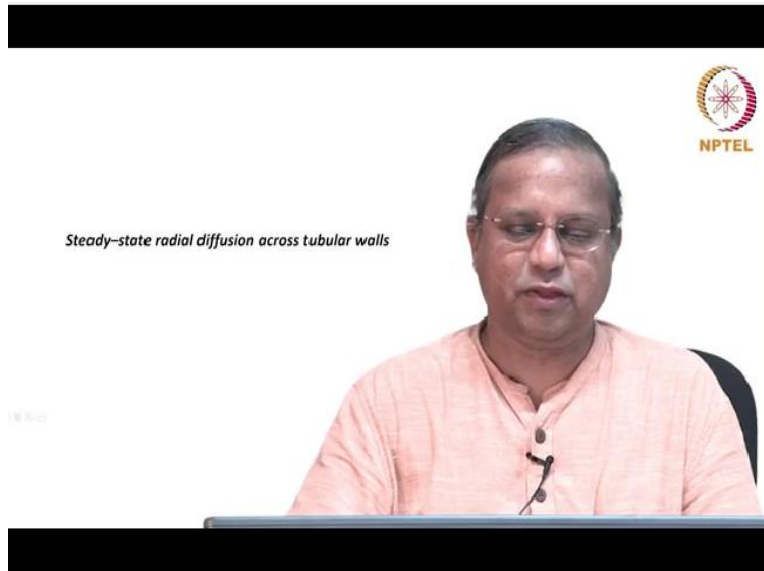


Transport Phenomena in Biological Systems
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Lecture-12
Steady-state Diffusion across Tubular Walls

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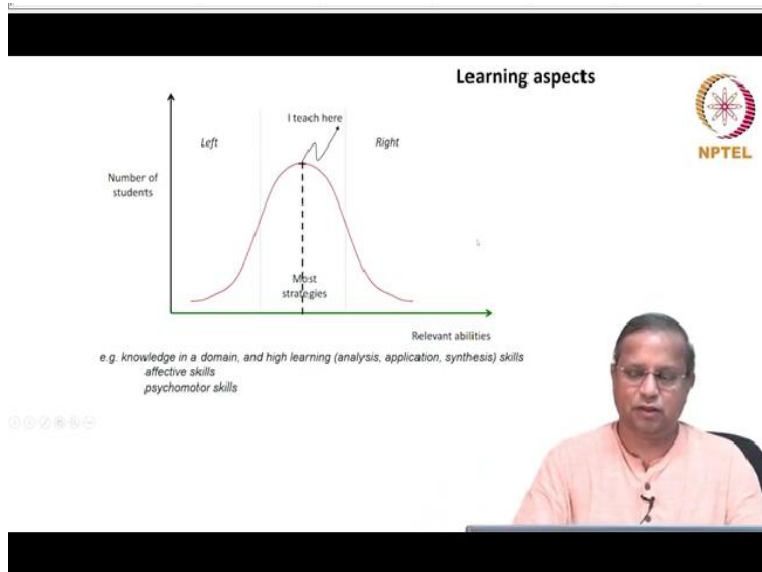


Welcome, today, let us start looking at steady state radial diffusion across tubular walls. To recall a little bit, we are looking at mass flux, we said that there are 2 major aspects or 2 major approaches to solve relevant problems in this area. One is through what is called a shell balance approach. We write material balances over a representative shell for the system of interest and then use those balances to get to useful expressions which can give us insights.

And it also help us in first design then operation of these systems, we earlier did both these approaches while doing the conservation equation approach, we derived the conservation equation that is necessary for us to do this approach and then we applied that to a membrane, cuboidal membrane that is a thin membrane and therefore, we could use the rectangular Cartesian coordinate system to analyze that situation.

That of course, has many different applications as we have already seen in the last class. In this class we will start looking at the application of the same steady state diffusion, steady state means the properties at a particular point in the system do not change with time, steady state diffusion across tubular walls. So, the system is going to be a cylindrical system. A cylindrical system, therefore, we need to use cylindrical coordinates and so on.

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Before we start doing that, I think I need to tell you something about the way I teach, because we have gone through quite a few lectures in this course. Some of you may have found this very easy, may have felt that I was repeating too many things and so on and so forth. Whereas, others may have felt a little lost, both are very natural, the majority would have felt fine with it.

This I can say with confidence based on experience honed by a feedback that I have received both in earlier courses done in this fashion, the NPTEL courses. I have done about 4 already, as well as through classroom teaching and so on so forth, where we get direct feedback, feedback can be of many forms, one is direct feedback, then we get to see how people have understood based on the performance of the exam.

Based on the way they answer questions in class, the way they understand things in class and so on so forth. Based on all those things, I have a pretty good idea to teach at a certain level, where a majority of students would feel comfortable, whereas, these 2 would also happen, let us try to

understand that a little better. So, that, you know, the expectations can be appropriately honed, and you could tune your approach to this course, to get the maximum out of this course.

I also have an interest in the learning process and therefore, I spent time understanding these things. This is from a published paper or the work towards a published paper which is subsequently published. So, let us look at the learning aspects, in a group or in a population if you want to call it so, of anything beyond 15 to 20 people, 18 to 20 students, whatever I am going to say is very nicely valid.

If you plot the number of students or number of people in the population under consideration on the Y axis and what I call the relevant abilities on the X axis, it is typically a variation in the form of a Gaussian curve that you see here, you know, the bell shaped curve. What this means is that there are few who have lower element abilities. There are a few who have high relevant abilities and a majority of the population will have an ability at a certain level, which can be considered as the average ability of the population .

The most number of students as indicated by this point on the Y axis, this is what you see time and again, you can say it with confidence. Sometimes this is slight skew and all that. Let us not get into that. But this is a very good first approximation to make for this kind of behavior, for this kind of an insight that we are trying to get into a population. By relevant abilities, I mean the following.

It could be knowledge in a domain, it could be high learning, that is analysis, application and synthesis skills. It could be also something called effective skills, the attitude that you bring to learning. It could also include psychomotor skills; how good you are with your hands to get things done and so on and so forth. I am looking at some sort of a combination of these aspects towards learning transport phenomena alone.

That is what I mean by relevant abilities. I am going to limit the relevant abilities to those that are appropriate for this course and therefore, let me say the relevant abilities to the transport phenomena in biological processes course or biological systems course . So, you see a distribution

something like this between number of students and relevant abilities. And as I said earlier, you could draw a line here.

And you could call the students who have a higher set of abilities as people on the right or right students and let us say, the students who have lower than the relevant abilities as left students, this is natural. There is nothing wrong about it. This is the way a population behaves. And majority of people are here, a majority of the learners of this course would also be here, I can say it with full confidence.

There are various strategies that we employ. I may not have told you much, but there are so many strategies that have gone into the design of this course that we present the course and so on and so forth. And most of those strategies are for improving the learning of the majority of students who are at the average level . I have done some work on improving the learning of the right students, as well as improving the learning of the left students.

And some of those are also included in a way in this course, this medium does not allow the numbers especially the huge numbers, does not allow me to effectively handle the right students or the left students exclusively which I do in a normal class. I can handle up to let us say 80, 90 or 100 students and take care of these people very clearly, of course, I do not mention who they are in the class and so on and so forth.

But I know and I can take care of these people through ways, which I have developed over many years. Unfortunately, I cannot do that here . So, let me be satisfied with addressing the most number of students, the numbers of these and the students right and left students are small anyway, as given by this distribution or as shown by this distribution. I teach at this level, and this I have gained through experience and feedback.

I know intuitively how to teach at this level and that is what I do here. Students who are right students would find this boring . They would have gotten whatever I said in the first go and they would feel that, why is this person repeating so much , but that is part of the deal. It is a class that I am addressing. And then there are these left students who genuinely will feel lost, these students

need to put in that extra effort, go over the material a few more times, that is all as needed. You go over the material a few more times and then it will become much easier. This is only for transport phenomena, people who are here for transport phenomena may be very good and something else, which I mean, not even you know, I might completely be bad at. So, it is entirely dependent on the particular aspect that we are focusing on in this case transport phenomena that is all.

Some of my left students are very good sports people. Some of my left students are very good artists, musicians and so on so forth. And some of my left students do very well in other courses, whereas they might find the requirements of this course not to their orientation. That's it. There is nothing wrong with it. So, that is the way the things are I teach here and people who are here probably can move forward at a faster pace.

You do not have to, you can fast forward things and look at things in a typical class in a face to face class, I give exercises which take care of these students. Unfortunately, those exercises cannot be given on a very large number kind of a situation. For the left students, the only suggestion that I have is please go through the material a few times and that should help you significantly.

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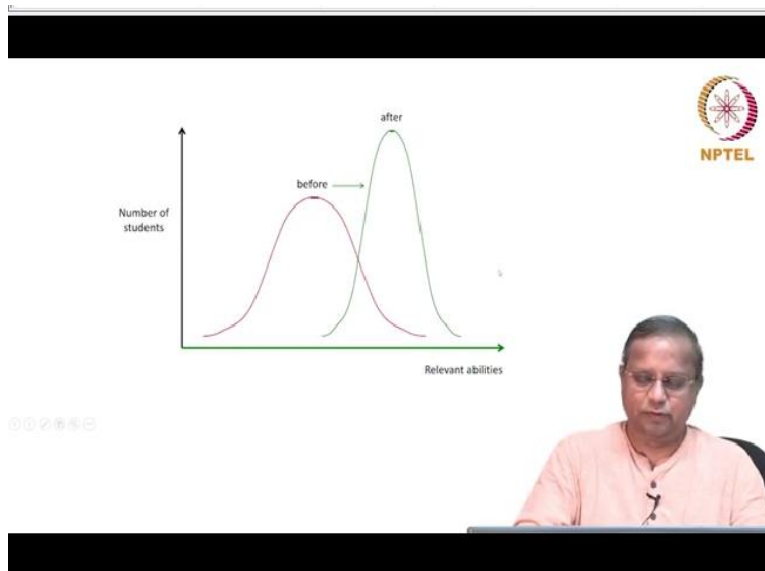
The slide features a central comparison between 'Unlimited time' and 'Limited time'. The text 'Unlimited time' is positioned above 'vs.', which is above 'Limited time'. To the right of this text is the NPTEL logo, a circular emblem with a stylized sunburst and the acronym 'NPTEL' below it. In the bottom right corner, there is a video inset showing a man with glasses and a light-colored shirt speaking. The slide is framed by black bars at the top and bottom.

What typically happens in this course as well as in standard courses that we give in classrooms is that we have a limited time of a semester, where we have this material, the students need to pick

up this material. If we had had unlimited time, then we could give enough time, give enough grooming and so on, so forth, help them, things like that. So, that even the person who finds it the most difficult can get to a certain degree of expertise to be comfortable in the course or to reach a certain level of expertise in the course.

But unfortunately, we do not have this unlimited time, we have a limited time, typically of a semester. Therefore, what we do is we use grades to differentiate between students and so on so forth. Personally, I do not like it but that is the practical way in which things happen, because mainly because of the limited time.

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Ideally, we would like things to be this way. If you look at the same graph the number of students versus the relevant abilities, before the start of the course, if the distribution are something like this, at the end of the course, I would like the distribution to move to the right, of course, because I would like the students to have picked up the abilities relevant for the transport phenomena in biological systems.


And a narrowing of the distribution so that the difference between the left students and the right students is minimized. This is what I am actually after and this is what I do in all my courses. I try to do this in this course in a certain way given the limitations of this format. So, I thought I should

let you know this so that the expectations are clear and your approach is appropriate to get the best out of this course .

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In certain conditions of respiratory difficulty, a drug is administered through the nasal cavity, continuously, at an appropriate dose to reach the lung tissue by passing across the bronchiole wall. The concentration of the drug in the air present in the lumen of the bronchiole is c_0 at steady state. The drug concentration in the lung tissue on the other side of the bronchiole wall is needed to be c_0 for effectiveness. The inner and outer radii of the bronchiole are R_i and R_o , respectively. Derive an expression for the radial drug flux at the inner wall of the bronchiole that is needed to ensure effectiveness of the drug.



Let us move forward, steady state diffusion across tubular walls is what we are going to look at. And one of the strategies that we normally use I am telling you this openly here, I am not going to do that in each part of the course, there are so many strategies, and they have all been worked out in a certain way. If you look at a certain way of doing things, there might be several different strategies associated with it.

So, I am not going to do that. And since we just talked about it, let me tell you the strategy. There is something called problem-based learning. Problem-based learning presents a problem first, and gives you the information to understand the material itself in the context of that problem. That is what problem-based learning is and that is one of the things that I have done in this course, even in this format, to improve the learning.

And this is the way I do it, I throw the problem at you. You think about it, you form your thoughts about it. And that also triggers a few modes of learning which are normally absent when you just give the information and then of course, we pick up the information, strategies and so on, that are required to solve that and thereby we learn something more basic and that hopefully improves understanding, application and so on and so forth.

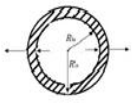
I may not mention many of the strategies that I normally use just this one, fine. Let us get back to this. The problem here is in certain conditions of respiratory difficulty, high time, it's very apt now, given the COVID-19 situation, in certain conditions of respiratory difficulty, a drug is administered through the nasal cavity continuously, at an appropriate dose to reach the lung tissue by passing across the bronchiole wall .

You all know this; you are all bio people. You know that the air goes through the trachea and then through the bronchi, which branches onto the bronchioles which ends up in the alveoli and that is where the gas exchange happens between the air and the blood, which pass through the blood vessels that line the alveoli. We are looking at these cylindrical bronchioles, especially the bronchiole wall(Refer the video for the picture).

So, this is given continuously at an appropriate dose to reach the lung tissue by passing across the bronchiole wall. The concentration of the drug in the air present in the lumen of the bronchiole is c_b at steady state. The drug concentration in the lung tissue on the other side of the bronchiole wall is needed to be seen c_0 for effectiveness. In this case, we are just looking at the bronchiole, we have not gone to the alveoli level.

So, inside the bronchiole, let the concentration be c_b and it has to be c_0 on the other side of the bronchiole wall for effectiveness. The inner and outer radii of the bronchiole are R_b and R_o respectively. Derive an expression for the radial drug flux at the inner wall of the bronchiole that is needed to ensure effectiveness of drug . If you want, you can pause the video here read it once more to understand to make a picture of what is happening here.


I have provided some picture, you can complete the picture in your own minds . Pause go ahead . Hopefully, you have a picture of the situation here in your minds clearly. Now let us look at this.
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Solution

This is a cylindrical system – it will be easier to work with cylindrical co-ordinates
 System: bronchiole wall
 Species: the drug

A mass balance of the species on our system. Here, we can directly use the equation of continuity in cylindrical co-ordinates equation B2 from Table 2.3.2 - 1



$$\begin{aligned}
 &= 0 \text{ (SS)} \quad \Rightarrow 0 \text{ (} v_r = 0 \text{)} \quad \Rightarrow 0 \text{ (} v_\theta = 0 \text{)} \quad \Rightarrow 0 \text{ (} v_z = 0 \text{)} \quad \Rightarrow 0 \text{ (} c_1 = f(\theta) \text{)} \\
 &\frac{\partial c_1}{\partial t} + \left(v_r \frac{\partial c_1}{\partial r} + v_\theta \frac{1}{r} \frac{\partial c_1}{\partial \theta} + v_z \frac{\partial c_1}{\partial z} \right) - D_1 \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_1}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 c_1}{\partial \theta^2} + \frac{\partial^2 c_1}{\partial z^2} \right) = R_1 \quad \Rightarrow 0 \text{ (no rxn)} \\
 &D_1 \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_1}{\partial r} \right) \right) = 0
 \end{aligned}$$

r is the only independent variable now – we can replace the partial derivatives with the total derivatives

$$D_1 \left(\frac{1}{r} \frac{d}{dr} \left(r \frac{dc_1}{dr} \right) \right) = 0 \quad \text{Eq. 2.4.2. - 1}$$

$$c_1 = Kc_b \text{ at } r = R_b \quad \text{Eq. 2.4.2. - 2}$$

$$c_1 = Kc_o \text{ at } r = R_o \quad \text{Eq. 2.4.2. - 3}$$

K = distribution co-efficient, the ratio of the drug concentrations in the two phases at equilibrium (identify phases in Figure)

The solution, so this is the cross section of the bronchiole, a bronchiole is like tubular, if you cut across it and look at it from the side, it is going to look as 2 concentric circles, the outer radius at R_o from here and the inner radius of the bronchiole wall being R_b , this is the inner part, this is the outer part and the hashed portion is the bronchiole wall(Refer to the picture on the video).

We are interested in the drug passing through the bronchiole wall from the lumen, the inside of the bronchiole to the outside of the bronchiole. This is a cylindrical system as you could see and therefore, it may be easier to work with cylindrical coordinates. Yes, it is going to be easier to work with cylindrical coordinates. If you draw a rectangular Cartesian coordinate system, how would you handle the variation in these curved paths and that becomes very messy.

That is the reason why we have a totally different coordinate system to handle these aspects. So, the system is the bronchiole wall which is already hashed here, the species is a drug that transfers from here to here and let us write a mass balance of the species on our system, system is a bronchiole wall. And here we already derived, gone through the pain, we have derived something that can be directly applied.

And we have it of the form that can be directly applied in cylindrical coordinate system in the table that was given to you earlier, hopefully you have made a copy of the table, you could refer to that and if you look at that table, equation B2 table 2.3.2 - 1, it will be something like this.

Cylindrical coordinates

$$\frac{\partial c_A}{\partial t} + \left(\frac{1}{r} \frac{\partial}{\partial r} (r N_{Ar}) + \frac{1}{r} \frac{\partial N_{A\theta}}{\partial \theta} + \frac{\partial N_{Az}}{\partial z} \right) = R_A \quad (\text{B1})$$

When c and D_{AB} are constant

$$\begin{aligned} \frac{\partial c_A}{\partial t} + \left(v_r \frac{\partial c_A}{\partial r} + v_\theta \frac{1}{r} \frac{\partial c_A}{\partial \theta} + v_z \frac{\partial c_A}{\partial z} \right) \\ - D_{AB} \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_A}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 c_A}{\partial \theta^2} + \frac{\partial^2 c_A}{\partial z^2} \right) = R_A \end{aligned} \quad (\text{B2})$$

You do not have to remember any of this, you already have that in the table, you just see that, it fits in, this is the cylindrical coordinate system. Therefore, that form of the material balance equation needs to be valid and therefore we take it directly here. Now, let us start seeing which of these terms are relevant in this particular case. Let me start you out. This of course is $0 \left(\frac{\partial c_A}{\partial t} = 0 \right)$ as we are analyzing steady state situation.

And therefore, any time derivative is set to 0. We already know that there is no fluid motion, there is fluid motion of course, the air is flowing in the lumen, in the axial direction or the z direction there is certainly a flow, but that z direction is not the direction of interest for us, we are looking at the r direction for the transport. Therefore, in that direction there is no motion, there is no bulk motion, there is no convective motion of the fluid.

And as long as you do not have bulk motion, convective motion, the motion of the fluid itself, these velocities which correspond to such motion can directly be set to 0. In fact, in the entire chapter here, these terms will be 0, these will come in only in the 6th chapter, just to make it clear to you, these are convective or bulk motion parameters v_r , v_θ and v_z that all be 0, till we get to the 6th, to the last chapter.

So, if you have, I hope you have understood the bulk motion, convective motion particle, the fluid itself needs to move, v_r , v_θ and v_z are the velocity components of the fluid motion. Even though the fluid is not moving across the wall the species is moving by diffusion rate I hope you got that. So, because of that v_r , v_θ and v_z are all 0.

That is what c_A is, needs to be the same at a certain radial position at all the angular positions right. Therefore, c_A is not a function of θ and therefore, that goes to 0. There is radial symmetry here. At any radius, if you look at the concentration of the drug, it has to be the same. Similarly, we are not interested in the z aspect at all we assume that there is no change in the concentration of the drug over the length of the bronchiole that we are considering.

And therefore, of the length of the system that is the bronchiolar wall that we are considering and therefore, that goes to 0 right. So, this is not the lumen, this is the z axis of the system which is the bronchiole wall, there is no variation in concentration we are considering a situation where there is no variation in the concentration of the drug in the lumen and therefore, there can be no variation of the concentration of the drug on the wall.

And therefore, that goes to 0. And of course, there is no reaction happening here it is a simple diffusion, simple transport of the drug from the inside of the lumen to the outside of the lumen, and therefore, that goes to 0. So, in one step, we have this by canceling the terms, we have the relevant equation that we need to consider, that makes it simple, you could also do a shell balance, you needed to have considered cylindrical shell in the space.

And then that balances over it and then arrived at this 0, or you would have arrived at the same thing after about 4 pages of working, . So, it is a little cumbersome that is all, but we already have this and there are no difficulties of the kind that we mentioned earlier in an area and so on and so forth. Therefore, this is fine. So, this is the equation that we need to work with, there is the only term remaining, as given below.

Consider Eq. B2 from Table 2.3.2-1

$$\frac{\partial c_A}{\partial t} + \left(v_r \frac{\partial c_A}{\partial r} + v_\theta \frac{1}{r} \frac{\partial c_A}{\partial \theta} + v_z \frac{\partial c_A}{\partial z} \right) - D_{AB} \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_A}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 c_A}{\partial \theta^2} + \frac{\partial^2 c_A}{\partial z^2} \right) = R_A$$

$\begin{matrix} = 0 \text{ (SS)} & = 0 \text{ (} v_r = 0 \text{)} & = 0 \text{ (} v_\theta = 0 \text{)} & \begin{matrix} = 0 \text{ (} c_A \\ \neq f(z) \end{matrix} \\ \nearrow & \nearrow & \nearrow & \nearrow \end{matrix}$
 $\begin{matrix} = 0 \text{ (} c_A \\ \neq f(\theta) \end{matrix} & = 0 \text{ (} c_A \\ \neq f(z) \end{matrix} & = 0 \text{ (no } r \text{ in)} \end{matrix}$

Hence

$$D_{AB} \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_A}{\partial r} \right) \right) = 0$$

Since r is the only independent variable here, we can replace the partial derivatives with total derivatives. Thus

$$D_{AB} \left(\frac{1}{r} \frac{d}{dr} \left(r \frac{dc_A}{dr} \right) \right) = 0 \quad (2.4.2-1)$$

The boundary conditions are

$$c_A = Kc_b \text{ at } r = R_b \quad (2.4.2-2)$$

$$c_A = Kc_o \text{ at } r = R_o \quad (2.4.2-3)$$


where K is the distribution coefficient, i.e. the ratio of the drug concentrations in the two phases at equilibrium. For Eq. 2.4.2-2, the phases are the air inside the bronchiole and the bronchiole wall. For Eq. 2.4.2-3 the phases are the air outside the bronchiole and the bronchiole wall.

There is no variation in θ and there is no variation in the z . Since r is only independent variable, the partial derivatives can be replaced with total derivatives, r is the only variable that is going to vary. Therefore, I am just replacing the partials with the total derivative as given in the equation 2.4.2 - 1. And this being a differential equation, we need 2 boundary conditions. This is a second order differential equation. So, we need 2 boundary conditions to solve. The boundary conditions are at r equals R_b which is the inside wall, c_A , the concentration of the drug in the membrane is K times the concentration of the drug in the lumen(c_b) right.

K is the partition coefficient; we have already seen the concept of a partition coefficient earlier. So, just take the same thing or if you need to understand that go back to the previous problem the diffusion across a flat membrane and then understand the partition coefficient. This is equation 2.4.2 - 2 the boundary condition. The other boundary condition is on the other side at R equals R_o ,

which is the outer wall, c_A equals Kc_0 . c_0 needs to be the concentration here. Therefore, the concentration on the membrane would be the partition coefficient times c_0 and that is what this is we will call this equation 2.4.2 - 3 right, for completeness, the ratio of the drug concentrations in the 2 phases are at equilibrium and of course, we have already identified those in the figure.

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Solving Eq. 2.4.2 - 1 (derivative in Eq. 2.4.2 - 1 = zero, implies $r \frac{dc_A}{dr} = \text{constant, say } C_1$),

$$c_A = C_1 \ln r + C_2 \quad \text{Eq. 2.4.2 - 4}$$

Substituting the boundary conditions,


$$C_1 = \frac{K(c_b - c_0)}{\ln\left(\frac{R_b}{R_a}\right)}$$

$$C_2 = Kc_b - K(c_b - c_0) \frac{\ln R_b}{\ln\left(\frac{R_b}{R_a}\right)}$$

By substituting C_1 and C_2 in Eq. 2.4.2 - 4 and by rearranging,

$$c_A = Kc_b - K(c_b - c_0) \frac{\ln\left(\frac{R_b}{r}\right)}{\ln\left(\frac{R_b}{R_a}\right)} \quad \text{Eq. 2.4.2 - 5}$$

Therefore, the flux at R_b

$$\bar{J}_A = -D_{AB} \left. \frac{\partial c_A}{\partial r} \right|_{r=R_b} = \frac{D_{AB} K (C_b - C_0)}{r \ln\left(\frac{R_b}{R_a}\right)} \bigg|_{r=R_b} = \frac{D_{AB} K (C_b - C_0)}{R_b \ln\left(\frac{R_b}{R_a}\right)} \quad \text{Eq. 2.4.2 - 6}$$


,Now let us solve this. The derivative of the whole thing being equal to 0, right that is what this is implying that this derivative needs to be a constant. So, the derivative of a constant, of course is 0. And that's the way by which this whole expression can be equal to 0. And therefore, $r (dc_A/ dr)$ has to be a constant. Let us call $r (dc_A/dr)$ as C_1 .

On solving Eq. 2.4.2-1 (note that for the derivative in the equation to be zero, $r \frac{dC_A}{dr} = \text{constant}$, say C_1), we get

$$c_A = C_1 \ln r + C_2 \quad (2.4.2-4)$$

Using the boundary conditions, we can get

$$C_1 = \frac{K(c_b - c_o)}{\ln\left(\frac{R_b}{R_o}\right)}$$

$$C_2 = Kc_b - K(c_b - c_o) \frac{\ln(R_b)}{\ln\left(\frac{R_b}{R_o}\right)}$$

If you are unclear, I would like you to stop the video here. Go back substitute these boundary conditions c_A equals Kc_b at r equals R_b and c_A equals Kc_o at r equals R_o into this solution here and find out C_1 and C_2 and convince yourself that it is indeed the case .

Now by substituting C_1 and C_2 back in this and by rearranging, we will get,

$$C_A = Kc_b - K(C_b - C_o) \frac{\ln\left(\frac{R_b}{r}\right)}{\ln\left(\frac{R_b}{R_o}\right)} \quad (2.4.2-5)$$

Thus, the flux at R_b

$$\bar{J}_A^* = -D_{AB} \frac{\partial C_A}{\partial r} \Big|_{r=R_b} = \frac{D_{AB} K (C_b - C_o)}{r \ln\left(\frac{R_b}{R_o}\right)} \Big|_{r=R_b} = \frac{D_{AB} K (C_b - C_o)}{R_b \ln\left(\frac{R_b}{R_o}\right)} \quad (2.4.2-6)$$

And therefore the flux at R_b which is what we are required to find as a part of this problem, is nothing but a diffusive flux which is given by the Fick's first law - $D_{AB} \frac{\partial c_A}{\partial r}$ at r equals R_b . We

obtained an expression for c_A and that should be first substituted in the flux equation and then differentiated with respect to r . And then we substitute $r = R_b$. So, we have a nice concentration profile which is typically what we look at first depending on what we need for our analysis or design.

And then in this case, we are looking at the flux. What I would like you to do is please use a spreadsheet software such as Microsoft Excel or something like that and plot this and see what the variation of c_A is with r . That would be interesting that would provide insights into the way the concentration varies in the wall of the bronchiole; like looking through microscope, a really clear way to understand that better and so on.

And interestingly in this we have seen earlier also, the flux is nothing but all constancy, D_{AB} is a constant, K is a constant, c_b is given, constant. c_b is the drug concentration the lumen, c_0 is the drug concentration in the tissue on the other side of the bronchiole wall, all are constants here. For a given bronchiole, R_b and R_o are fixed and therefore, the molar flux of the drug turns out to be a constant at steady state.

So, these are some nice insights that we can draw which can be used in any way that you need for your purpose. Good. So, we have looked at some learning aspects first to get an idea of as to how to approach this course. And then, we saw the application of the conservation equation to a cylindrical system, in this case a drug diffusion across the bronchiole wall. When we meet next we will take things for you, see you.