickly summarize this. So, we did this and there is no reason for us to repeat. So, theta equals A cos hyperbolic x plus B cos hyperbolic sin hyperbolic phi x. So, there is no reason for us to repeat. So, del theta del x would be 0 at x equals 0.

So, b could turn out to be, and theta would be this and all you need to do is apply this boundary condition at this end and you will get your solution. So, I did this without the gamma out here, but you can just put the gamma in there and it would not make any difference to your equation.

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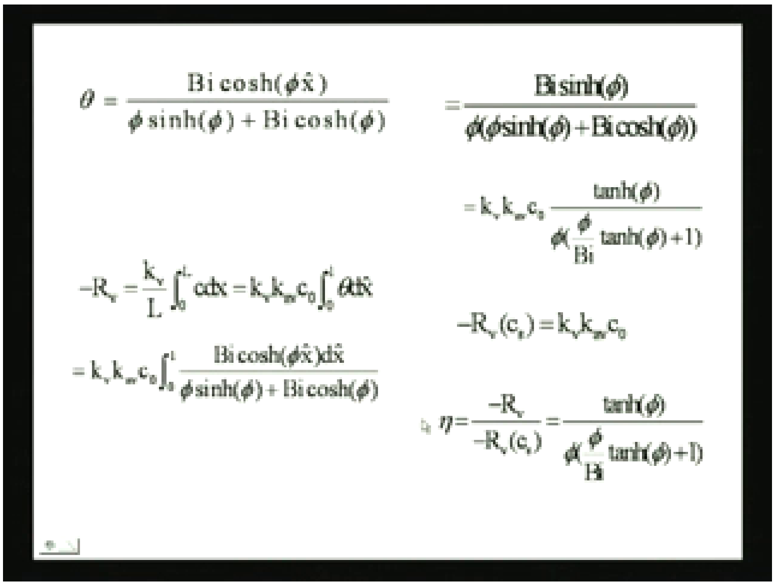

So, this would be your theta that you get at the final thing the, but again without the gamma and if you put the gamma in here if I remember yeah. So, it will come over here the biot number it would come with a suffix of gamma. So, it will be biota number times gamma cos hyperbolic x and this. So, what I want you to do is just you know go and redo this and see whether gamma comes in. I am sure it comes in over here, but just for you to check now. So, this is once you write it in this form then you can you can write it in the tan hyperbolic form as well. Because sin hyperbolic over cos hyperbolic and then you get the tan hyperbolic phi over tan hyperbolic phi and so on.

And these are values at x equals one. So, this is general theta and this is evaluated at x equals one the surface concentration. Now why do I do them? Because I need to evaluate the eta the effectiveness factor. So, I just need to evaluate that. So, my R v the average volumetric average is given by k v over l times integral of this from 0 to one which is integral of this is the little complicated integral and then eta comes out to be tan hyperbolic phi over phi over biot number tan hyperbolic phi plus one this is this is what it comes out to be this is because R v C s is this number. So, this gets canceled with this over here and this is what remains.

So, I think you know we are doing a little probably little fast today. So, I would stop here, but I think we will probably we might is it clear to everybody or do we need to go back to it rather next select next lecture what I want you to do is. Just go back and put this gamma over here, that we had. There is a gamma out here. So, you just and as you see that my intuition tells me that you know the gamma comes here with the cos hyperbolic term. So, wherever there is a cos hyperbolic term the gamma would come there, and then you can just then the rest is easy. But again you know this integrals are not very easy you know that is that is the problem, when integrals are actually not very difficult either, because this is just cos hyperbolic. So, the denominator is something you do not need to worry about. So, this is just cos hyperbolic the integral of that would be sin hyperbolic, but we you know the thing is that we can really go through each of these steps in this class.

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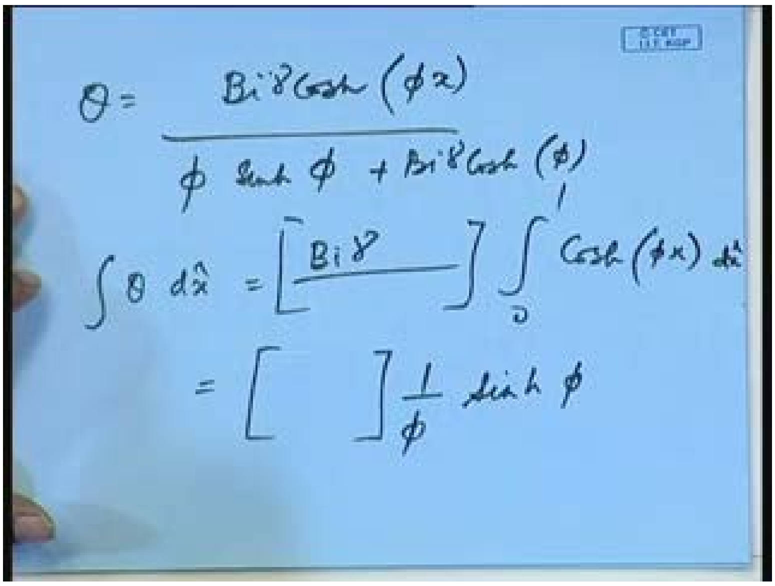

So, if you want I still have a couple of minutes or if you want I can go through this. So, theta equals biot number, cos hyperbolic phi x times phi. I guess the gamma would come here and here that is my guess. So, if you do that then the integral of theta d x hat would be simply biot number gamma over this entire denominator. I am not writing it because of lack of time integral of cos hyperbolic phi x d x hat from 0 to 1. So, which would be this whole thing in square brackets over one over phi sin hyperbolic phi once you put the integrals out there.

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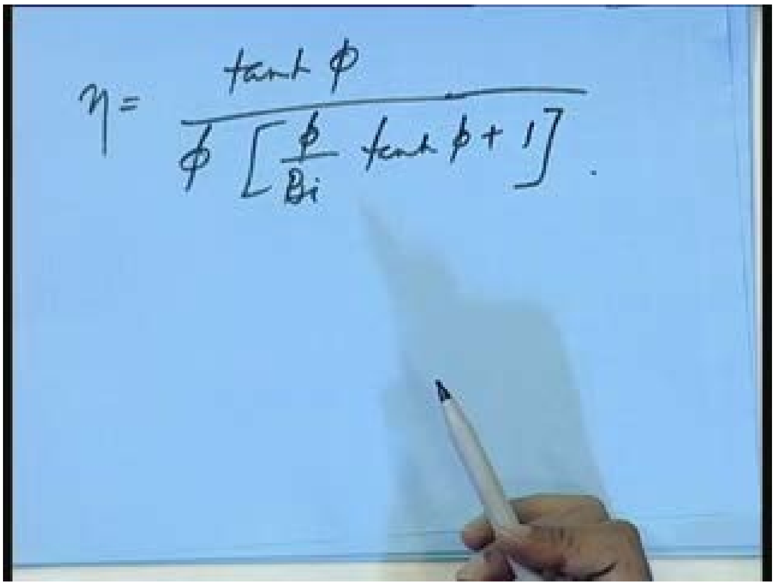

So, you what you get is your eta comes out to be tan hyperbolic, because the sin hyperbolic and the cos hyperbolic you can take this in denominator, tan hyperbolic phi over because there is a there is a phi out here. So, that would come. So, phi times phi over biot number tan hyperbolic phi plus 1. So, what I want you to do is, you know as a as homework today is to go, and add the gamma, and go through these steps because unless you go through these steps yourself. You know this is not something that you will take away from the class. So, just go through these steps, because you know as I said in a in that in the test, for example, you might have to do all these calculations very quickly within a short period of time and then there is only one way of being able to do that is which is do them yourself. So, I want you to go through these steps, and if there are problems I will recap that in the first 5 minutes of the next class, otherwise I will start with something else. So, I will stop here. Thanks.