Biochemical Engineering

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Module No. # 01

Lecture No. # 17

Effectiveness Factor in Immobilized Enzymes

Immobilized enzymes and this is hopefully the last lecture on immobilized enzymes and the thing that, we are going to look at today is the effectiveness factor, the calculation of the effectiveness factors. So, the effectiveness factor, what is it signify? It signifies that, what is the total amount of reaction that is occurring over the total, a maximum amount of reaction that could have occurred right. So, that is a that is a idea for immobilized enzyme effectiveness factor sorry. So, we did look at effectiveness factors under in certain geometries and so on.

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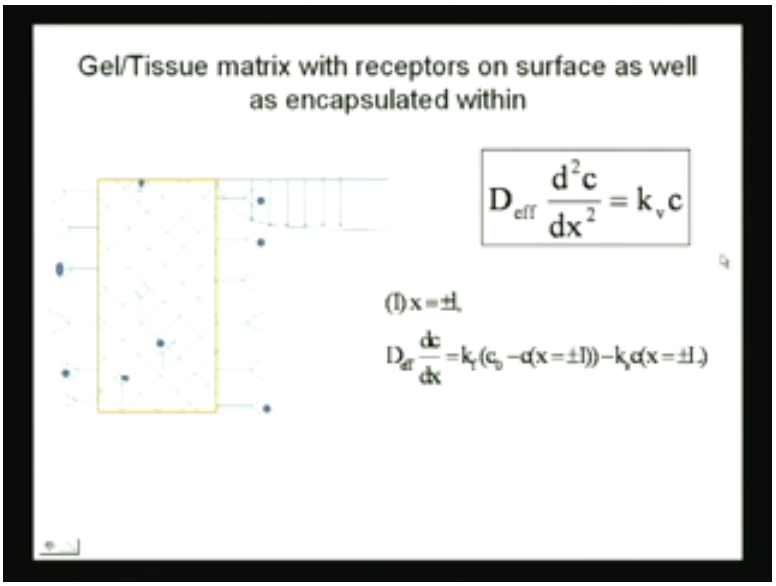

So, if you go to the slide, this is the last thing we did if you remember, we looked at encapsulated enzymes with reaction taking place both inside and outside and it was little complicated in terms of the boundary condition, and we took a simple geometry.

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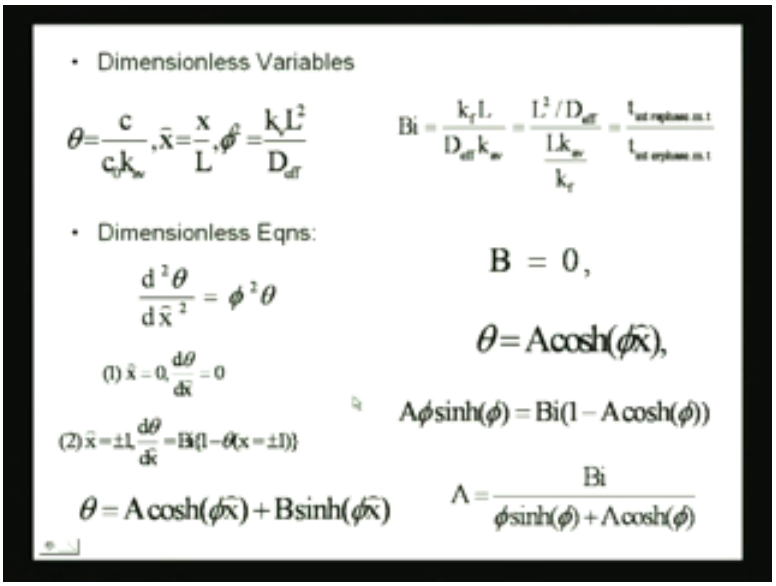

And then we go ended up with an equation like this, del del theta del x square equals phi square being the Thiele modulus phi square times theta and the boundary, condition the boundary condition included the biot number, which is the ratio of mass transfer, external to internal mass transferred times and then based on that, we got the solution and everything and we found the effectiveness factor.

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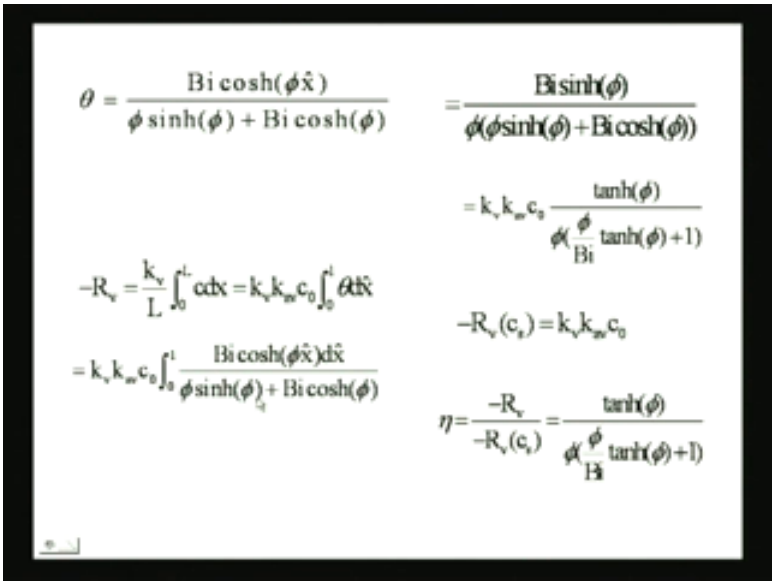

Now, what we are trying to do, what we are going to do in today's lecture is, try and obtain the general expression for the effectiveness factor. And I told you, while we derived the effectiveness factor for, I think with a normal slab or something that it comes out to be tan hyperbolic phi over phi and I told you that, this is an expression that you could use for different kinds of geometries, provided you make certain changes to phi, that is, you define phi in terms of the effective effective length L. And so, your length L is going to be the length for a slab, how the length for a slab, for a sphere is going to be something else, for radius is going to be something else, and we will figure out how to do that today. So, that is the first thing we will to do today.

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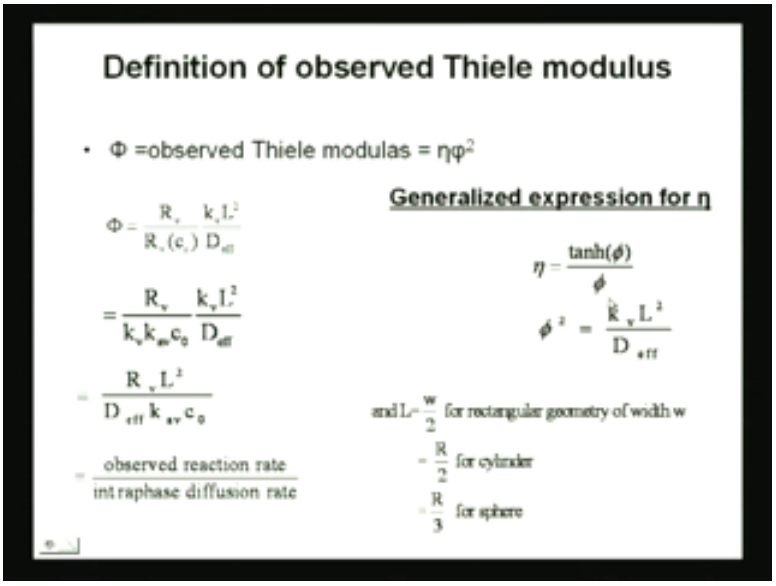

So, my observed Thiele modulus, so now, we come up with the with the expression for observed Thiele modulus. So, if you remember, we had the Thiele modulus which had the reaction reaction times k times can diffusion time scale over reaction times scale right.

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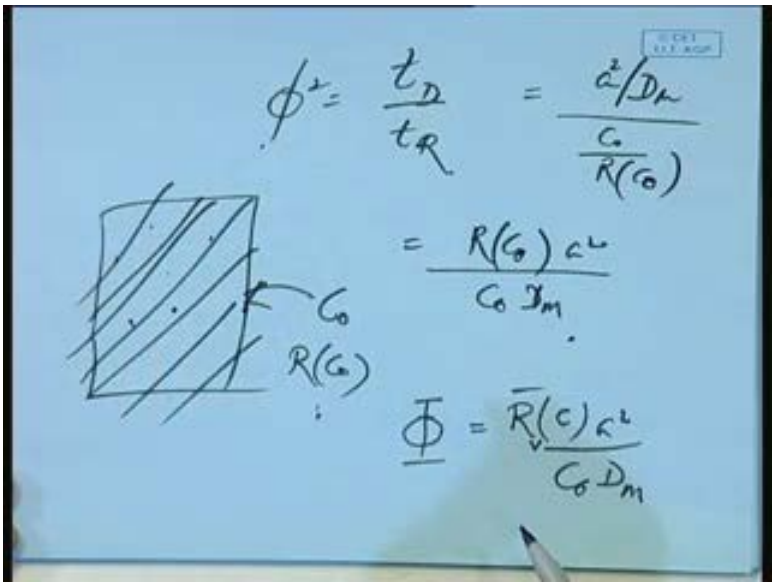

So, or in other words, if Thiele modulus is very small, then it means that, what is the mean that diffusion is Thiele module is much larger than 1, it means reaction is much faster than diffusion. And if Thiele module is much smaller than 1, it means reaction is

much slower than diffusion right. So, but the thing is, if you look at it that, Thiele modulus essentially is, therefore diffusion diffusion reaction time over diffusion time right, say if reaction time is very small, then sorry. So, Thiele modulus should be diffusion time over reaction time, so phi square equals t D over t R. So, which is a square over D M divided by, what is the reaction time C naught over R C naught right. So, this turns out to be R C naught times a square over C naught D M fine.

So, what do you find over here is that, if the reaction rate is faster, so Thiele modulus is essential is proportion to the reaction rate. Now, this, what is this reaction rate, the question is what is this reaction rate? When you when you write Thiele modulus, you write the reaction rate in terms of C naught right, what is the C naught, what is the concentration?

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Yes, that is what is typically taken. So, the Thiele modulus essentially is the maximum concentration of the initial concentration of the boundary concentration. Now, that obviously, is not a true representation of what is going on in the system, why is that? Because, of boundary concentration is much higher and this concentration inside is much lower, because of diffusion limitation of mass transfer limitation. So, what we want to come up with is an expression for the observed Thiele modulus. So, the actual Thiele modulus is R c or R c naught is square over you know D M C naught, but that is the intrinsic Thiele modulus, the actual Thiele modulus at the observed Thiele modulus is should be based on, not the reaction rate evaluated at the surface, but what, but the?

Intrinsic (( ))

No, no the intrinsic reaction rate is one of that is evaluated the surface.

Maximum actual (( ))

Actual reaction rate which means, but which point you know inside the matrix, the reaction rate varies from point to point right, the actual reaction rate at which point?

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No, the concentration is maximum is the exit, at the surface. So, then there is no point, then the Thiele modulus Thiele modulus is defined and the based on the concentration of the surface, concentration is maximum of the surface, let me draw this and matrix you know I think I do not know, why you are confused. So, this is my concentration at the surface, let us call the C naught. So, my Thiele modulus is defined on sorry reaction is defined on this intrinsic reaction rate is defined based on that, and my phi square is defined based on this reaction rate. What I am trying to say is that, this is not the correct representation of the Thiele modulus, the if I want to call my observed Thiele modulus as this, then this should be a square C naught over D M is fine, then something else over here reaction rate evaluated somewhere else, where where is it evaluated (No Audio from 6:16 to 6:26), where should this be evaluated? Because it it varies from point to point right, see let us understand two things that, the surface reaction rate is not a true representation.

So, that is the maximum reaction rate possible, because the concentration is maximum there and the concentration inside the matrix is varies from point to point, then varies from point to point, because of mass transfer limitation. Now, which point, this also very straightforward answer and should come up with as really groggy, I mean you know at which point should should this concentration, we measured that? They varies from point to point, you agreed with that or not, then which point should be measured it right.

It should be in average.

It should average yes it is whether a volume average typically evolving average. So, this is what we have the R c the average of that. So, you take at different points and then take the average of this, as simple as that. So, how can I write this, now I have, once I have gotten this.

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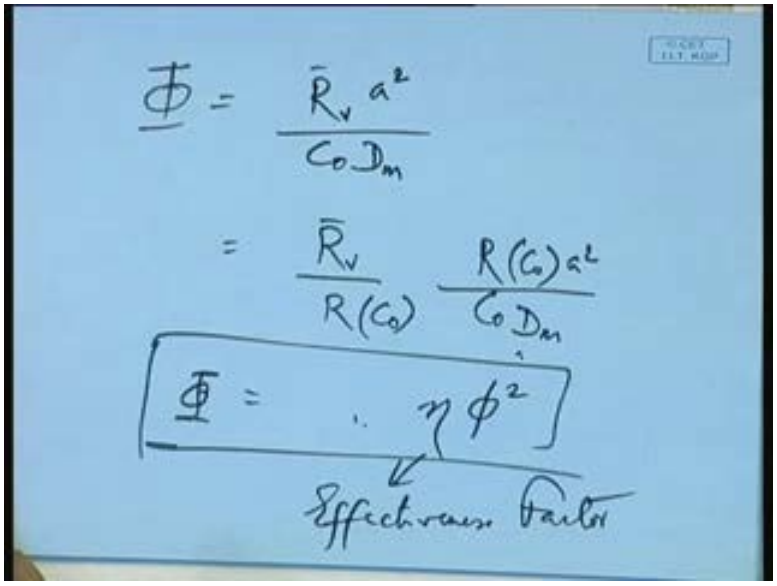

So, this calls this R v, I am not putting the c in there fine. So, this I can write now as right, so this is my phi square what is this, what is the R v?

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Yeah, effectiveness factors.

So, my observed Thiele modulus is actual Thiele modulus or intrinsic Thiele modulus, times the effectiveness factor. So, this is what we have on the screen as well, just the same thing what I showed you. So, this is done here, if you see what I did was for the general reaction and what I shown here is for first order reaction. So, just R v c naught is represented by k v time c naught, and this is what you have, I think I think there is a, this k v cancels out this, there is a do not worry about this on the screen, I think there is a mistake there, it should be should not k v actually, because k v is in the denominator anyway yeah. So, this is correct that, observed reaction rate over interface diffusion rate.

So, observed Thiele modulus is the effectiveness factor, times the actual reaction, the intrinsic reaction rate, which is the observed reaction rate. So, effectiveness factor times intrinsic reaction rate is an observed c reaction rate. So, the observed the Thiele modulus is observed reaction rate over interface diffusion. So, this expression is correct over here, and there is a problem with k v over here, so this is, these are not correct. So, this expression is correct if you want to write that, but what we wrote is essentially write

before on the paper. So, now we come to this concept of the generalized expression for eta, which is something that I mentioned to you in the class or the class before, that is that you can come up with different expression for eta for each of the geometry, but those are hard to remember. So, what we want is a generalized expression of eta which you want to remember and the generalized expression in that, the phi that is there, the Thiele modulus of phi square that is there, it is defined in terms of the length scale of the system and this is known as what is this phenomenon known as? I used a word last time.

Shape normalization.

Shape normalization right. So, for different different shapes you can come up with the same same expression and as I said before, what I did say, that expression that we are going to use is not going to be completely accurate for all shapes, but it is very going to be very close to accurate. So, there is going to be 5, 10 percent error may be, but even with 5 to 10 percent error you pretty close. So, because you can in shape normalization you cannot have 100 percent accuracy. So, the expression that, we are going to use is this, eta equals tan hyperbolic phi over phi and does does it ring a bell? Yes, it does, because this is what we had obtained in the first calculation right when we did the slab yeah. So, transfer you know in a in a mass transfer in a reaction in a slab. So, what is the difference that is going to be here? The difference is that, phi that we are going to have is going to be defined not necessarily in terms of the length, but in terms of length scale, that are related to other geometry. So, what are those? So, phi square is defined as this set this is the first order reaction and if it is not a first order reaction, how do you redefine your phi square, this were first order reaction and if it is not, then what you do? I just did it few 10, 5 minutes back.

R v L c square over c naught R at c evaluated at c naught L square divided by c naught d effective right. So, now this L that, you have over here phi square. So, why I am trying to tell you this, why I am trying to define that is, because it is not that all reactions of first order right. So, and you should be able to define the Thiele modulus for reaction which are not first order right. So, for reaction which is not first order, for Thiele modulus is defined just away, I wrote on paper few minutes back, R c naught R of c naught times L square divided by D effective c naught right and this is L that is here is half the width for rectangular geometry. So, if your width, say 2 b or something then you L is b, half the width, it is have the radius for a cylinder and one third the radius for a sphere. So, this is

something that you need to remember, I do not expect to you remember all the formulas, but this is the important formula that you need to remember eta is tan hyperbolic, phi over phi, phi square is R c naught L square over D effective c naught or equals k v L square over the D effective for first order reaction L is w over two for rectangular geometry, half of the width, half the radius for cylinder and one third the radius for sphere, so this is something I want you to remember.

Now, what we will do is, we will in you know we have looked at different cases before and what I am going to do with the use of this observed you know general form, general shape normalized formula and the previous formula, this going to look at limiting cases, how do how do limiting cases help us, because it help us help us calculate the asymptotes of the system.

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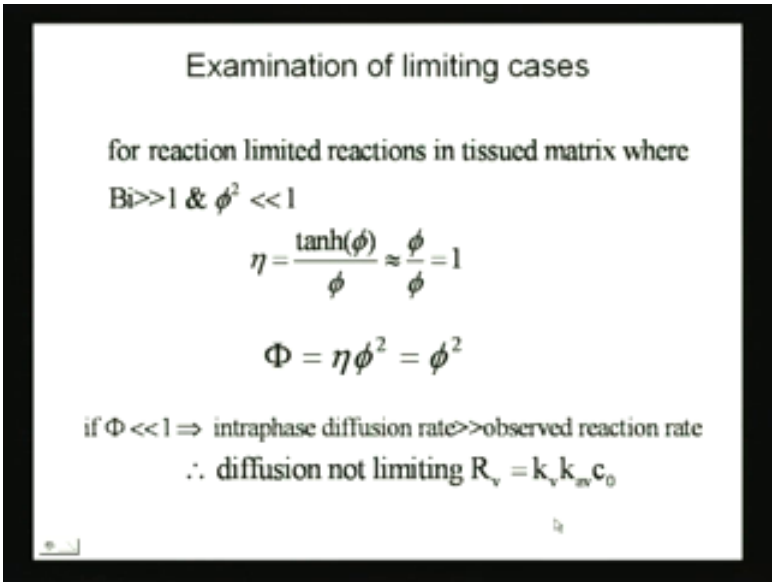

So, first case that we are going to look at is, where the biot number is much much greater than 1 and phi square is much much lesser than 1 or in other words, the system is completely reaction limited. So, for reaction limited, what do you need, you need phi square is much much lesser than 1 or in other words in other words, why the why the two conditions necessary, phi square is much much lesser than 1, 1 means that, the reaction time scale v is much much greater than the interface diffusion time scale using phi square small much much smaller than 1? Why you need the other condition? (No Audio from

14:18 to 14:30), Why you need the second condition? (No Audio from 14:31 to 14:40) And a second condition involve biot number right, what what is Biot number?

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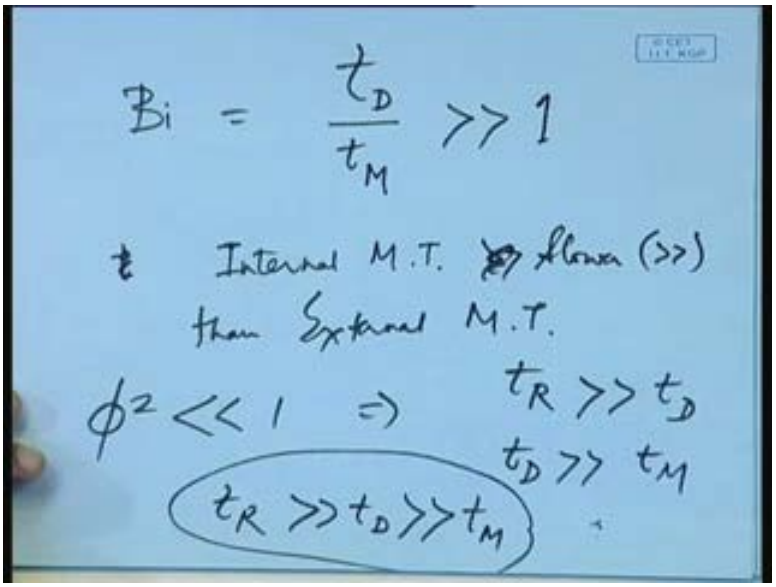

Bio number is

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t

(( ))

Interface over

(( )) which is the surface limit (( ))

Yeah

(( ))

T d over

T (( ))

T

M

M maximum, yeah. So, this is much much greater than which means at the, what is it mean?

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Now, you should be able to tell.

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Slow huh

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Slower, yeah internal mass transfer is much much slower much much slower right. Now, can you make a sense of what what I am trying say here? So, phi square much much smaller than 1, means that t R is much much greater than t D right and fine you see, what I am saying here, you seen now, so what you get, is that clear? So, why why we need this, now is that making sense? You have three times scale, then in order to define a system as completely reaction limited, you have to show that the reaction time scale is a smallest of all three, it is not enough to show that, the phi square that you have over here.

For example, it is much much smaller than 1, means this and this implies the t D is much much greater than t M. So, it is not enough to say that, the reaction is much much slower than diffusion, internal diffusion; you have to also show that, reaction is also much much slower than external diffusion, so which means that, the reaction has to be the rate limiting step. So, this is something that you need to understand that, when we have two processes in the system, it was enough to show that one of the processes is slower than the other, in order to call it a reaction limited or mass transfer limited. When you have three processes in the system, in order to call the call the system completely limited by one of the process, you have to show that, the process is smallest of all three, is that clear?

So, that is why you need two criteria, one is biot number much much greater than 1, another one phi square much much smaller than 1, fine. So, once we have said done that, now we can make the approximation. So, if it eta is tan hyperbolic phi over phi, now phi if phi is much much small, if phi square is smaller than 1, then phi square phi is even smaller than 1, and phi over. So, tan hyperbolic phi goes to phi fine. So, then you have

eta of 1. So, eta of 1, what is what is it mean that, the concentration eta almost going to close to 1 means, since concentration, since there is no mass transfer limitation are hardly in mass transfer limitation, both internal and external the concentration inside the matrix is more or less close to the surface concentration is the what I means right. So, which means is the reaction is more or less taking place at the, close to the surface concentration fine. So, then the Thiele modulus, observed Thiele modulus equals say intrinsic Thiele modulus, because observed Thiele modulus eta times intrinsic Thiele modulus. So, as a result, observed Thiele modulus is same as the intrinsic modulus right.

So, if my observed is, so if my intrinsic Thiele modulus is very small, small much much smaller than 1, then my observed Thiele modulus is also much much smaller than 1, because we just showed that they are equal. Now, this mean that inter phase diffusion is now, so what does the phi square much much smaller than 1 means, that inter phase diffusion is much much faster than reaction right. So, now this is the case, and inter phase reaction is much much faster than inter phase diffusion sorry is much much faster than reaction, intrinsic reaction. Now, if big phi equals small phi square, then it means that inter phase diffusion is much much faster than observed reaction as well, is that clear? Should not be any confusion, because eta is the ratio of observed reaction to intrinsic reaction.

Now, eta means once eta equals 1 means, that of observed reaction is equal to intrinsic reaction. Now, if the phi square much much lesser than 1 means, inter phase diffusion is much faster than observed intrinsic reaction, it also it is also much faster than observed reaction fine. So, this is one of the limiting case we did, remember this. So, we will get go to the next case, so diffusion is not limiting, this very straightforward.

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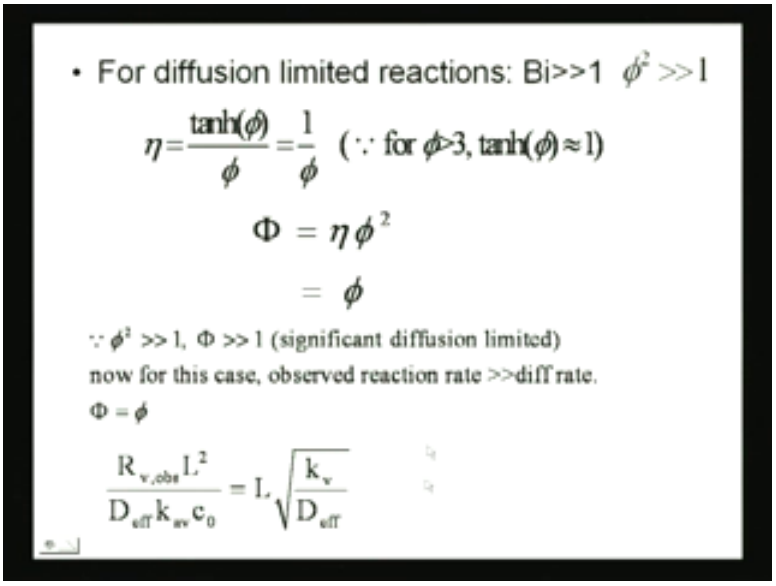

So, the second case that we look at is the other limit, not a complete limit, but you know to some sort. So, biot number much much greater than 1, and phi square much much greater than and so on. So, you have to do tell me very quickly, so I already gave you the definitions of both, you have to tell me, in this case, which one is the limiting one, it is already written. But you have to show that, which one is the limiting, which after the three processes, t D, t M and t R, which one is the limiting one.

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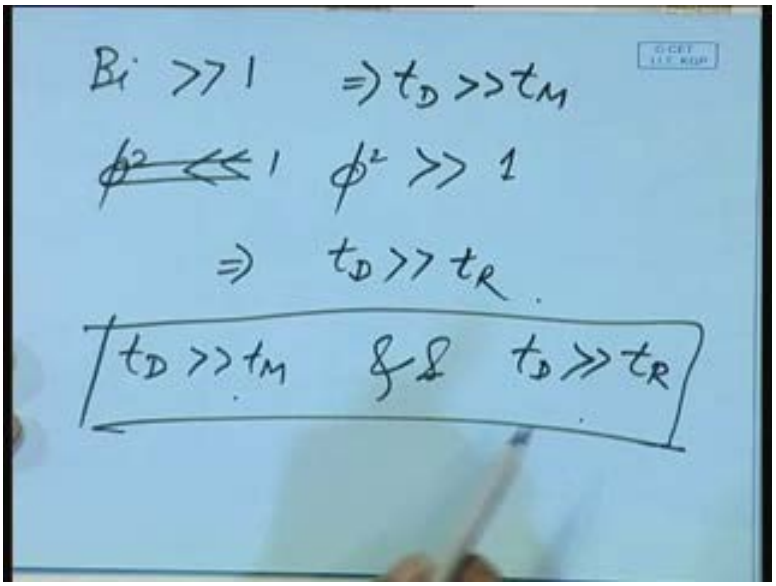

So, here biot number is much much greater than 1 which means, t D is much much greater than t M right and phi square is much much less than sorry phi square is much much greater than one phi square is much much greater than one which means that t D is much much greater than t r. So, which means t D is much much greater than t m and and t D is much much greater than t R now I cannot write the kind of inequality I wrote before because I do not know really relationship here between t M and t R, but one thing I know is that, t D is the slowest of all is the smallest.

So, it is not limited by internal diffusion, so it is always like this. So, whenever a relationship is given or some inequalities have given between these two numbers, you have to use these two numbers very quickly to figure out which is the largest time scale or in other words, which is the rate limiting step. So, if that is the case, now for a (( )) pretty straightforward again, the phi square is much much greater than 1 and we presume that, it is much much greater than 1, we presume that phi square is greater than 9, say if phi square is greater than 9 or in other words, phi is greater than 3, then tan hyperbolic phi equals 1.

So, tan hyperbolic phi is 1, for all phi is larger than 3 fine. So, you can go on, put that over here and what you find this, eta goes 1 over phi, eta is inversely proportional to the square root of the intrinsic Thiele modulus, phi is remember, the square root of the intrinsic Thiele modulus. So, how do you obtain the observed Thiele modulus now, you simply multiply this by, multiply the intrinsic 1 by eta. So, observed Thiele modulus is eta times phi square, now eta itself is 1 over phi. So, this turns turns out to be phi right, eta itself is 1 over phi. So, (( )) this this comes out to be phi.

Now, what we find from from this is that, phi square much much greater than 1 and this implies that, big phi also that is if intrinsic Thiele modulus much much greater than 1, then the observed Thiele modulus is also much much greater than 1 right, because though it is not as high in terms of the, I mean it is not as high as phi phi is, because it not equal to phi square, but it goes square square root of the Thiele modulus. So, with the square Thiele modulus is 100, then the observed Thiele modulus is 10, why do you think so? Can you can you explain physically that, last time what we had that, the observed Thiele modulus equals intrinsic Thiele modulus, but this time we do not have that, we have that it is not equal to, but it goes the square root of the intrinsic Thiele modulus. So, can you explain that, physically? Why does it not go as the directly, is not directly

proportional, but it is goes square root of that, because of internal diffusion limitations. So, because of diffusion limitations, the concentration gradient is not uniform inside right, even if it smaller than or, than the external 1, it is not uniform inside. So, as a result the observed Thiele modulus is smaller than the intrinsic Thiele modulus is smaller than the intrinsic Thiele modulus it s large, even intrinsic Thiele modulus is large again is this is large, but because there are diffusion limitations present in the system, what is it mean? It means that the, if phi square is much much smaller than larger than 1, it means that reaction is very fast in system right.

So, reaction is very fast, as a result the concentration is not going to be very high, if the concentration is not going to be very high inside, if the reaction is very fast. But still what this means is that, if there are internal limitations diffusion limitations present in the system, then this going to be concentration profile, is not going to uniform, is not going to be very high, but even without the small number, you can have profile, you see what I am saying. So, that is that is what I trying to say, it is not a uniform number, it is it is there is going to be a profile, but it is going to be a small number, because concentration is reaction is very fast, so this is what we get.

And so, what we can do is, if we want to measure experimentally the last thing you see on the page here where the pointer is. So, if you want to measure experimentally, what is the observed reaction rate is, because this is something why do you want to measure, then this how you do it. So, observed reaction rate, so what you do is, you put this side, the left hand side, you just substitute the observed Thiele modulus; the right hand side you substitute the square root of the intrinsic Thiele modulus.

And based on that, so L cancels out over here one of the L's. So, you get the observed observed reaction rate equals square root of k v over D effective, one D effective cancels out here sorry. So, square root of k v time D effective times k v C naught over l. So, this is my observed reaction rate, because why why do I am, why do you want to measure, because see intrinsic reaction rate is easy to measure, how? Because, if you simply measure the rate constant which is easily available, you can measure the intrinsic reaction rate, if its first order reaction, it is just proportional to that times the C naught.

But observed reaction rate is very hard to measure, why is that? Because, you took take a pallet or something or immobilized enzyme and at each point, you have to inside the

matrix it to go and measure the concentration, then into multiply by the rate constant and then you have to average it out over the volume, which is a very hard thing to do. So, that is not the best way to measure. So, even we are trying to figure out, what could be the other ways of measuring the observed reaction rate and this is one of the ways that we find over here is that, you can measure the intrinsic reaction rate, D effective diffusion coefficient length of the matrix and the concentration and we find the formula to, without measuring the observed reaction rate, actually we find the formula to be able to evaluated, so this is (( ))

So, we do not measure the observed reaction rate. So, earlier what was going to trying to doing, they are trying to solve the whole problem and everything and obtain the concentration profile and and, so experimentally is very hard to measure. So, there are two ways, one is to actually solve for the concentration profile in the system theoretically and use that to measure my observed reaction rate right, because observed reaction rate is the integral of the rate constant time is the concentration over the domain, so that is one procedure.

The second one is, to be able to measure it in terms of other parameter, which is what we are trying to do, but remember that is something you can do only in limiting cases. In limiting cases, where one of the three processes, internal diffusion, external diffusion, external mass transfer, internal mass transfer and reaction, one of the three processes is very very slow as compared to the other two; only in those limiting cases, can we do it. So, this is what we get, so the observed reaction rate is what we said just now, k v time D effective square root of time that times k a v times C naught over L fine.

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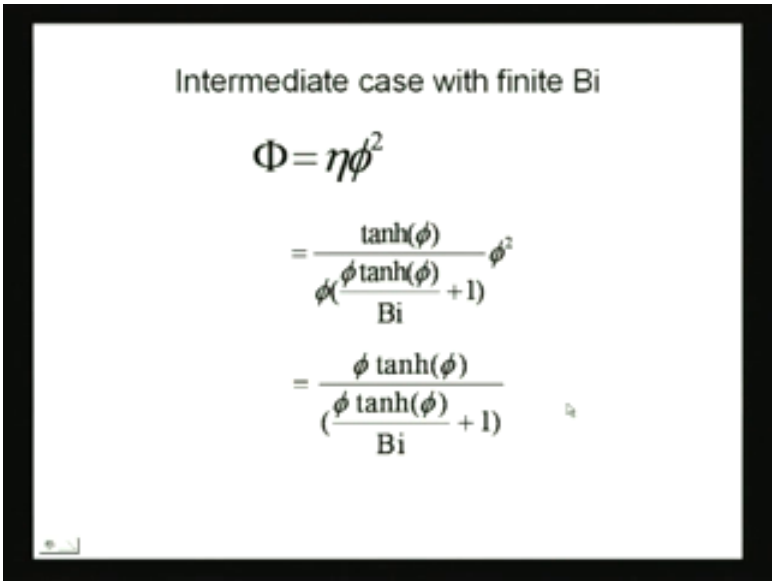

So, let us do the last case, I think this is the one which is the case with finite biot number. So, we did the case of very large biot numbers, but what happens in the case of finite biot number, it formula that we used before was, where there was no external mass transfer limitations right. You remember, let us go back this one that we used over here, why did we use it? Because, it it there is no external limitation, because all these cases that we considered before, the Biot number was much much greater than 1 which means, there is no external limitation. Now, if there are external limitations, we derived let us see yeah here. So, this is the expression we derived right this is, so if if you look at this expression, what happens in the in the limit of biot number going to infinity, this goes to tan hyperbolic phi over phi. So, this is the expression, general expression. So, in this expression is a limit of biot number going to infinity or very large, this goes tan hyperbolic phi over phi, which is what we used over here for the last calculation, because we looked at the two limiting cases; in both limiting cases, biot number was much larger than 1.

So, now we look at the intermediate case. So, the biot number is not very large, it is not going to infinity which means that, we have to use the whole expression, it can tan hyperbolic phi over phi, it has to be tan hyperbolic phi over phi multiplied by this factor over here, so 1 over phi tan hyperbolic phi over biot number plus 1. So, I suggest you right, this expression for eta, you have it before also, but just for the sake of remembering, you write this. So, phi square cancels out in numerator and denominator

one of them. So, you get phi time hyperbolic phi divided by phi time hyperbolic phi over biot number plus 1, then we what we are going to do is, we are going to do some special cases on phi. So, biot number is finite over here, but we can take limits on phi. So, what did we do last time, last time we assumed biot number to be infinite and then took two limits of phi, phi much much smaller than 1, much much greater than 1, here we will assume biot number to be finite and then, we can take limits on phi fine.

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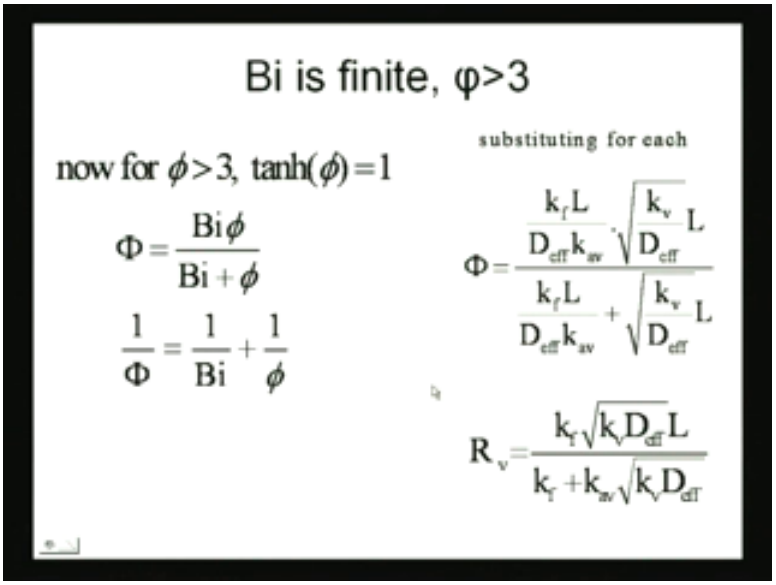

So, the first limit we take again is phi greater than, much much greater than 1, it does not even have to be much much greater than 1, as we showed last time is just if it is phi square is greater than 10 or something, then we can assume this tan hyperbolic phi over phi and there is lot of simplification that is possible, so biot number. So, observed Thiele modulus is biot number times phi divided by biot number plus phi. So, what do you find over here, if you take the observed Thiele modulus, 1 over phi would be, 1 over phi is one over biot number plus 1 over intrinsic phi 1 over big phi would be 1 over biot number plus 1 over intrinsic phi, what is it suggest, physically what is it suggest, and we have done something like this, not exactly the same, but something like this before.

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Which two resistances?

(( )) both mass transfer

Two mass transfer resistances are in series, but look at this carefully, there are not exactly in series, this is not the summation of the linear sum, this is the mass, you can signifies this is the mass transfer resistance, then it become, this one looks like the diffusion resistance, but square root of that, because actual diffusion resistance would be given by 1 over phi square, it is it is a summation of the resistances, but not as linear sum of the resistances, one is linear then the other one is goes square root of it, this is what you need to remember. So, this for finite biot number with phi square much greater than, I mean basically 10 would work out, phi square 10 would work.

So, next our our aim always is you know, what we are trying to do is, trying to find out what my observed Thiele modulus or in other words, what my observed reaction rate is based on other quantities, because I do not you know I want to be a little you know, I am lazy. So, I do not want to be measuring the actual reaction rates. So, what I do, is very straightforward simply in this formula I go and put all my D effective, d in biot number and the intrinsic Thiele modulus, expressions for them, in terms of the effective diffusion coefficient and the mass transfer coefficient k f L, the length, k average and you know which is the partition coefficient and everything and this is a formula that I get recheck and use.

So, this is this is one limit, that we are looking at and to go a little quick today, because you know finish this little bit fine. So, now you are R v that is your reaction rate, observed reaction rate, you can measure in terms of this and this is expression that you get. So, if you want you can write it down, so this is proportional to the k f is mass transfer coefficient, k v the partition coefficient, D effective diffusion and length. So, we did then, so first we did the biot number much much greater than 1. Next, we did biot number finite and the last thing we will do in the limiting cases is biot number small, what happens in the limit that, the biot number is very smaller or other words, it is limited by the external mass transfer.

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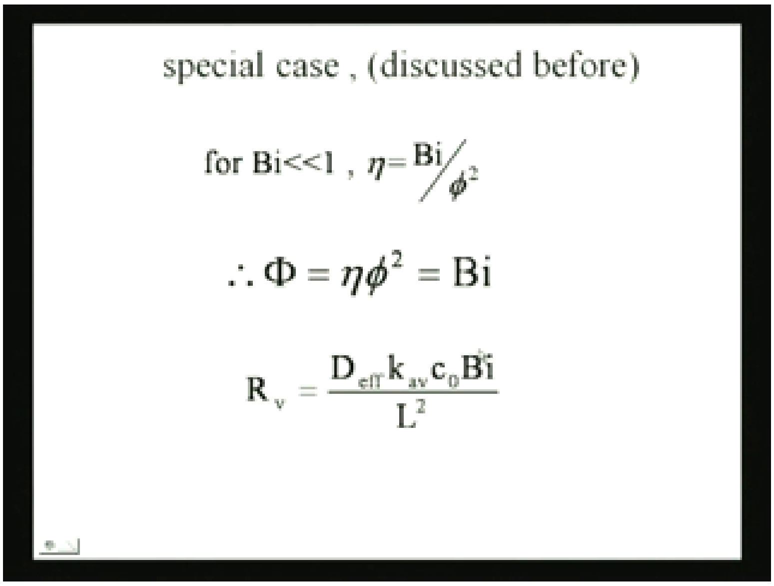

So, if biot number is very small, then eta over here let us go back and look at that formula eta that you that you have over here goes phi square, I think this is very small, then this remains. So, I think biot number over phi square right, this goes to the numerator biot number goes. So, if you take biot number, so we will have, phi tan hyperbolic phi plus biot number and 1 goes to the numerator. So, this one you can neglect, so you will get biot number over phi just yeah I think no yeah no no sorry, this is we are looking at the observed Thiele modulus. So, let us look at the, if you look at only the eta, then you will have biot number over phi phi square right phi square phi square,(()) yeah Bio number over phi square, because right.

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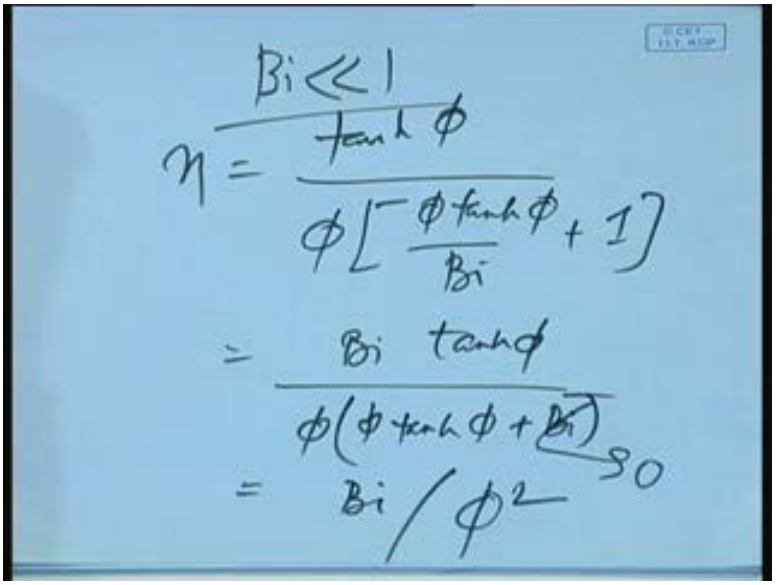

So, you are running out of time, but, so eta equals tan hyperbolic phi over (No Audio from 34:32 to 34:50). So, in the limit of biot number going to very small, this is a term you neglect and you end up with biot number over phi square. So, this is the third limit biot number much much smaller than 1. So, we did first biot number much much greater than 1, then finite and this is the third limit clear.

So, let us go quick, so if that is the case, then big phi that is observed Thiele modulus which is eta times phi square, say simply biot number which means what? Which means that, it s only limited by external mass transfer coefficient, then observed Thiele modulus is independent of reaction, internal reaction and it is only dependent on the external mass transfer.

So, the R v that we trying to find out over here is, D effective k a v c naught biot number over L is L square and what you find over here, look look at this very interesting that, it depends only on the external mass transfer, why? Because, biot number already has D effective which will get cancel with this D effective and we only, we are left with external mass transfer coefficient, is that clear? right. So, because biot numbers itself has D effective in it, so 1 over D effective or something like that, which will get cancel, then L square will get cancel. So, what it means is that, the observed reaction rate, what you observed, is dependent only on the external mass transfer.

So, whatever is the, it rate of external mass transfer is the rate of external, these are rate of reaction. So, if you have 3, 4, 5 or n number of processes in series right in series, that is the most important thing. If you have n number of processes in series and if one of them, one of these process is limiting, then the rate of the overall process equals to the rate limiting process right something you know. So, this exactly what we have over here. So, biot biot number very very small means, the external mass transfer is limiting and because the external and internal mass transfer are internal mass transfer reaction are parallel, but internal external mass transfer is in series with these things.

So, if external mass transfer is limiting and is the is the slowest step, then the overall rate of reaction equals to the rate of external mass transfer right, this is things that we can derive intuitively we can come out with intuitively, but these are very concrete ways of coming showing this.

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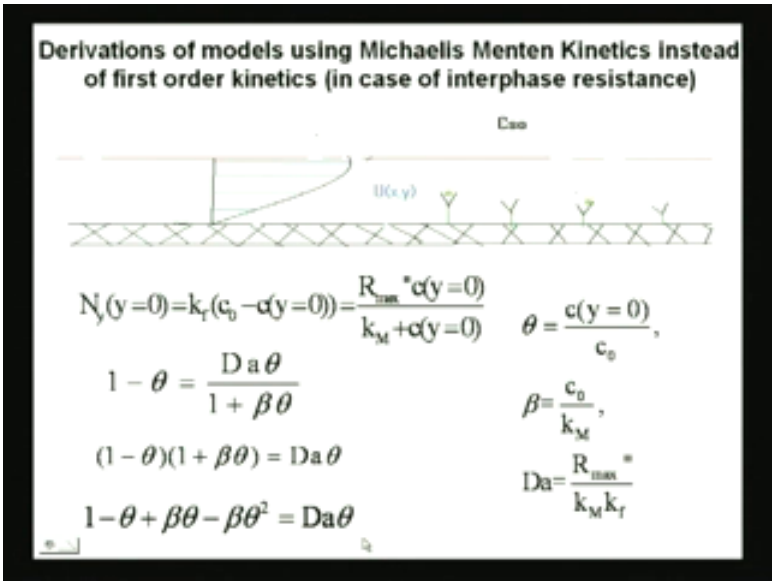

So, in the next two minutes, we have what we will do is, we will show the derivation of the model using Michaelis-Menten kinetics instead of first order. So, what had been we have been doing till now is that mostly using first order kinetics.

So, as I said what are what is our objective? Our objective is to actually predict what happens in a Michaelis-Menten kinetics, because that what is important you know in immobilized enzyme, but we have no way of predicting that, the reason being that, these non-linear equations and we can solve them. So, what we do is, we predict the two

asymptotes of the zeroth order and the first order, we had not done zeroth order in many cases, because it is much easier to solve and what we find in zeroth order is that, we did some cases what we found that the effective mass sorry effectiveness factor equals?

1.

1 for zeroth order the reason being that, there is plenty you know the zeroth order itself means that is the plenty of substrate inside. So, we look tomorrow at the first order and also with some case of the zeroth order and we know that actual case is is kind of bounded by these two. So, what we do is, there one single case which we can actually solve analytically using Michaelis-Menten kinetics. So, just as an one example, the last example of this chapter, we will solve this case using Michaelis-Menten kinetics and this is the case where you have the external, you have the surface reaction taking place.

So, this is this is that old example, if you remember that, we had with we have them (( )) enzyme over here, we have the matrix over here and then enzyme is immobilized on it, this using receptors which are covalently attached to the surface and the substrate is coming in and reacting over here. So, this is the only case where we can use Michaelis-Menten kinetics and still get analytical solution. If you remember, there were two approaches to this, what was those two approaches, we did this, the two approaches we have we have taken to this; one is the boundary layer approach using the diffusion reaction equation, and the other one was the mass transfer coefficient approach, we did like three, four classes back, three classes back I think.

So, the diffusion reaction equation, boundary layer convection, diffusion reaction equation using boundary layer theory is not something you can solve analytically for a non-linear reaction, it is not even something that you can solve analytically for a linear reaction, let alone and non-linear one. So, obviously that is ruled out, if you want to get an analytical solution. So, the one that we are left with, is mass transfer coefficient, use the mass the coefficient, so let us do that.

So, this is if you remember that this was our, so you know this this was our boundary condition, Liza just tell me if you have any problem with this? That, this was a boundary condition that, at any at y equal 0 at this point, the flux that N y at y equal 0 was k f, that is mass transfer coefficient times c naught, minus c naught is boundary is outside the boundary layer, the concentration outside the boundary, C s o is given in the picture, here

I just refer to it as c naught, but same thing, so c c naught minus the concentration at y y equals 0 at the surface right, so that is the amount of material that is coming in. Now, what was the reaction previously? The previously, the reaction we looked the first order reaction which means that it was some k v times c or k times c k as time c, now we are looking at Michaelis-Menten kinetics which is non-linear. So, before we actually go on solve this, try and solve what we do is, make the system dimensionless and it is important, this is really important in this case, it is not out of fancy that we do it. So, how we make it dimensionless, you have to do slightly careful here.

So, theta is a new dimensionless concentration, which is the concentration at the surface divided by the concentration outside the boundary layer c y at c at y equals 0 divided by c outside the boundary layer c naught, beta is a new a new variable that you define which is c naught over k M, this is again you know dimensionless variable c naught over k M, and Damkohler number over here and you have to be careful with this, is defined as a R max the double prime here signifies, this is surface reaction, typically it is nothing to do with derivatives typically R is R is used or R double prime is use for surface reactions and R v or R triple prime is use for volumetric reactions, so again nothing to do with derivatives over here.

So, Damkohler number over here is given as R max double prime over k M times k f, k M the being the Michaelis constant and k f being the mass transfer coefficient over here. So, this is something new, we have not defined Damkohler number in this way previously, why because, we did not have non-linear reaction we never handle the non-linear reaction before. So, this is the first time we handle a non-linear reaction (( )) we come up these sets of variables and you will see that, how these variables, why you might want to ask me that, why do you, how do you come up with this variables at this point of times theta is very straightforward, but these two variables are not the straightforward, the dimensionless variables and why do I come up with that, once I recast the equation in dimensionless form, you start to see that why I do that. So, now see, so what I have done, I have k f. So, this only, this part of the equation that that is there, this this this part over here, so this is the one that I will, I make dimensionless.

So, k f c naught minus c equals R max c over k M plus c. So, k f if you take to this side in the on the right hand side, then you get R max over k k f right remember R max over k f is this side here. So, this side gives you, so divide the equation both sides of the

equation by c naught. So, this will give you 1 minus theta right, so this will R max. So, divide both sides again by k f k M. So, you will get Damkohler number over here on the denominator times theta, this k M goes from the denominator, because you you divided that plus beta times theta, so beta, because beta comes, because of c naught and c naught and k M, because you divided the both sides by k M and theta comes, because of c over c naught. So, c over c naught is that fine or you do not want me to go through the step fine right.

So, now it is pretty straightforward for me, what I am going to do this is a quadratic equation and I am going to solve it directly. So, why have to put to the equation you know that form and quickly get the solution. So, this is the quadratic form that we have 1 minus eta plus 1 minus beta theta equals Damkohler numbers time theta and then you will get once you open the bracket, you will get 1 minus theta plus beta theta minus beta theta square equals D a theta, if you collect the coefficients.

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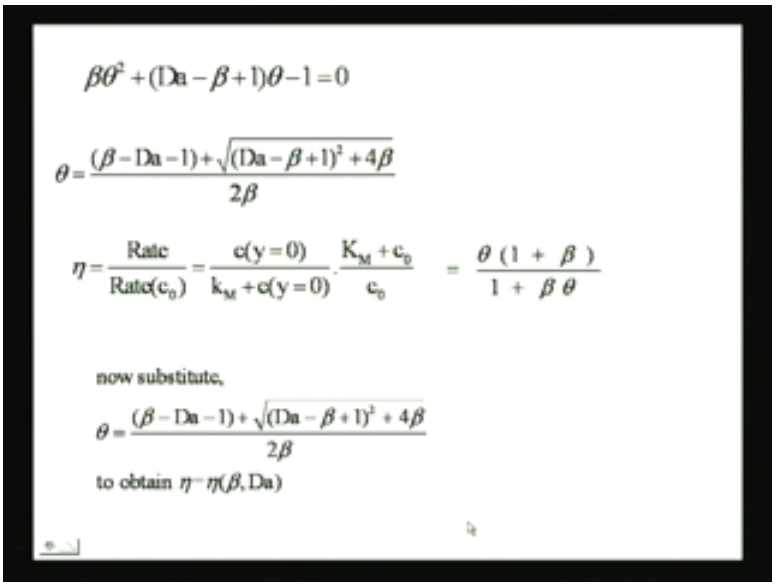

So, then you will get the final form of the quadratic is beta theta square plus D a minus beta plus 1 time theta minus 1 (No Audio from 44:26 to 44:36) fine. So, then once you solve this, this is your this is your expression for theta, beta minus D a minus 1 plus D a minus beta plus 1 square plus 4 beta square root of that by 2 beta, the reason you neglect the other root is, because it is not feasible, it is not in the physical ranging fine.

So, then what you are suppose to do is, find the rate, the eta, the effectiveness factor again. So, the eta is here if you remember the way we defined it before is that, eta at the surface concentration divided by eta had it been at the concentration outside the boundary layer right. So, eta at c s or c at y equals 0 sorry rates at c c s or c at y equals 0, divided by rate at c equals c naught fine. So, slightly different from before, because of the non-linear nature, you get c y c at y equals 0 divided by k M plus c at y equal 0 times k M plus c naught over c naught right, no problem. So, now we can express these in terms of beta, remember right, because beta was defined as k M over c naught if you remember.

(( ))

C yeah c naught by k M yeah c naught by k M. So, this is what we do, you can divide the whole thing by c naught by k M. So, theta times 1 plus beta over 1 plus beta theta fine. So, now once we substitute this, you can get your expression for eta, if you already got your theta, you can substitute that that back over there and you can get your expression for eta. So, which is again pretty non-linear expression, because that is what is expected (No Audio from 46:24 to 46:32), fine.

So, the last thing we will do today is, you written this down? Ok. So, the last thing we will do today is, try and plot this.

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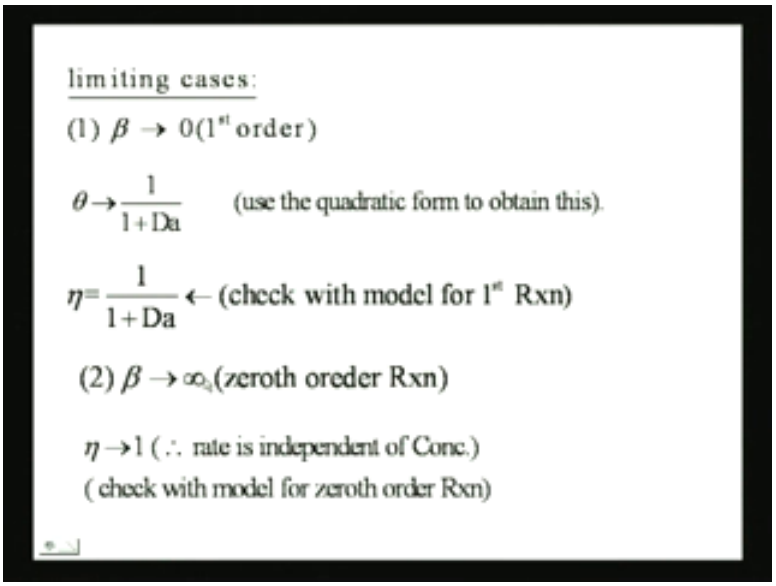

So, oh before that, I think we have to do some quick limiting cases. So, the limiting cases are things that you know, that beta going to 0, it is a first order reaction beta going to what value it is a zeroth order reaction?

(( )) one

No not one what?

Infinity.

Infinity right. So, beta going to infinity is the zeroth order reaction though, so if you if you look over here. So, beta going to 0 and you know you can check over here. So, for example, here this was an expression, so beta going to 0, it is first order reaction; beta going to infinity, you had a zeroth order reaction, not beta equal to 0 right, beta equal to 0 is the first order, beta going to be infinity is the zeroth order. So, theta if you put that in the quadratic form and this is something that you just again you know, we do not have a lot of time.

But this is something, this not very straightforward, if you if you want theta going to one over D a this is not very straightforward, this this I think you can get from then you can get from the quadratic form, but is there is another one that you it is not so easy. Let me go through this and then, because we do not have really a lot of time. So, let us go through this quick and then if there is a problem with the calculations, I will come back to it.

So, theta for this case, beta going to 0 that is first order, it goes to 1 over D a 1 over 1 plus D a and the eta, therefore comes out to be 1 over 1 plus D a. So, here for example, if you go and put that, so beta beta equals 0 you have put in. So, this is simply equals to theta right eta is simply equals to theta. So, your theta goes to 1 over D a, how do you 1 over 1 plus D a, you can put it in the quadratic form and get this and eta will be 1 over 1 plus 1 over 1 plus D a again, because it is equal to theta. The other case is, beta going to infinity, the zeroth order reaction, now this is the this is, there is a little problem in getting this solution. For example, this is a quadratic form right, now with with beta going to 0, for example, this is your solution that you get with beta going to 0, you can see what is a problem with beta going to 0, you cannot put this, that is what I said the slight problem over here.

So, you cannot put this directly in to this form right, because beta is in the denominator. So, what you need to do is, you put your beta equals 0 in the quadratic form itself, fine and then you get theta straight away equals 1 over 1 plus D a. So, this is just quick little trick, is that clear Liza? You cannot put it directly in to the quadratic form, because this will blow up if do, so just put it, no, you cannot put it in the solution, put it in the quadratic form and get it.

Similarly, beta going to infinity the, also you have to put it in to the in to the in to the quadratic form and get this and what you will get is eta going to 1, beta going to infinity, eta going to 1 and this is something that, why I am doing this two limiting cases, because these are two limiting cases, I have already solved before, if you remember that, eta going to 0, eta goes to 1 over 1 plus D a, for beta goes to 0, that is the first order case. I did separately and then I did the zeroth order case where I have told you that, eta goes to 1, the reason eta goes to 1 is, because the there is no effect of boundary layer, essentially and the concentration at the surface equals the concentration at the boundary layer.

So, why I am doing is, this whenever you do a non-linear problem, this is usual thing that you do always that, whenever you do a non-linear problem, it is important to check the two limits, two asymptotic limits of the non-linear problem with the two solutions that you know. So, that is what we are doing, we just checking with the two solution that you that you know to make sure that is works a, and b is to figure out that it stays within the limit.

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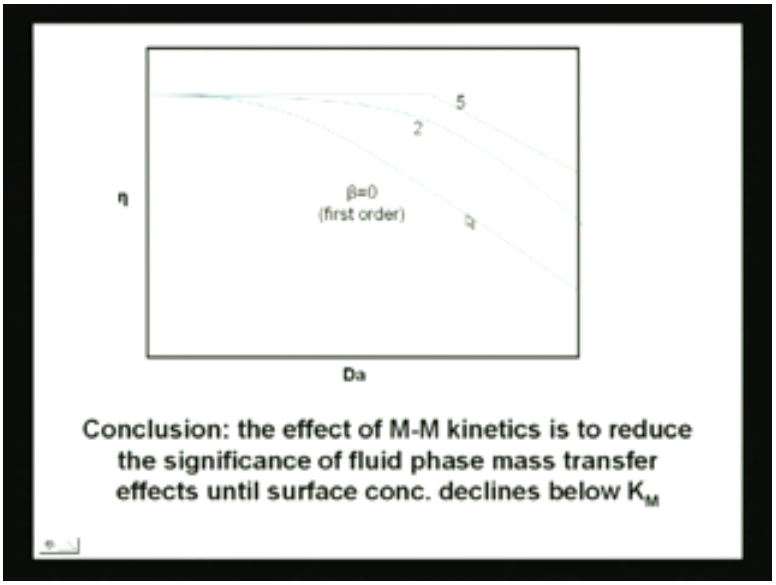

So, the last thing I will show you is the plot of eta versus beta. So, this is the plot for the first order reaction this is the plot for the first order reaction beta going to 0 and this is eta equals 1 you know, I should have written that, but I have not, so please make a note over there. So, this is the line of eta equals 1, the parallel the line parallel to the x axis. So, for eta going to infinity, what to do you have, you have this line extending all over. So, what happens is that, as beta starts to increase or in other words, the system tends away from first order towards zeroth order. So, Michaelis-Menten kinetics means, it is somewhere within the zeroth and the first order right, a fractional order.

So, this is the first order and as soon as beta is a number greater than 0, a positive number it means the order is fractional, as it tends to become fractional, the eta, the effectiveness factor increases. So, which means that Michaelis-Menten kinetics essentially improves the effectiveness of the immobilized enzyme. So, this is the very important in you know thoughts that we want to take away from this whole chapter, because the reason that we are trying to do is that, we have shown you first order, we shown 0 the order, but what is the effect of Michaelis-Menten kinetics?

So, the conclusion that, we have and this is essentially the conclusion of this chapter also, the effective Michaelis-Menten kinetics is to reduce the significance of fluid phase mass transfer effects, until surface concentration declines below K M. So, if the, what do you mean until surface concentration declines below K M, what it means is that, if

reaction is very fast and is being depleted very fast, then at some point of time, there substitute is going to be taken away and the surface concentration is going to decline below the below the value that is given.

So, if it is unless that really happens, unless in the in the Michaelis-Menten constant kinetics, the surface concentration decreases to that kind of value, it always improves, if you look at this graph, this is the first order reaction Michaelis-Menten is always going to improve which means that, it reduces the, so the kinetics itself is such that, the effect of mass transfer is reduced, because of that. So, the mass transfer effect that you have, in the first order reaction is more than the mass transfer effect that you would have in Michaelis-Menten.

So, come to think of it, is not very it is something that is quite intuitive, the reason is quite intuitive is that, the think of this, the mass transfer effect or mass transfer limitation that system would have on zeroth order reaction is less much much less than the first order reaction right. So, when the order goes fractional, it hurts less, again you think of this in this way, the mass transfer effect that a system will on a second order reaction is more than first order reaction right. So, higher is the order of the system, then higher is is the effect that it mass transfer limitation has on the on the system right.

So, lower is the order of the system, lower is the effect of the mass transfer limitation has, and come to think of it Michaelis-Menten is is a complicated kinetics, but the effective order is the fractional order right. So, because it is fractional order that mass transfer has less effect than that, it would have in first order, so this is one of the important. So, we do first, zeroth order, we do first order all through the chapter and, but this is one of the important things that we take home.

So, if is there any quick question on, what we did. So, just to summarize, we did surface reaction, we did with the started with reaction outside, you know we took a sphere on which the matrix, spherical matrix on which the enzyme sorry immobilized from surface and we looked at outside, concentration, variation then we took a system where matrix was immobilized inside, we took a system with a matrix was immobilized on a flat plate on the surface, we took a system where all these three things, two things where coupled, it was on the surface, it was inside, then we looked at different geometry, we looked at the effect of zeroth order, first order and find the effect of Michaelis-Menten.

So, this is in the natural, what we did in the last four, five lectures in this in this chapter. So, tomorrow, we will start a new chapter on microbial growth and so, if there any quick question I will take it right away, then we will stop this and so, we will continue tomorrow with a new chapter, thank you.