# Biomechanical Engineering

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**Module No. # 01**
**Lecture No. # 14**

## Immobilized Enzymes (contd.)

We will to start off from where we left in the last class, which was we are doing the diffusion reaction model if you remember. So, let me go back a little bit and try to show you what we are doing.

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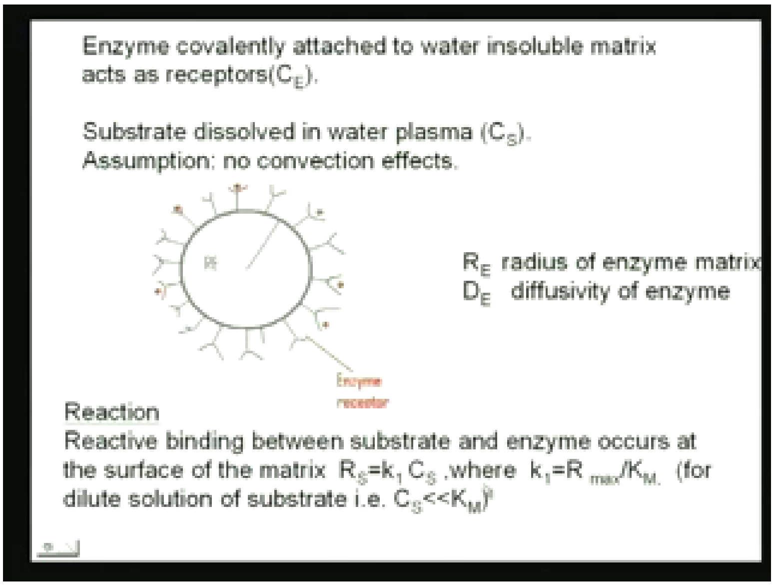

Enzyme covalently attached to water insoluble matrix acts as receptors($C_E$).

Substrate dissolved in water plasma ($C_S$).
Assumption: no convection effects.

$R_E$ radius of enzyme matrix
$D_E$ diffusivity of enzyme

Reaction
Reactive binding between substrate and enzyme occurs at the surface of the matrix $R_S=k_1 C_S$ ,where $k_1=R_{max}/K_M$. (for dilute solution of substrate i.e. $C_S<<K_M$)

So, this was the, this was what we are looking at a matrix, an immobilized matrix which is insoluble in water and on this the enzymes are attached covalently, as receptors and these red dot set here are the enzymes, R E being the radius of the enzyme, matrix D E being the diffusivity of the matrix. So, this is what we are looking at.

Now, what we wanted to do, we wanted to model this system and try and understand how this process of transport and reaction was occurring, so what did we decide? We decided that the diffusion is occurring from anywhere in the solution to the surface of the enzyme and reaction is occurring at the surface of the enzyme right. So, the reaction is the surface reaction essentially, and because enzymes are kind of rooted or kind of you know fixed to to the surface, so their reaction would occur at the surface of the enzyme and the rate of reaction equals the rate of diffusion, mass flux to diffusion at the interface, so it is so simple model.

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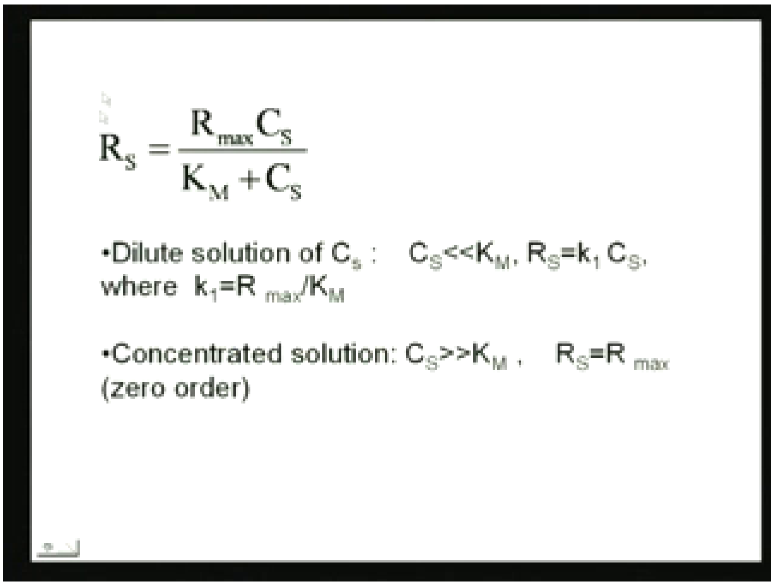

$$R_S = \frac{R_{max} C_S}{K_M + C_S}$$

- Dilute solution of $C_s$ : $C_S << K_M$, $R_S = k_1 C_S$, where $k_1 = R_{max}/K_M$
- Concentrated solution: $C_S >> K_M$ , $R_S = R_{max}$ (zero order)

So, let us go to the, so what we did was you know just some of you were not there, then just to the wrap up, on that and so, summary on that. So, the problem that we face here in these in, when we talk about immobilized enzymes is that, these are diffusion reaction system, so diffusion and reaction or convection and reaction, so some kind of mass transfer and reaction are occurring simultaneously in the each enzyme.

So, it is much harder, when you are trying to actually solve the equations of transport and reaction in these enzymes is much harder, because it is a simultaneous diffusion reaction or convection reaction problem, unlike before in the soluble case, where it is simply the reaction problem. Now, this will essentially lead, so this what we are doing now immobilized enzyme will essentially lead to O D E or P D E to be solved. Now, the problem is that, the reaction kinetics of the enzyme what you see on the screen here, it is a Michaelis Menten kinetic, that the reaction kinetics of the enzyme, now this is inherently non-linear. So, if you want to solve with set of O D E or P D E with non-linear terms, you cannot do it analytically and we cannot do it in the in the, as a part of the course.

So, what we do is, we do what we did one of things that we did before, which was to look at the two extreme ends of the problem, which is the two accent towards it is the problem, which is the very small value of C S where the system is first, call as a of first order of kinetic in a very large value of C S, where the system follows the second zeroth order kinetics.

So, what is the advantage, the advantage is that, the actual order, the real order of the system is a fractional order between 0 and 1, and if we can specify or we can find the two boundaries that the two bounds of the solution, so your real solution is going to be bounded by these two solutions.

So, if we can find out the two bounds of the solution, between the zero order and the first order we are sort of in business. So, that is what we are trying to do, and most of the problems that we are going to solve here, we are going to solve it first using the zeroth order kinetics or first order kinetics and then, using zeroth order kinetics and we understand that, how real kinetics and real solution lies between these two. So, our our actual solution would be bounded by the two solutions that we get over here.

So, that is a strategy that we will follow, now if you want to do these on your own with the real kinetics, what you have to do is, simply go and solve this numerically fine.

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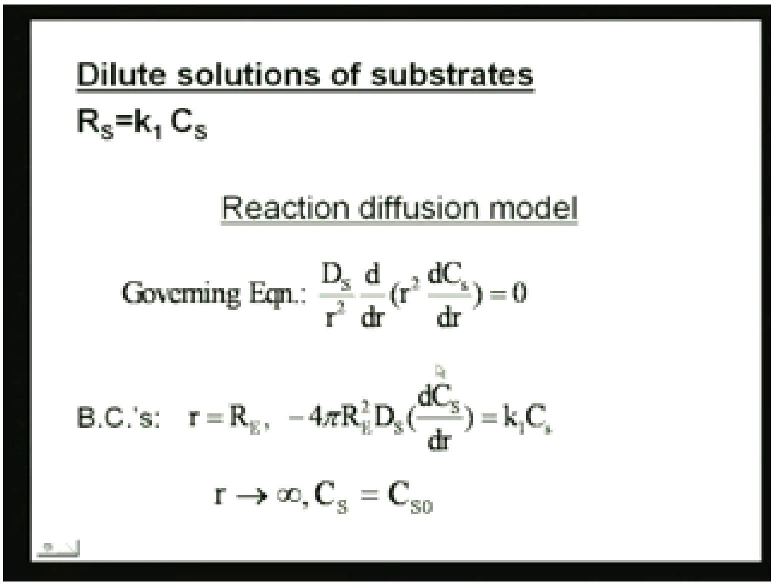

Dilute solutions of substrates

$R_S=k_1 C_S$

Reaction diffusion model

Governing Eqn.: $\frac{D_S}{r^2}\frac{d}{dr}(r^2\frac{dC_s}{dr})=0$

B.C.'s: $r=R_E,\quad -4\pi R_E^2 D_S(\frac{dC_S}{dr})=k_1 C_s$

$r \to \infty, C_S = C_{S0}$

So, the diffusion reaction model is what we looked at, now I went and and talked about the diffusion reaction model in the Cartesian, and the spherical, and the cylindrical coordinates. So, here what we take is, we take a matrix which is cylindrical. So, the diffusion reaction equation is in the cylindrical coordinate to remind you on more time, we are not solving inside the cylindrical, spherical matrix, this is the spherical coordinate I am sorry. So, we are not solving inside the spherical matrix, to remind you one more time, we are solving outside the spherical matrix. Now, then why do we take a spherical coordinate? We can take any coordinate further matter for the two, for the for the sake of the, for what? For the sake of the…

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For the sake of a?

Simplicity

Simplicity of what, with respect to what, why is this spherical coordinate is not simple? You know the Cartesian coordinate is lot simpler than spherical. So, we could have gone for the Cartesian coordinate, but we go for a spherical coordinate, why do we do that?

Simply to solve we should

Yeah but, which point, that what point does it make it simple, which part? It is not easier you know look at the look at the spherical coordinate equation. So, this spherical coordinate equation is not any easier, if I had taken a diffusion times del to C del x square or del (( )) you know 1 over r del del r of r del C del r.

(( ))

No but, if we took.

(( ))

Cartesian be two way, two two coordinates that is that is the one thing that is correct, but you know you can also take just normal to the surface that kind of thing, just one kind of yes, but you are in the right direction, but that is not the point. So, I mentioned this in the last class, it is for the sake of simplicity of the boundary conditions, see the boundary is spherical. So, that is something you have to you have to realize, that the the the sphere is like, the matrix is sphere like this and the reaction is occurring on the boundary on the surface of this sphere, and the surface of this sphere is, you know it is it is a spherical surface right.

So, as a result of which the boundary condition is on the spherical surface. So, if you take, you can take any geometry outside in the in the fluid if you want, but when it comes to the boundary conditions, if you have a spherical boundary condition, a spherical coordinate, it helps with the spherical boundary condition, otherwise you have to transform from a spherical boundary condition to a Cartesian boundary condition which makes life lot more difficult.

So, that is why we take this form, now the boundary conditions as we discussed, one is the flux equals reaction rate, that is, we are, so this is we are doing at the limit of small substrate concentration where the, as the result of which the reaction rate is first order. And the other boundary condition is that, far away from the matrix, far, very far away from the matrix, the concentration is a constant. So, this is where we stop now, we go on and what I want you to do again you know is to put your pen to your paper and try and quickly solve this, integrated first and then put your boundary conditions in there and see what you get.

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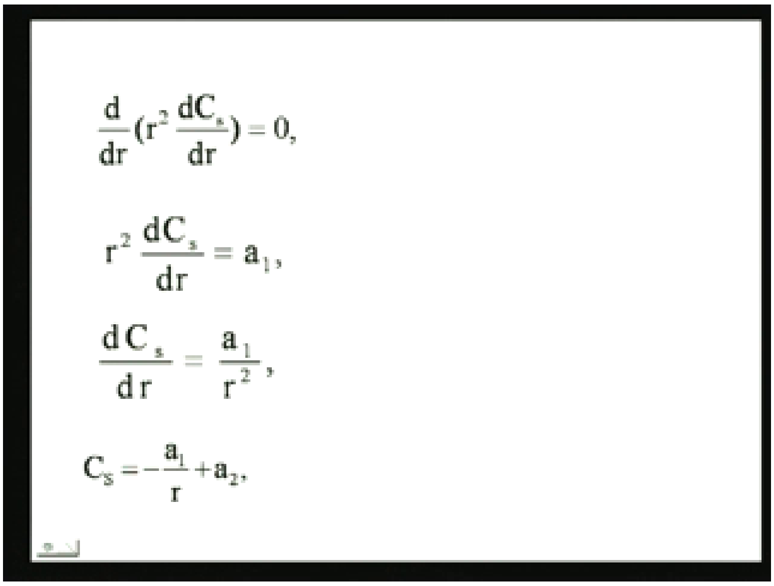

$$\frac{d}{dr}(r^2\frac{dC_s}{dr})=0,$$

$$r^2\frac{dC_s}{dr}=a_1,$$

$$\frac{dC_s}{dr}=\frac{a_1}{r^2},$$

$$C_s=-\frac{a_1}{r}+a_2,$$

So, this is the equation that you need to solve, this integrated very quickly first time. So, if you integrate it first time, you get r square del d C s d r equals constant right (No Audio from 7:22 to 7:32), can you obtain the value of this constant right, this step? No, because you have a, what kind of boundary condition, one is a Dirichlet boundary condition fine, the other one is the?

(( ))

Robin’s boundary condition yeah mixed robin’s boundary condition. So, you cannot, so get this C D R at initially right away, you need to solve the whole thing and which is what we are trying to do (No audio from 07:56 to 08:29).

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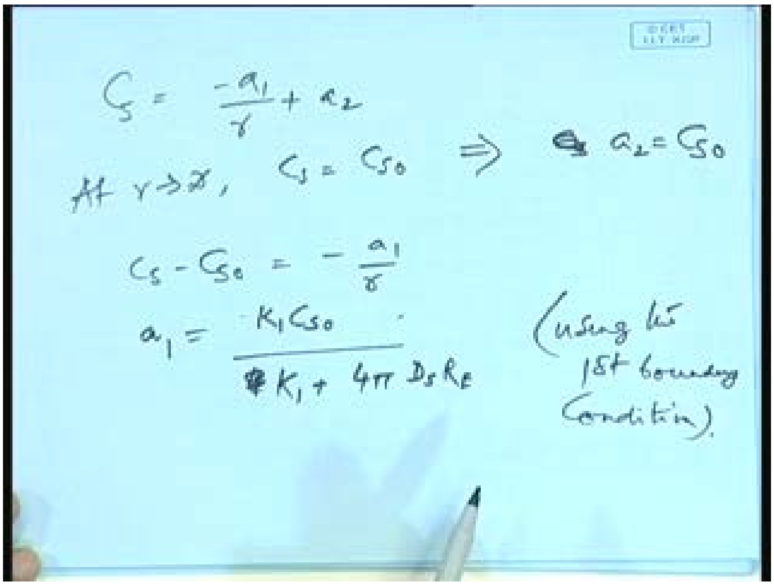

$$C_s = \frac{-a_1}{r} + a_2$$

At $r \to \infty$, $C_s = C_{s0} \Rightarrow a_2 = C_{s0}$

$$C_s - C_{s0} = -\frac{a_1}{r}$$

$$a_1 = \frac{K_1 C_{s0}}{K_1 + 4\pi D_s R_E}$$

(using the 1st boundary condition).

So, C s is something like this, you get. So, C s this is what you get, now use the second boundary condition, r going to infinity C s equals C s naught, which means that, C s means a 2 equals C s naught. So, C s minus C s naught equals minus a r 1, a 1 over r. And so, a 1 equals (No audio from 9:16 to 9:43), you get that, after using the first boundary, use the second boundary condition, get your C s minus C s naught as this, and then you plug this back into the first boundary condition.

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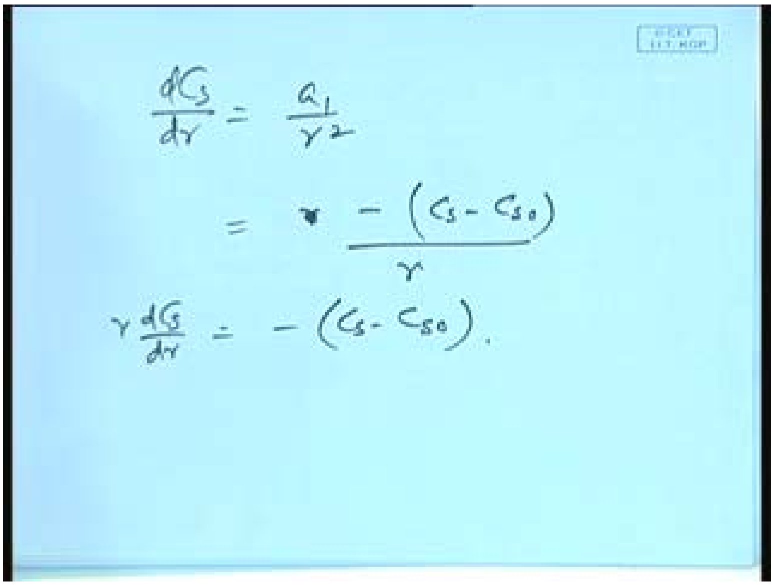

$$\frac{dC_s}{dr} = \frac{a_1}{r^2}$$

$$= \frac{-(C_s - C_{s0})}{r}$$

$$r\frac{dC_s}{dr} = -(C_s - C_{s0}).$$

So, you you forgot then, your del, d C s del r equals a 1 over r r square sorry fine. So, then you can put this back from here, which is that, a 1 equals minus C s minus C s naught over r right. So, r fine then you can just use this boundary condition at r equals R E fine. So, let us go to the screen and I have the solution for you.

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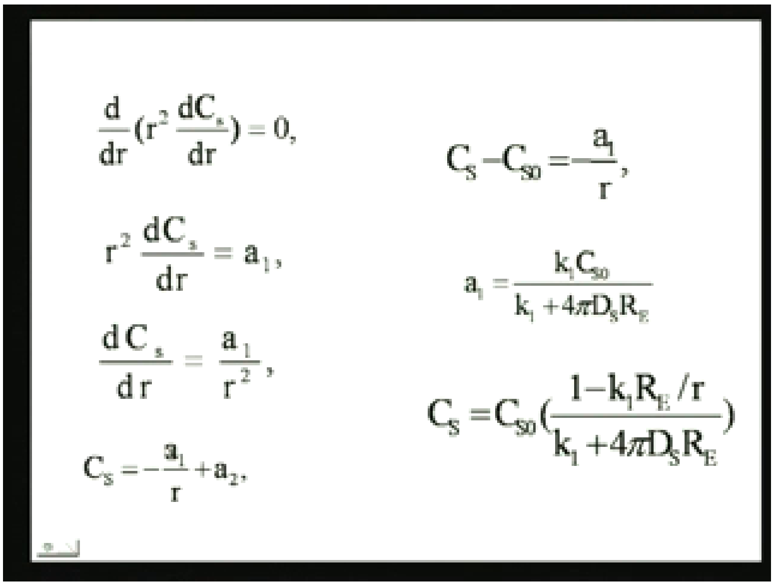

$$\frac{d}{dr}\left(r^2\frac{dC_s}{dr}\right)=0,$$

$$r^2\frac{dC_s}{dr}=a_1,$$

$$\frac{dC_s}{dr}=\frac{a_1}{r^2},$$

$$C_S=-\frac{a_1}{r}+a_2,$$

$$C_S-C_{S0}=-\frac{a_1}{r},$$

$$a_1=\frac{k_1C_{S0}}{k_1+4\pi D_SR_E}$$

$$C_S=C_{S0}\left(\frac{1-k_1R_E/r}{k_1+4\pi D_SR_E}\right)$$

So, this is the final solution that you have, which is C s equal C s naught times 1 minus k 1 R E over r over this denominator, get that or is too quick, we just make a note even if it little quick (No Audio from 11:05 to 11:26), up to this is fine right up to this is fine, all you need to do is, now replace this into the first boundary condition and just do a little bit of algebraic manipulation (No audio from 11:35 to 11:42).

So, now you get your C s as C s naught times s number. So, what are we trying to find here, you know those few who were there in the last class, one of the major aims is, and trying to quantify the reaction rate, what reaction rate, which reaction rate?

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Yeah, the observed reaction rate, the intrinsic reaction rate could be different, but there is an observed reaction rate, not the surface reaction rate, but an observed reaction rate.

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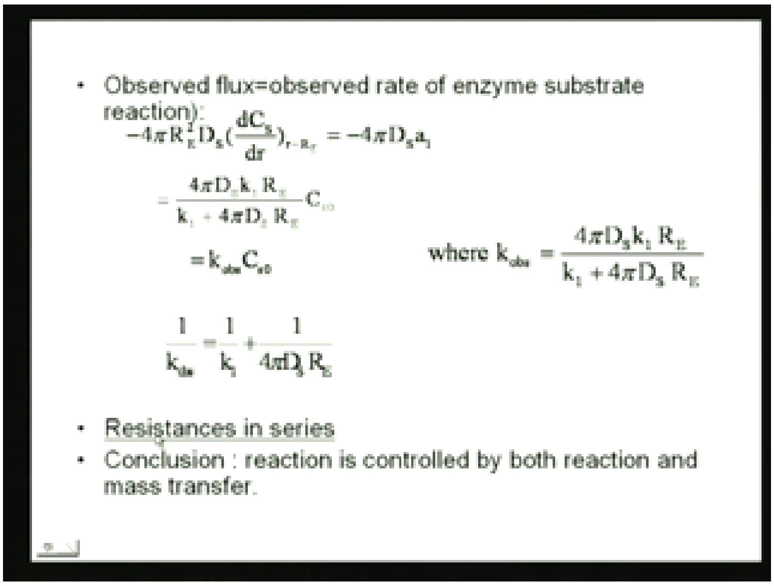

- Observed flux=observed rate of enzyme substrate reaction):

$$-4\pi R_E^2 D_s \left(\frac{dC_s}{dr}\right)_{r=R_E} = -4\pi D_s a_1$$

$$= \frac{4\pi D_s k_1 R_E}{k_1 + 4\pi D_s R_E} C_{s0}$$

$$= k_{obs} C_{s0} \qquad \text{where } k_{obs} = \frac{4\pi D_s k_1 R_E}{k_1 + 4\pi D_s R_E}$$

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{1}{4\pi D_s R_E}$$

- Resistances in series
- Conclusion : reaction is controlled by both reaction and mass transfer.

So, observed reaction rate or observed flux is equal to observed rate of surface substrate reaction. So, this is this is my observed rate of flux which is, minus 4 pi R E square times D s del del C s del  r d C s del d r, at r equals R E fine, is that clear with everybody? So, that you can, because you you calculated that your r times d C s d r, just now we calculated r times d C s d r equals a 1. So, you can put put that constant from there and you a 1 we got a here this, just now we got this, that r times d C s or r times d C s d r equals a 1, a 1 over r sorry. And so, you can put that over here here, so R E, r square times d C s d r equals a 1.

So, this you are trying to evaluate it, r equals R E right. So, you get R E square time d C s d r equals a 1. So, 4 pi D s is there, (()) times simply times a 1. So, we have calculated what a 1 is, so you can put that back over here and this is what you get, is it clear to everybody, that little algebra? Now, what is this, trying to show here, this is, see in ideal case, if you did not have mass transfer limitations, what would your reaction rate be, it simply should be?

(( ))

k yeah k 1 into C s, C s?

C s naught.

C s naught right k 1 into C s naught

But what this is showing is that, look at this number over there, that denominator is larger than the numerator, so this is the fraction. So, what this is showing is, this is smaller than k 1 and why that smaller? Because of the mass transfer limitation right, is that clear to everybody, Lisa? So, that is what we had, we are trying to achieve.

So, all this calculation, we are trying to achieve what is my actual reaction rate so that you can have a intrinsic reaction rate, which is the ideal reaction rate, that you would like to have over there, but then life is not ideal and you know the reaction rate that you get over there is not the ideal reaction rate, it is lesser than the (( )) that is called the observed reaction rate and what we are trying to calculate here, is how much less is observed reaction rate than the actual reaction rate, so this is what we get.

Now, if you look at this, what we can do is, we can take an inverse of this, the reason is that the, so I can write it as k observed times C s naught. Now, if what would my 1 over k observed would be? 1 over k observed would be 1 over yeah. So, you you take the inverse of this, so do you see what I am trying to approach at?

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Right.

(( ))

So, 1 over k observed equals 1 over k 1 plus 1 over pi D s R E. Now, 1 over k 1 is a is a, which resistance?

Reaction (( ))

Reaction resistance, for a simple reaction and 1 over 4 pi D s R E is mass transfer resistance, so yes. So, this is one of the cases, I am not sure if you have done such an example before, where you have done examples where reaction two two say, mass transfer resistances or two heat transfer resistances are in series. But I am not sure; you have done a case where one heat transfer resistance or one mass transfer resistance is coupled with a reactive resistance.

So, if you have, then it is an interesting thing, otherwise this is this is one of the examples where you look at that, it is it is called reaction in series, but the only difference is that, the reactions is the, resistance is in series. But the only difference is that, the two resistances and the three resistances that we are considering are not necessarily of the same type. So, your reactive resistance out here and a mass transfer resistance and you are adding them up, to get your total resistance. Now, so this is the reaction is controlled, so this is an intermediate, so if you go you know, let me go back to that slide here.

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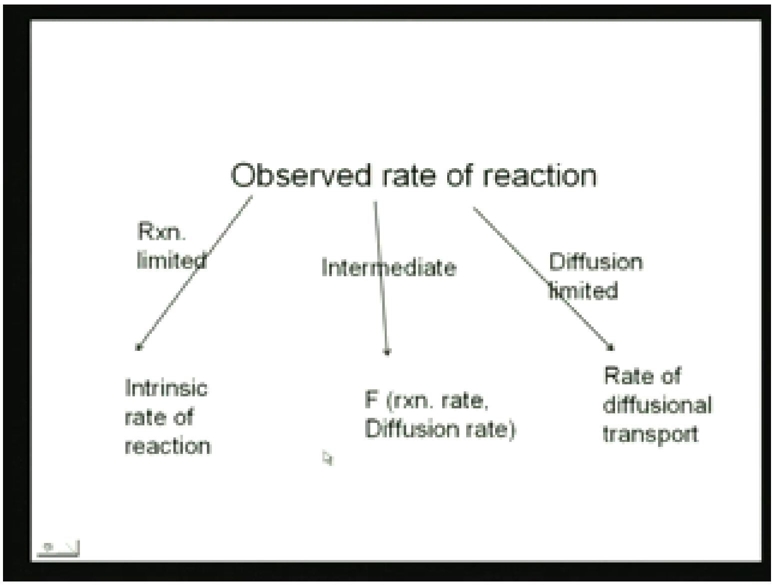

Observed rate of reaction

So, the observed rate of reaction, we decided could be it same as intrinsic rate of reaction if the system is diffusion limited, could be same as rate of diffusional transport if the system is diffusion limited and could be intermediate, that is, depending both on reaction rate and diffusional rate, if it is in the intermediate regime. So, it turns out that for this particular case, what we are doing here.

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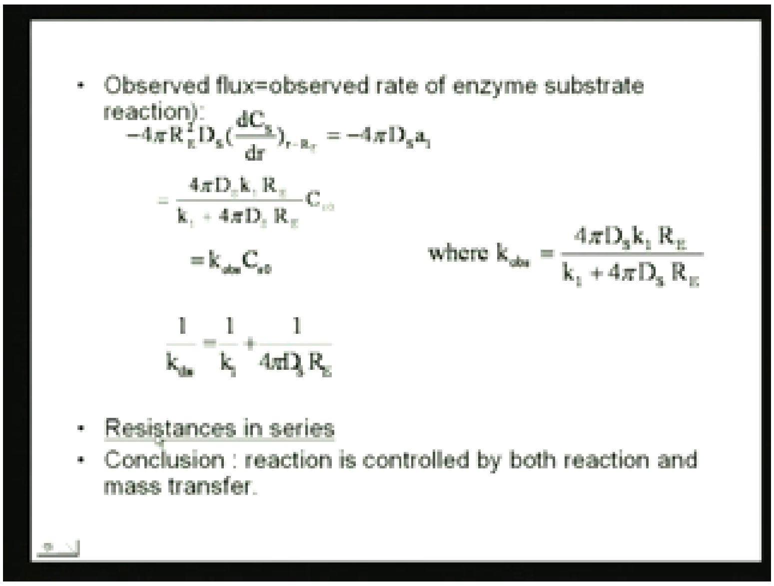

- Observed flux=observed rate of enzyme substrate reaction):

$$-4\pi R_E^2 D_s \left(\frac{dC_s}{dr}\right)_{r=R_E} = -4\pi D_s a_1$$

$$= \frac{4\pi D_s k_1 R_E}{k_1 + 4\pi D_s R_E} C_{s0}$$

$$= k_{obs} C_{s0} \qquad \text{where } k_{obs} = \frac{4\pi D_s k_1 R_E}{k_1 + 4\pi D_s R_E}$$

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{1}{4\pi D_s R_E}$$

- Resistances in series
- Conclusion : reaction is controlled by both reaction and mass transfer.

And is in the intermediate regime and another result, the reaction is controlled both by the the observed reaction. So, to say this controlled both by the intrinsic reaction and the mass transfer and the total resistance that you get in the system, is a combination of these two resistances. Now, when I say combination it could be different kinds of combination and one of the things that you have to understand very clearly is that, why do we get resistances in series, can you tell me? Why are these resistances in necessarily in series over here?

Because the diffusion occurs, means the substrates (( ))

Right and then

Call to the (( ))

No, first the diffusion occurs.

(( ))

And then the reaction occurs, right that is a right answer.

So, see the resistance is that, the way you write your mathematics is only and only governed by the process. So, when you say that, the react resistances are in series, it automatically means, it should hard back to the fact that, the processes are in series, that that is the point you know, it is not that, it is not you know god's gift to biochemical engineering, that all resistance they are going to be in series all the time, they need not be in series.

But it is that, the processes are in series which is what he said just now, that first the diffusion occurs and then it is followed by the reaction, as a result resistances are in the series. Why I am trying to tell this is that, I am typing to impress upon you the fact that, do not close your eyes and write resistances is in series all the time, try and see if the processes are in series.

Now, this is a very you know, this is an effort saving exercise that if you understand if the, whether the processes are in series or not, then you can figure out what the resistances are and you can write down the total resistance right away, without doing all these calculations. You see, once we do the calculations, we try and want to come out with conclusion that we can use in a generic way. So, but you can skip the calculation, provided you were right with the physics.

So, if the resistance is, if the processes are in are in series, then resistances could be in series a and b is that you have to have to also check what kind of you know, what kind of coordinate system you are working at.

So, even if the resistances are in series, the way they would look in a Cartesian coordinate, is different from the way they would look in a cylindrical coordinate, is different from the way they would looking at spherical coordinate. So, these two things you have keep in mind when you use this, one is check the process, if they are in series, then you can resistances in series concept and send next, check the coordinates system and then use this.

So, that is one thing we want to do, what I want to do is, do the other limit. So, we did the other limit of the small small concentration, which is gives you first order kinetic. Now, let us do the limit of the large concentration, which will give you zeroth order kinetics.

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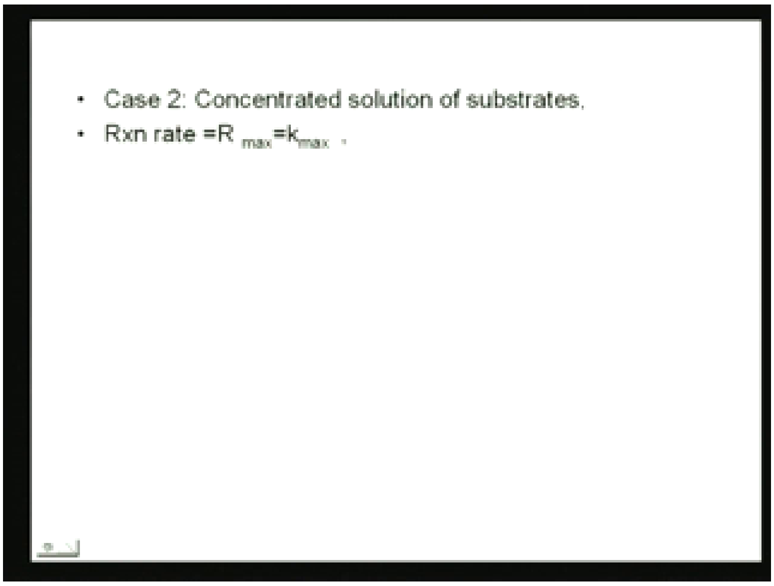

- Case 2: Concentrated solution of substrates.
- Rxn rate $=R_{max}=k_{max}$ .

And this is very straight forward. So, in zero order kinetics, what happens, the reaction rate is the constant. And the (No audio from 19:47 to 19:55), so the reaction rate is constant equals R max and let us just represent that by k max, the reason is, because we just wanted to be in terms of a rate constant. So, what would be my governing equation now?

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It is still the same, which is, can you write that, do remember, do you write that, what is it? (No audio from 20:23 to 20:31).

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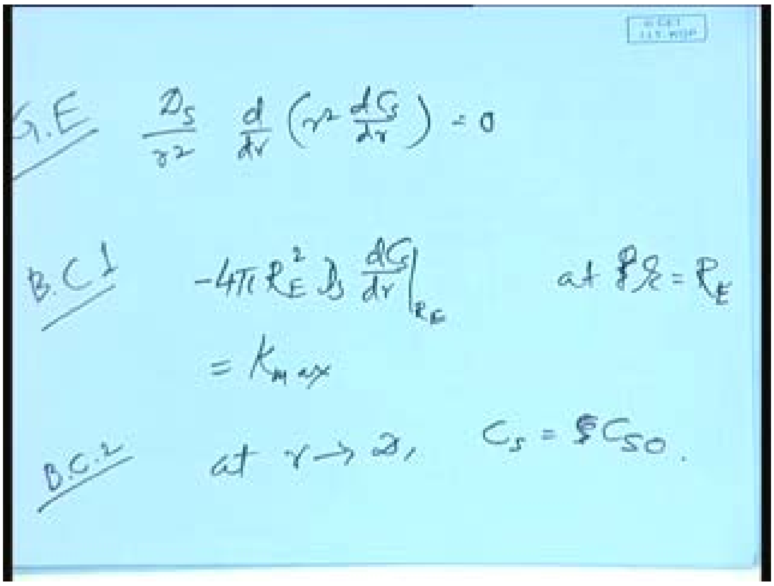

G.E $\frac{D_s}{r^2}\frac{d}{dr}\left(r^2\frac{dC_s}{dr}\right)=0$

B.C 1 $-4\pi R_E^2 D_s \frac{dC_s}{dr}\Big|_{R_E} = k_{max}$ at $r = R_E$

B.C 2 at $r \to \infty$, $C_s = C_{s0}$.

In still in this spherical coordinate and what is the governing equation? D s by r square d d r of r square d C s d r equals 0 yeah. So, what would be my, that is my governing equation, boundary condition 1 could be at r equals R E, what is my boundary condition? 4 pi.

(( )) 4 pi R E square.

4 pi R E square D s into del C s del R equals, that is the only difference now, equals equals k max and B C 2 would be simple, same at r going to infinity, C equals C s equals C s naught (No audio from 21:29 to 1:50). Now, you can quickly solve this, the same thing. So, C s equals C s naught plus a 1, a 1 C s naught minus a 1 over r, I think, that is what you will get (No audio from 22:01 to 22:10).

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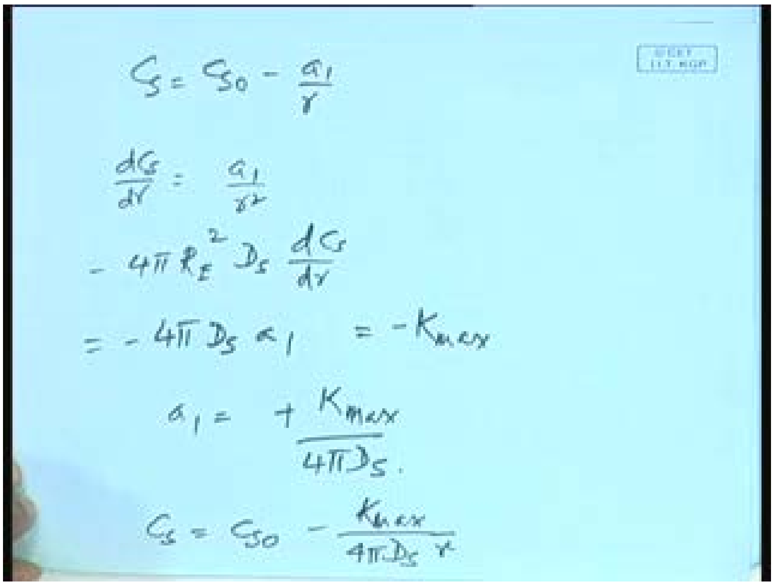


$$C_s = C_{s0} - \frac{a_1}{r}$$

$$\frac{dC_s}{dr} = \frac{a_1}{r^2}$$

$$-4\pi R_E^2 D_s \frac{dC_s}{dr}$$

$$= -4\pi D_s a_1 \quad = -K_{max}$$

$$a_1 = +\frac{K_{max}}{4\pi D_s}.$$

$$C_s = C_{s0} - \frac{K_{max}}{4\pi D_s r}$$

So, the C s equals C s naught minus a 1 over r and so, d C s d r equals a 1 over r square. So, 4 pi R E square D s d C s d r equals, this equals minus 4 pi D s into a 1 right, this is what you got which equals K max. So, a 1 equals minus K max over 4 pi D s ((No audio 22:59 to 23:34)) I think I think there is a sign thing, so this should be plus.

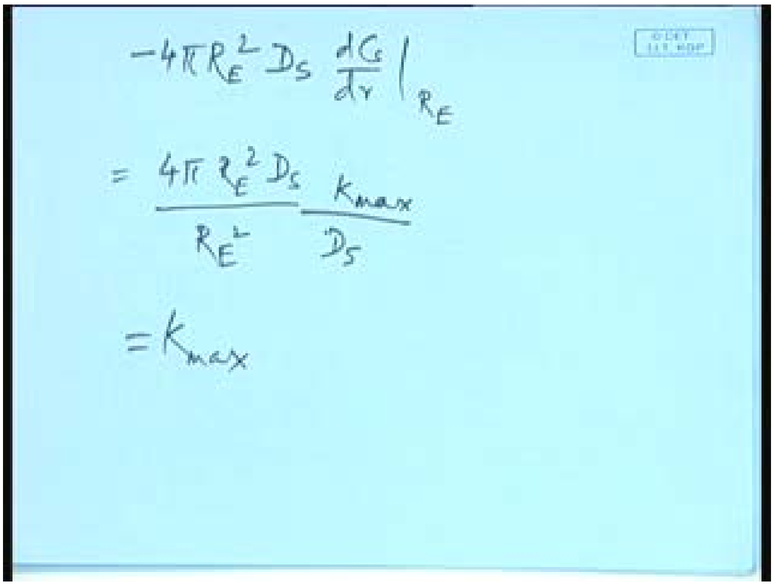
(())

Huh.

Minus (( ))

This should be minus, I think and that this should be plus. So, C s equals C naught minus K max over 4 pi D s over r. Now, so this is what we wanted, we want that profile and then, you have to calculate the flux right.

(Refer Slide Time: 24:26)



$$-4\pi R_E^2 D_s \frac{dC_s}{dr}\Big|_{R_E}$$

$$= \frac{4\pi R_E^2 D_s}{R_E^2} \frac{K_{max}}{D_s}$$

$$= K_{max}$$

So, what would you get? So, the for the flux, I mean this is the back calculation, but you have to still get the same thing 4 pi R E square D s times del C s rather equals R E equals 4 pi R E square D s times over R E square and into that is a (( )) thing 4 pi D s to K max and over D s right (No audio from 25:05 to 25:18), through we feel kind of short change right after doing all the all the analysis we kind of feel short changed, because we started with this, this was one of our boundary conditions, you see why I am saying.

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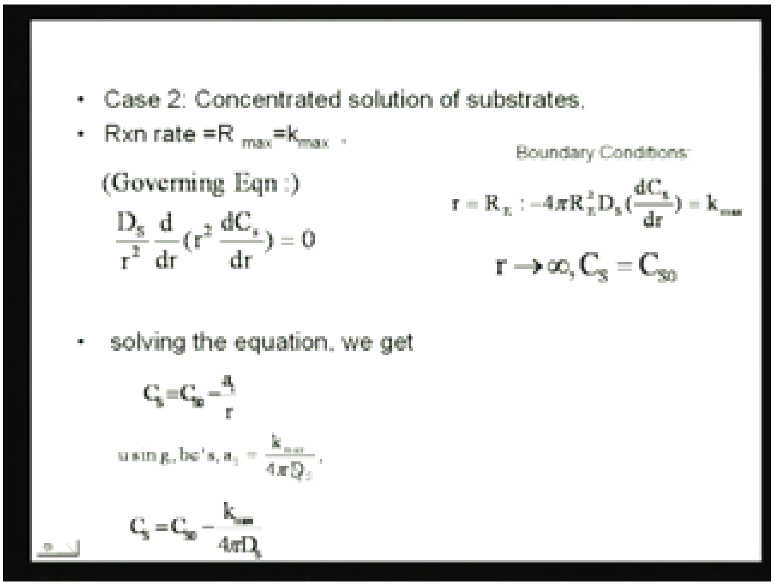

- Case 2: Concentrated solution of substrates.
- Rxn rate $=R_{max}=k_{max}$ .

(Governing Eqn :)

$$\frac{D_S}{r^2}\frac{d}{dr}(r^2\frac{dC_s}{dr}) = 0$$

Boundary Conditions:

$$r = R_E : -4\pi R_E^2 D_s(\frac{dC_s}{dr}) = k_{max}$$

$$r \to \infty, C_S = C_{S0}$$

- solving the equation, we get

$$C_s = C_{s0} - \frac{a_1}{r}$$

using, bc's, $a_1 = \frac{k_{max}}{4\pi D_s}$,

$$C_s = C_{s0} - \frac{k_{max}}{4\pi D_s}$$

See, if you go to the screen, so look at this boundary condition out here. So, this was our boundary condition anyway. So, what what is a, what is a what is over here that is going on, what is what is going on here you know, there is a inherent physics that is there you know (( ))

(( ))

No, that is not the point yeah all the receptors could be associated within enzymes, but that that is that is not the point you know, there is something going on here, we have to you know we you do the calculation, then you figure out that as I said, you kind of feel short change and you thought that well, this was what was given to us and why did we have to all this and come back to the same thing. But the reason we did this is, because there is a slight physics of the problem that, we did not address at the beginning.

If we thought about it, then we probably would not do this exercise, because it is kind of redundant and what is that, I want you to after having done that, I want you to go back and figure it out for me, yes right there you know whatever if you look at this screen and whatever the equation is on this screen, it is there in that equation, you just have to read it out there (No audio from 26:53 to 27:06), what is what is the, what is this, mean this over here and whatever, what does the boundary condition mean?

(( ))

No, reaction rate is always equal to flux, that was there before also, but what is so specific or special about this one?

This one (( ))

Yes, that is right, what does it mean, what does it imply?

0 only.

I know it is 0, but what does it mean imply?

We do not have (( ))

Yeah, that means that, we do not have reactive resistance or in other words, at any point of time, there is enough amount of substrate, what does a zeroth order mean? Zeroth order is, you know I told you this before, there is no reaction such as zeroth order, you know reaction cannot be zero order, reaction is first order, second order, fractional order. So, zero order is a concept it is not not a reality, so that is what I am trying to say. So, when you say it is a zeroth order reaction, it does not mean anything, it is a it is it is a concept.

So, what does it concept mean, that zeroth order concept means that at any point of time there is so much substrate, acts the reaction in sight that, it is independent of the substrate concentration, you see what I am saying, it does not means that the reaction is zeroth order actually, it does not means that the reaction is actually independent of concentration, because it how would reaction occur? I mean this is a something that we discussed in the first or the second lecture, how do reaction occur if there is no substrate? Can you just make reaction happen, it is in without substrate? No, you cannot do that.

So, it is not possible to have reaction without substrate, when you say the reaction is zeroth order, you mean that there is so much substrate at the reaction side that, it is not inhibited or limited by a substrate at any point of time, that is when it means zeroth order, so which means that, it could be actually a first order reaction.

For example, here or any other order reaction, but if the amount of substrate is enough and it is a constant at the reaction side, then that can be absorbed in the K, you see what I am saying, that is that is that is you know mathematically speaking that is the idea that, there is enough of reactant at the reactant side and so much of reactant, that any point of time, it is more or less constant like, if you need 1 millimolar of reaction, reactant at the, at this a interface or for reaction and if you have one molar of reactant there and if you have 2 molar, if you have 10 molar, it does not matter.

For the reactant which in equals 1 millimolar, you know 100 millimolars or 1 molar or 2 molar is still the same. So, you can absorb all of that, because then it becomes like a constant, you can absorb all of that in the rate constant and get that. Now, what happens over here is that, so the, there is enough reactant, that is there at this, at the at the side. As the result, whether there are there are mass transfer limitations in the system or not, actually you know you did not say it right and I did not yeah I should not agreed with you that point, so we will come back to that this.

So, whether or whether or not, there are mass transfer limitations in the system does not make a difference. So, the only thing that matters is just the opposite, the only thing that matters is, the reaction resistance. So, the only resistance that is there is reaction resistance. So, my k observed is going to be equal to k max.

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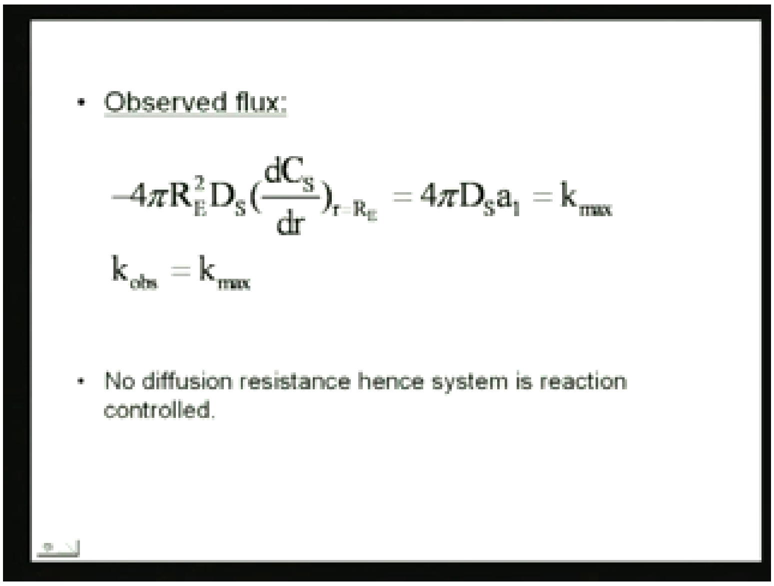


- Observed flux:

$$-4\pi R_E^2 D_S \left(\frac{dC_S}{dr}\right)_{r=R_E} = 4\pi D_S a_1 = k_{max}$$

$$k_{obs} = k_{max}$$

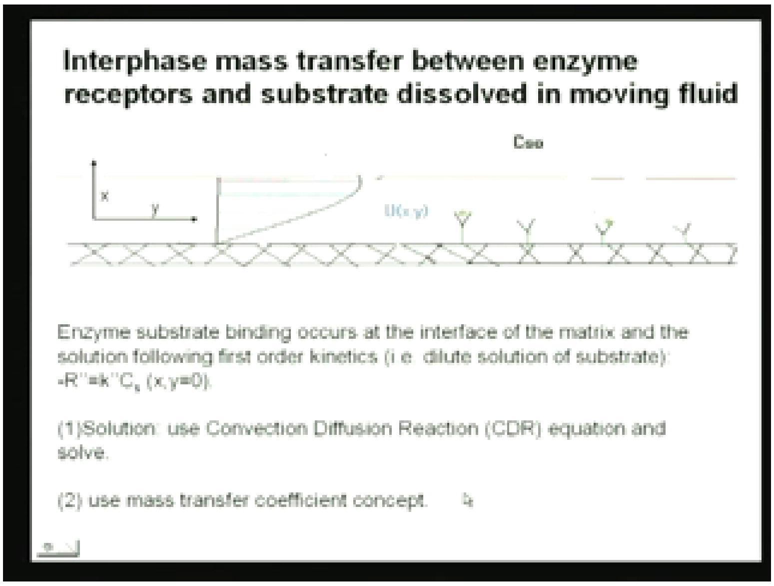
- No diffusion resistance hence system is reaction controlled.

So, let us go quickly, so my k observed equals k max. So, there is no diffusion or mass transfer resistance in the system at all, is that clear? So, this what we did is is gives gives us a way of understanding more fundamental mechanism of what really happens, when there is, when you say it is a zeroth order reaction, which is that the mass transfer resistance.

As soon as you say it is zeroth order, which it means that you are supplying enough reactant to the reaction side and the only way you can supply enough reactant to the reaction site is, when you are overcoming the mass transfer resistant in a steady rate. And the only way you can overcome the mass transfer resistant at the steady steady rate is, when the mass transfer resistance is very much smaller as compared to the reactive resistance.

So, here there is no mass transfer resistance and as the result your k observe equals k max, is that clear. Is there any question? Is there any question on this, on what we did? So, we are going to next next topic, but before we do that, if there is any question, I will address, none, shall we move on?

(Refer Slide Time: 31:50)



## Interphase mass transfer between enzyme receptors and substrate dissolved in moving fluid

Enzyme substrate binding occurs at the interface of the matrix and the solution following first order kinetics (i.e. dilute solution of substrate): $-R''=k''C_s\ (x,y=0)$.

(1)Solution: use Convection Diffusion Reaction (CDR) equation and solve.

(2) use mass transfer coefficient concept.

So, the next thing that we are going to do is, interface mass transfer between enzyme receptors and substrate, dissolved in a moving fluid. So, the major difference is in the first part that we did, we only considered diffusion and no movement of the fluid. So, it was, as if a static fluid was there and the enzyme matrix insoluble in it is dropped in it and diffusion on the reaction occurs. Here, what we are going to do is, we are going to look at moving fluids.

So, for example, you know if say this is the enzyme and there is there is fluid move, this enzyme is in your gut for example, you know some kind of enzyme is just a fell or something in that you have taken and it is on your on your on your, in your gut for example, and the fluid that that is there in the gut, it is moving right, you are drinking water and so on. So, there is movement of fluid in your gut; as a result, there will be convective effects now.

So, that is an added complexity that, we add in at this point and we do not you know do not include so much of diffusion in there, because the convective effects you know, you can do diffusion of course, but typically, the convective effect will always out way the diffusive effect, but of course, you can include diffusion. So, if you look at this picture over here, this is the now the matrix or one with the cross lines over here, this is the matrix matrix for of the enzyme of the, on which the enzyme is kind of attached covalently here.

So, these are the receptors and these are the enzymes and the fluid that you have that you have is flowing in this direction and you have the x and the y coordinates.

So, the enzyme, so what is happening here that, the enzyme substrate binding at the interface of the matrix and the and the solution (( )) obey for first order as I said this again the asymptote of the whole problem.

So, what I want you to do is, so there are two ways of you know solving it or may be one way, but one way with coupled with another way, which is the convection diffusion reaction equation and the next thing that you have to do is, to include the concept of the mass transfer coefficient. So, if you, you have to write, so first let me let me ask you, so where are you going to use the convection diffusion reaction equation first of all?

(( ))

It would be in the boundary condition that is correct. So, where is a, where are you going to write the convection diffusion equation then?

In the boundary layer

In the boundary layer right, so this is this is your solid. So, this goes back to the classical boundary layer problem, this is your solid, this is the liquid fluid that is coming in and you have a boundary layer that is that is created. And so, you have to write not a convection diffusion reaction equation, but a convection diffusion equation with a reaction at the boundary condition, we can still call it as CDR convection, because it is still you know convection diffusion and reaction all three are there, it is still called the convection diffusion reaction equation.

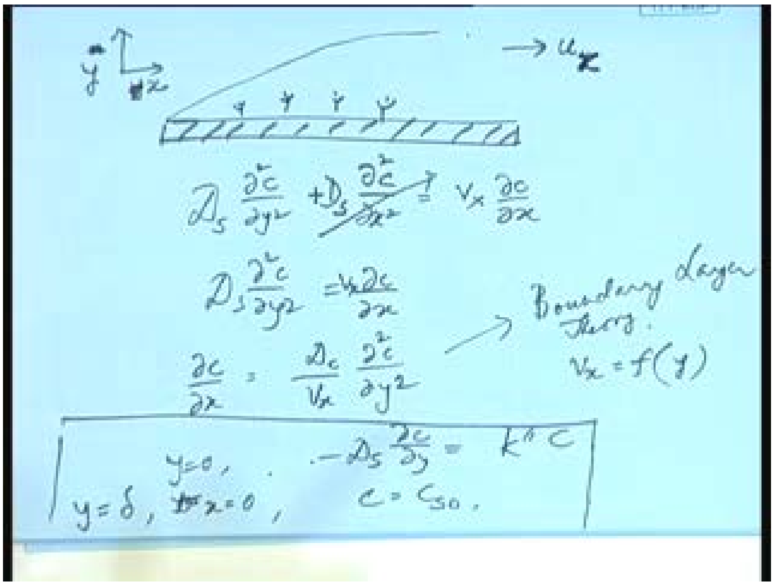
But the reaction is not going to be in the governing equation, the reaction is going to be in the boundary layer fine and you can solve it, the problem with solving it is it is little complicated and there are solutions possible for it and it is lightly complicated, the other option is the option of mass transfer coefficient.

So, we can use the mass transfer coefficient. So, if you know what the mass transfer coefficient is, mass transfer rate is from the fluid to the solid, then you can use a mass transfer coefficient, then in that case, what would be your basic concept, at any point of time, that is anyway your basic concept that that what are the two rates are there equal at the interface?

(( ))

So, the mass transfer whatever is coming in, because of mass transfer from the fluid into the into the solid equals what is reacting on the solid interface is that right. So, if you look here, whatever is coming in from here to here at this interface equals what is reacting. So, what I want you to do is, now first can you write from what you studied the CDR equation?

(Refer Slide Time: 35:53)



So, let me try and help you, so this is your solid and so, which direction the main velocity is in the y direction, let us say or shall we call maybe if you call this, call as let us call this x and this y, that is what it is done classically. So, if you write the convection and diffusion equation there will be two components; of course, the convection and the diffusion right. So, this is this is a fluids, for example (No audio from 36:29 to 36:35), and there is a (()) here, so what would be the terms, diffusion terms, same.

(( )) D s into del c a d a.

Ok, and

Conduction from v x into del C del x.

V?

V x into del C del x.

Do you say del del D s into del del 2 C del y square right and well I would you know why not this term as well, there is no reason for it, not to be there. You can neglect this term using scaling analysis in this direction and…

This will be very insignificant as (( ))

As yeah, that is what we have said initially that, when you have convection the diffusion terms one of the diffusion terms, you can neglect. So, that is the possibility that you can neglect this term and then, you if you if you neglect this and and D 2 s (No audio from 37:43 to 37:58) . So, do you know how to solve this?

(( ))

Yeah, but v x in the boundary layer is going to be a function of y, right v x in the boundary layer is going to be a function of y. So, if it is if it is a fully developed, you know and so, you know you can go back to the boundary layer theory and try to solve this and then at the boundaries, you have to use the boundary conditions. So, what kind of boundary conditions would that be?

Sir, (()) not given

Yeah at x equals at this surface

y equal to 0.

So, y equals 0, you will have what you will have? Minus D s del C del y equals.

(( ))

Huh tells you k double prime equals into C or something and…

X equals 0 (( ))

X equals

0.

Initially C s 1

C huh.

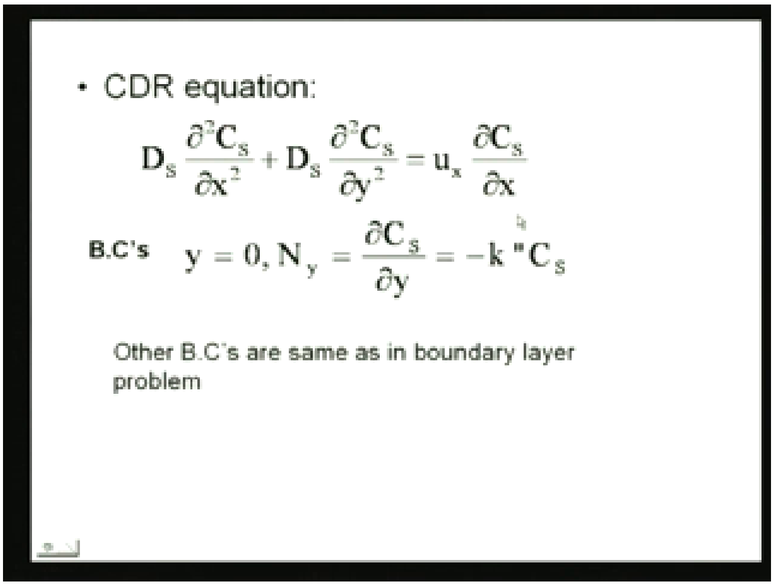
C equal to c.

C equals to C s naught or something and similarly, at y outside the boundary layer.

(())

y equals to delta y equals to delta, this is what we have, this is to view boundary condition fine. So, you can just go ahead and solve this, we are not doing this exercise in the class today, you can go ahead and solve this.

(Refer Slide Time: 39:42)



- CDR equation:

$$D_S \frac{\partial^2 C_S}{\partial x^2} + D_S \frac{\partial^2 C_S}{\partial y^2} = u_x \frac{\partial C_S}{\partial x}$$

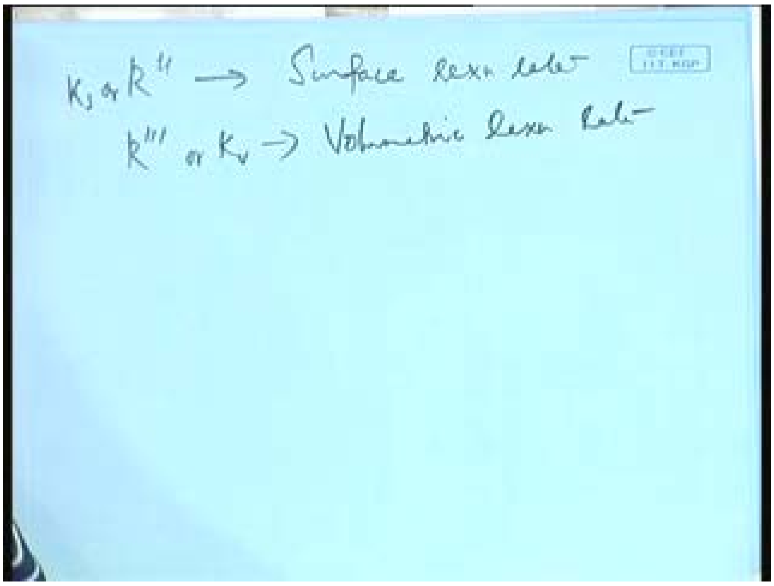
B.C's $y = 0, N_y = \frac{\partial C_S}{\partial y} = -k''C_S$

Other B.C's are same as in boundary layer problem

What we will do is, we will just use the straight forward concept of mass transfer coefficient that excuse me. So, this is what you do, straight forward concept of mass transfer coefficient and due there is a there is a slight error here, there should be D s times del C s del y equals k double prime, now why do I use k double prime?

(())

(Refer Slide Time: 40:09)



$K_s$ or $K''$ → Surface Rexn Rate

$K'''$ or $K_v$ → Volumetric Rexn Rate

Raded the surface, so k double prime is typically used for surface

(())

Reaction rate and k triple prime or K v is used as the

(())

So, k s or k triple prime is for a volumetric reaction rate. So, this double prime corresponds to the 2 D and triple prime corresponds to 3 D. So, other boundary conditions are in the same as a boundary layer problem.

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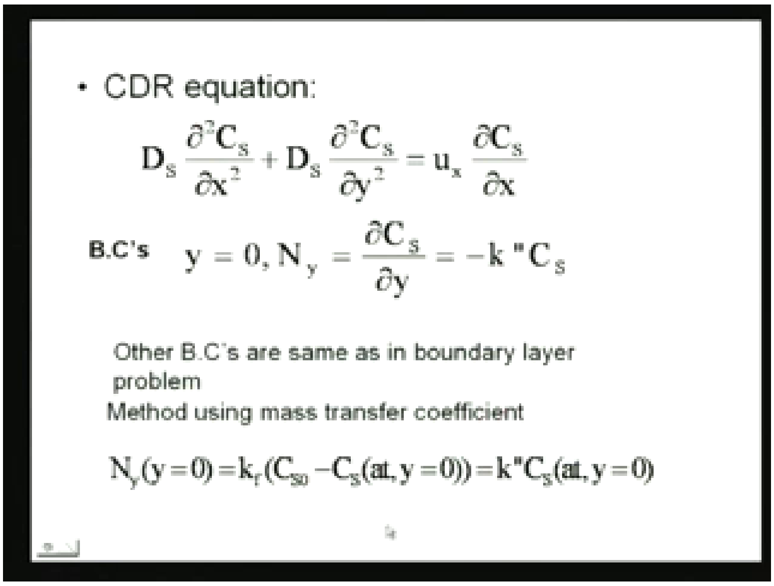

- CDR equation:

$$D_S \frac{\partial^2 C_S}{\partial x^2} + D_S \frac{\partial^2 C_S}{\partial y^2} = u_x \frac{\partial C_S}{\partial x}$$

B.C's $y = 0, N_y = \frac{\partial C_S}{\partial y} = -k'' C_S$

Other B.C's are same as in boundary layer problem

Method using mass transfer coefficient

$$N_y(y=0) = k_f(C_{S0} - C_S(at, y=0)) = k''C_S(at, y=0)$$

So, the second method that we can use is a method using mass transfer coefficient which is that you assume a mass transfer coefficient and the rate of mass transfer equals the rate of reaction, it is a very straight forward concept. So, this is what you do here, it is on your screen.

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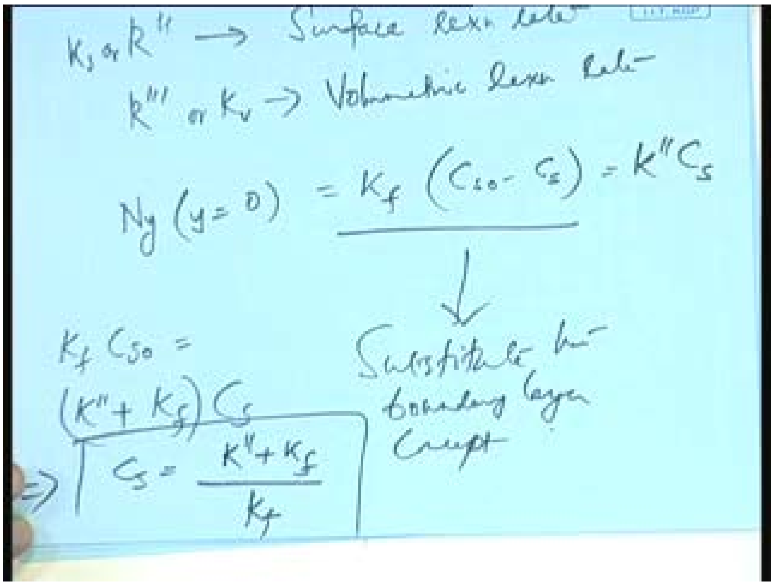

$K_s$ or $k'' \rightarrow$ Surface Rexn Rate

$k'''$ or $K_v \rightarrow$ Volumetric Rexn Rate

$$N_y(y=0) = \underline{K_f(C_{s0} - C_s)} = k''C_s$$

$\downarrow$

Substitute in boundary layer Concept

$K_f C_{s0} =$

$(k'' + K_f) C_s$

$$\Rightarrow \boxed{C_s = \frac{k'' + K_f}{K_f}}$$

So, N y at y equals 0 N y at y equals 0 equals some K f into C s naught minus C s equals K double prime which is C s, very straight forward that, so whatever is your outside the boundary layer, whatever is your concentration minus. So, then through the mass transfer coefficient you substitute the boundary layer concept at all, completely right. So, you just substitute the whole concept of boundary layer that is, C s naught minus C s whatever is a difference between outside the boundary layer and acts the surface, times some mass transfer coefficient for the boundary layer equals what is being consumed at the interface.

So, if you do that, then you can directly from this, for example, you can directly K f times C s naught equals K double prime plus K f times C s which implies that C s equals K double prime plus K f whole K f, is it fine? So, this is this is what you get.

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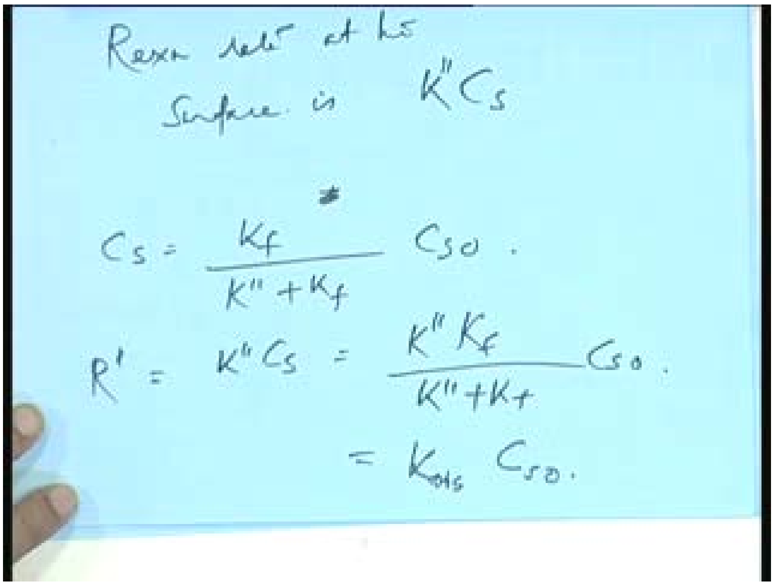

Rexn rate at the Surface is $K''C_s$

$$C_s = \frac{K_f}{K''+K_f} C_{s0}.$$

$$R' = K''C_s = \frac{K''K_f}{K''+K_f} C_{s0}.$$

$$= K_{obs} C_{s0}.$$

And once you get that, so what does it mean now? Your reaction rate and the surface is what is K double prime times C s fine.

So, k f did I did, I think C s naught equals this times C s and so, C s naught equals this times C s. So, C s equals K f over times C s naught fine, so your reaction rate is this. So, R equals R double prime, let us call that equals, k double prime times C s equals K double prime into K f over K double prime plus K f into C s naught fine which means that, if you take a inverse again. So, this is my K observed times C s naught fine.

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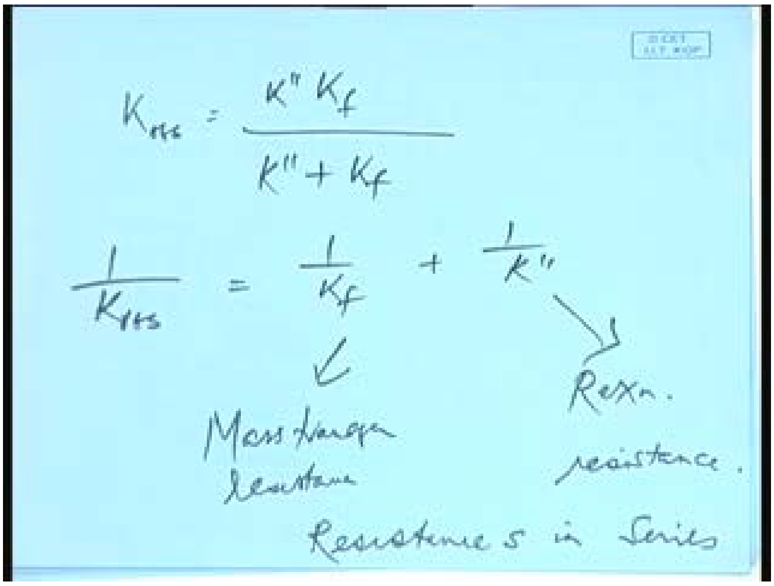

$$K_{obs} = \frac{K'' K_f}{K'' + K_f}$$

$$\frac{1}{K_{obs}} = \frac{1}{K_f} + \frac{1}{K''}$$

Mass transfer resistance

Rexn. resistance.

Resistances in Series

Now, K observed equals K double prime K f over K double prime plus K f are 1 over K observed equals (No audio from 43:50 to 44:05) is that right? (No audio from 44:08 to 44:22) So, you again figure out that resistances are in series. So, whether it is diffusion or convection, does not matter, as long as processes are in series, you can always add up resistances.

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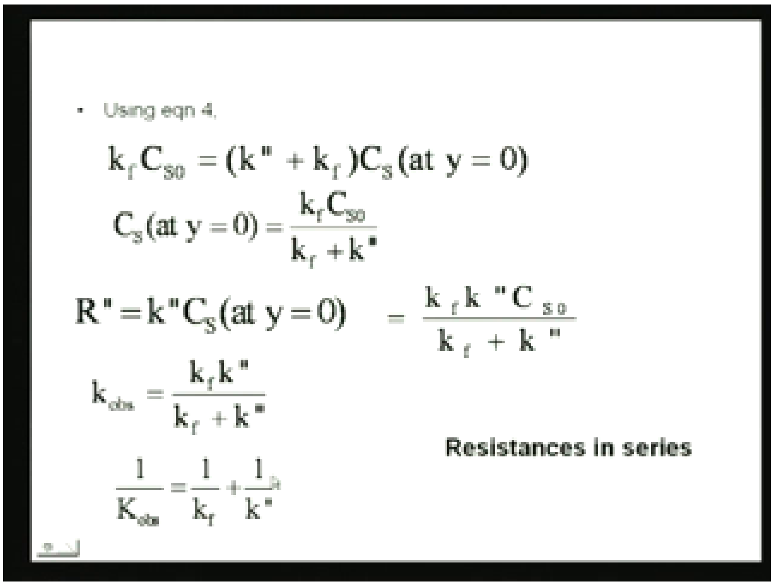

- Using eqn 4,

$$k_f C_{S0} = (k'' + k_f) C_S (\text{at } y = 0)$$

$$C_S (\text{at } y = 0) = \frac{k_f C_{S0}}{k_f + k''}$$

$$R'' = k'' C_S (\text{at } y = 0) = \frac{k_f k'' C_{S0}}{k_f + k''}$$

$$k_{obs} = \frac{k_f k''}{k_f + k''}$$

$$\frac{1}{K_{obs}} = \frac{1}{k_f} + \frac{1}{k''}$$

**Resistances in series**

So, just a quick time skill analysis we will do, these are the things that we all ready did, so no point going through them again. So, this is what we find that, 1 over K observed is

1 over k f plus 1 over k k double prime and therefore, the total resistance summation of the reactive resistance and the mass transfer resistance.

So, just after having done all this, let us have a quick look at the times scales that are there in the process, what did you do in the last class? Last class, we did the times scales that would, that were in you know the concerned times scales of, that are there in the system, what was the two time scales, the times scales of diffusion and the times scales of reaction, right.

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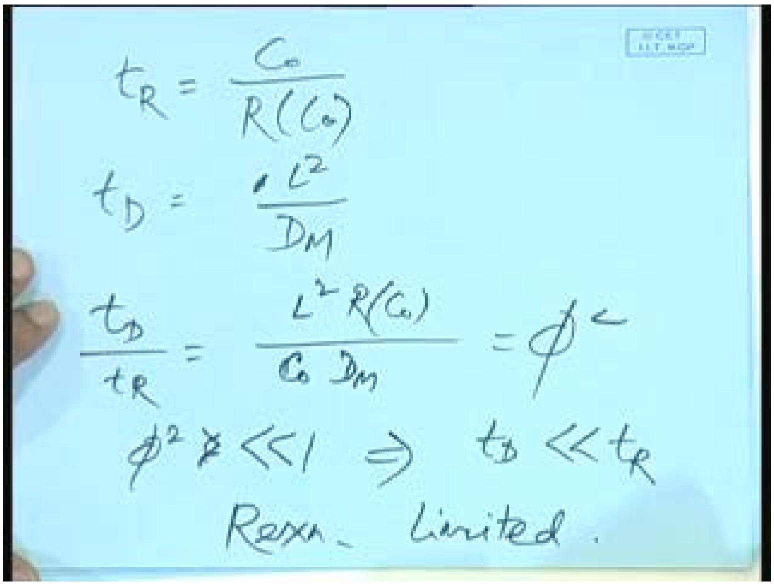

$$t_R = \frac{C_0}{R(C_0)}$$

$$t_D = \frac{L^2}{D_M}$$

$$\frac{t_D}{t_R} = \frac{L^2 R(C_0)}{C_0 D_M} = \phi^2$$

$$\phi^2 \cancel{>} \ll 1 \Rightarrow t_D \ll t_R$$

Rexn. Limited.

And can you go back to your notes and you know, just look what we did was the reaction time scale was C naught over R C naught, the diffusion time scale was L square over D M and then, we got the t D over t R I think we got, right L square R C naught over D M C naught D M right is that what we got? This is my Thiele modulus right.

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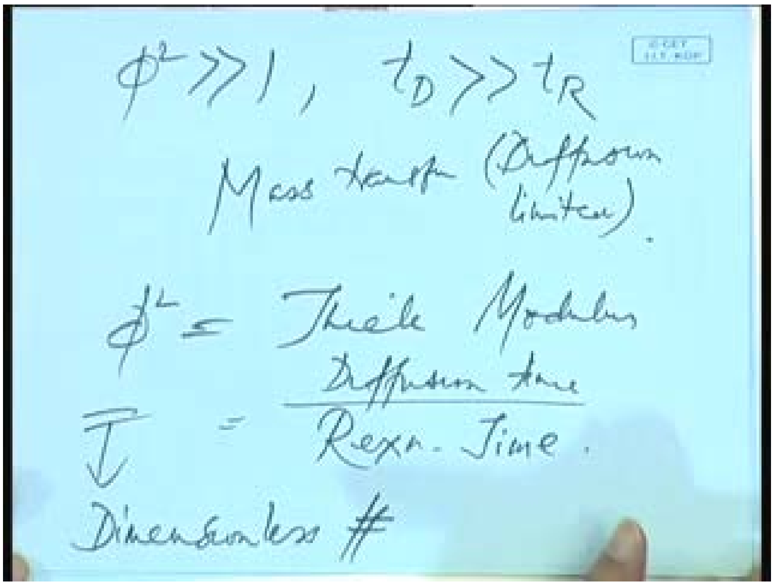

$\phi^2 \gg 1$, $t_D \gg t_R$

Mass transfer (Diffusion limited).

$\phi^2$ = Thiele Modulus

$= \frac{\text{Diffusion time}}{\text{Rexn. Time}}$.

Dimensionless #

So, for phi square much much less than 1, it implies that t D much much smaller than t R and the system is reaction limited right over phi square much much greater than 1, t D is much much greater than t R, and system is mass transfer or diffusion limited. Now, phi square is the Thiele modulus which is the ratio of diffusion time to reaction time, what we have to do today, this after this analysis is, slightly change this, why? Because the governing processes there were diffusion and reaction, the governing processes, the main dominant governing processes here are convection and reaction.

So, we have to the time scale that are involved, would be slightly different time scales and we have to come up with the different dimensionless number. So, Thiele modulus is what is a dimensionless number, it is a very important dimensionless number, actually and we will come up with another dimensionless number, can any of you guess what the dimensionless, the new dimensionless number is going to be?

(())

Yeah that is going to the number.

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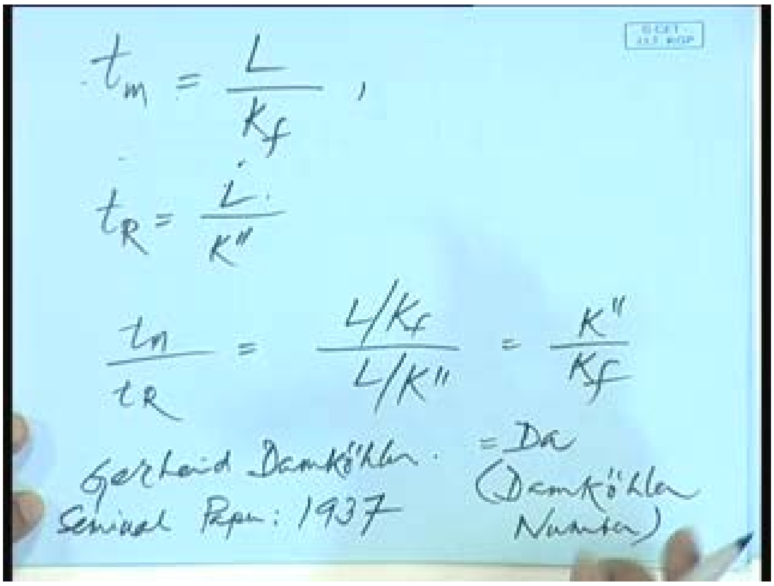

$t_m = \frac{L}{K_f}$,

$t_R = \frac{L}{K''}$

$\frac{t_m}{t_R} = \frac{L/K_f}{L/K''} = \frac{K''}{K_f} = Da$

Gerhard Damköhler. (Damköhler Number)

Seminal Paper: 1937

So, here what we do is, the mass transfer resistance is L over K f and the reaction resistance is L over K double prime, why is that? Why is the L coming in here, because it is a surface right. So, just to consider you know take that into account and if you remember my mass transfer coefficient and K double double prime, they have the same units right, so just to make this a unit of time. So, mass transfer coefficient, mass transfer time scale is L over K f and the reaction time scale is L over K prime.

So, my t m same way, t m over t R equals L over K f, over L over K double prime. So, K double prime and that is my, so Damkohler you know it is named after Damkohler, who is a very famous German scientist, German one of probably the most famous chemical reaction engineer ever, and his seminal paper was you know Damkohler's seminal. So, his name is, I think I remember it right Gerhard Damkohler and his seminal paper is in 1937.

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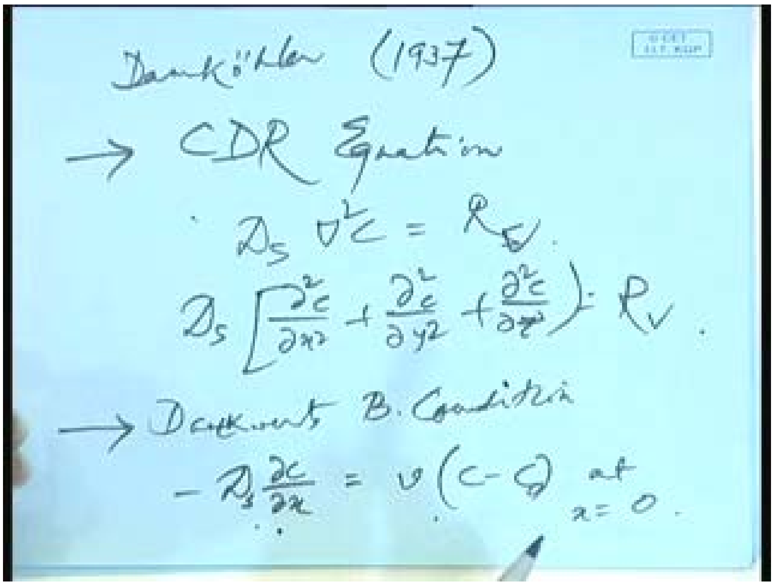

Damköhler (1937)

→ CDR Equation

$$D_s \nabla^2 C = R_v.$$

$$D_s \left[\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right] = R_v.$$

→ Danckwerts B. Condition

$$-D_s \frac{\partial c}{\partial x} = v(C - C_0) \text{ at } x = 0.$$

His major contributions are in this paper, this is probably the most famous paper ever written in chemical reaction engineering. Unfortunately, it was in German in that point of time and it took of, took many years for that paper to be translated and so, his main contribution is the most important contribution, is the CDR equation.

So, he is the one who wrote the CDR equation that, equation that we wrote write over here all the time is D s times laplacian of C equals R s or something, that equation that we write and he is the first one who wrote, he wrote it in the x, y, z coordinate. So, D s del 2 C del x square plus del 2 c del y square plus del 2 c del z square equals R v and if you think, come to think of it in 1937 to write something like that, was a big deal you know, because it is not just writing an equation it is coming to, bringing together the concepts that are embedded in that equations.

So, he was the first one who wrote the CDR equations, he was the first one who also wrote or maybe the second one after Lang mu, Lang mu wrote the first chemical engineer to get the noble prize. So, Lang Lang mu wrote till slightly before that, but he wrote the one which is known as a Danckwerts boundary condition and so, you know you know I wrote a whole paper just on the history of this chemical reaction engineering and how it evolved, all the way from the eighteenth century, so some point of time I can share that with you.

But so, all that is written there with details of which year, who discovered, which boundary condition. So, this is the mix boundary condition that we use all the time. So, minus D s del 2 s del x equals v times C minus C naught at x equals 0.

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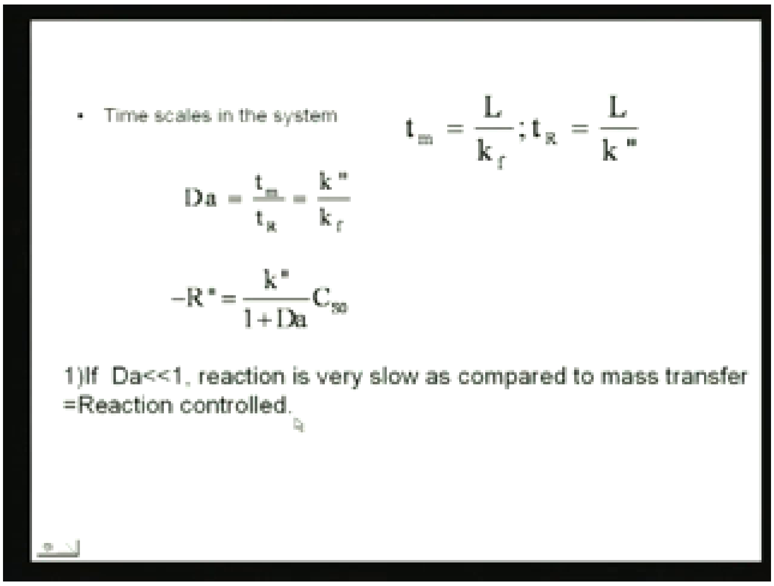


- Time scales in the system

$$t_m = \frac{L}{k_f};t_R = \frac{L}{k''}$$

$$Da = \frac{t_m}{t_R} = \frac{k''}{k_f}$$

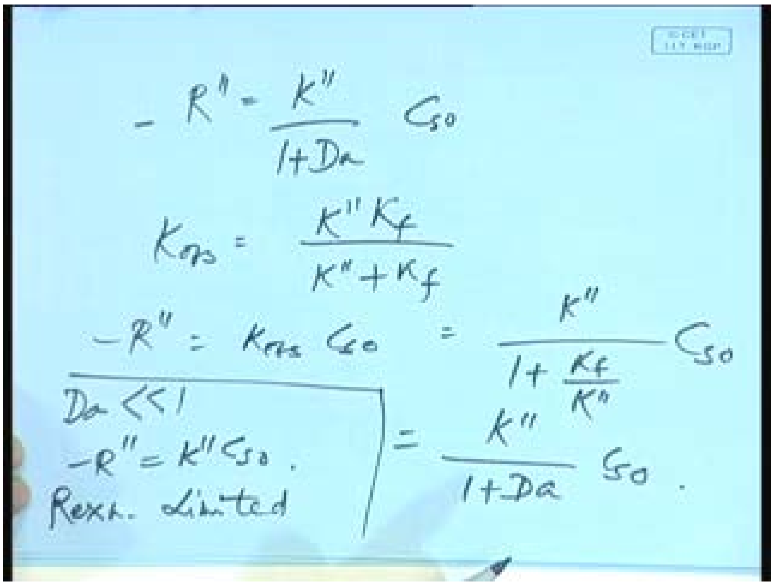
$$-R'' = \frac{k''}{1+Da}C_{s0}$$

1)If Da<<1, reaction is very slow as compared to mass transfer =Reaction controlled.

So, at the boundary of the reactor nor this plate, when both convection and diffusion are there, this is what you use, that is that del C del x that diffusion term equals the velocity times the difference in concentration. So, this was also founded by Damkohler. So, it is no wonder that, you know the most important number in whole of chemical reaction engineering is named after Damkohler and so, this were the, his two major major concepts.

And he brought in some other concepts it is a great paper and you know I one of my colleagues German helped me translate I mean he translated this paper for me and so, it it it is a very long paper, but it is a great paper. So, if you look at this screen now, so without further that you would, because we are running out of time.

(Refer Slide Time: 51:48)



$$-R'' = \frac{K''}{1+Da} C_{s0}$$

$$K_{obs} = \frac{K'' K_f}{K'' + K_f}$$

$$-R'' = K_{obs} C_{s0} = \frac{K''}{1 + \frac{K_f}{K''}} C_{s0}$$

$$= \frac{K''}{1+Da} C_{s0} .$$

$Da << 1$

$-R'' = K'' C_{s0} .$

Rexn. Limited

So, our reaction rate equals C s naught, why is that? Because, if I look back my reaction rate was given by, so K observed equals K double K double prime K f over K double prime plus K f. So, my R equals K observed time C s naught which is K double over 1 plus K f by double k prime, right. Because, so K double prime over 1 plus D a times C s naught right, so in this if D a is much much less than 1, then my R double prime goes to K double prime C s naught, is that clear.

So, what what is this now, this is reaction limited right, why is it reaction limited? Because the reaction rate that you get over here, is same as the reaction rate in the absence of mass transfer, which reaction limited means where it will mass transfer resistance.

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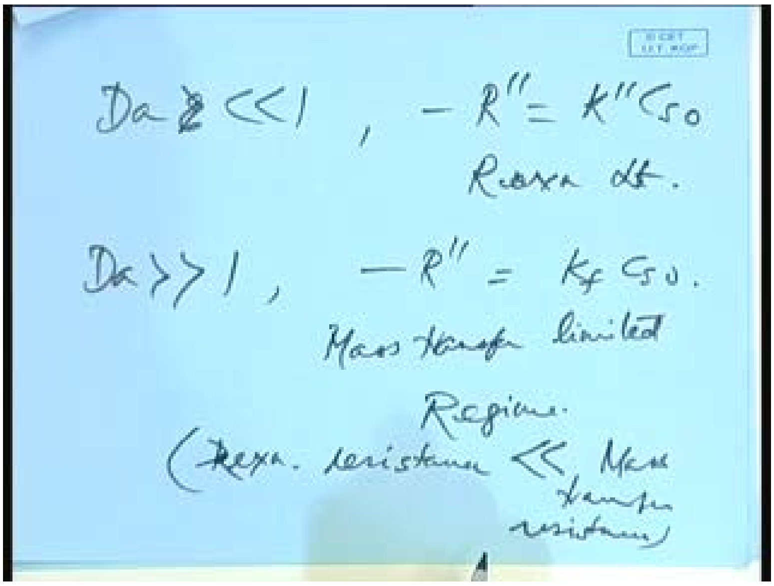

$Da \ll 1$ , $-R'' = k''C_{so}$

Reaxn. ltd.

$Da \gg 1$, $-R'' = k_f C_{so}$.

Mass transfer limited

Regime.

(Reaxn. resistance $\ll$ Mass transfer resistance)

So, let us look at the other end, so just to summarize. So, D a  much much much less than 1 minus R prime equals K double prime C s naught. So, reaction limited and D a much much greater than 1, then your minus R double prime equals equals  K f C s naught right, because it is it is much much greater than you take the inverse of that take the inverse of that and take the limit, because here if you if you look here, you cannot take the limit directly this will you know.

So, basically what you have to do is, put this over here. So, you will have K double prime over D a and then, substitute back in that. So, K double prime over D a and then D a equals K f over then K double prime over K f and then, you will get K f over C s K f over Cs.

So, this will be your mass transfer limited regime, which means that reaction resistance much much smaller than mass transfer resistance, because we have defined the way we have defined our Damkohler number is my mass transfer time over reaction time, so I will put this over here. So, the way we defined our Damkohler number is mass transfer time over reaction time. So, if I mass Damkohler number is very large, it means the mass transfer time you know is large and if it is very small, and then the reaction time is large. So, this is reaction rate over mass transfer rate, is that clear?

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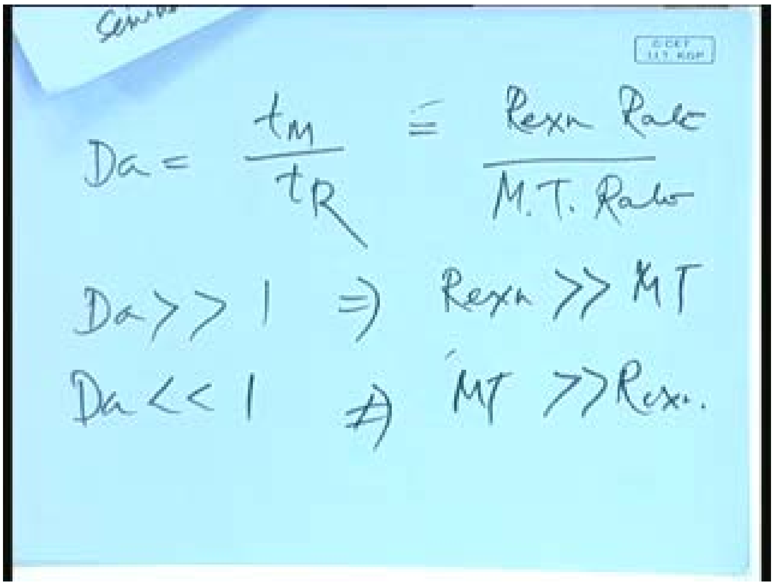

$$Da = \frac{t_M}{t_R} \equiv \frac{\text{Rexn Rate}}{\text{M.T. Rate}}$$

$$Da >> 1 \Rightarrow \text{Rexn} >> \text{MT}$$

$$Da << 1 \Rightarrow \text{MT} >> \text{Rexn.}$$

Let me write it clearly here, so Damkohler number equals mass transfer time over reaction time, equals reaction rate over mass transfer rate. So, if my Damkohler number is much much greater than 1, it means that reaction much much faster than mass transfer; if this is much much less than 1, it means mass mass transfer much much faster than reaction right. So, based on this, we can get the two asymptotes of mass transfer limitations and reaction limitations.

So, I think we will stop here and we will continue with the mass transfer coefficients at different different flows and then looking at interface mass transfer in next week's lecture, so thank you.