Transport Phenomena in Biological Systems
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Lecture - 14
Steady-state Diffusion with Reaction

Welcome back. Today we will look at slightly more complicated situation, okay. Steady state radial diffusion in spherical particles but we will add a reaction there okay. And this situation finds very many different applications as you can yourself see when we go through the actual situation. In fact, one of the applications is being presented as a problem here for us to consider. So steady state radial diffusion in spherical pellets with reaction.

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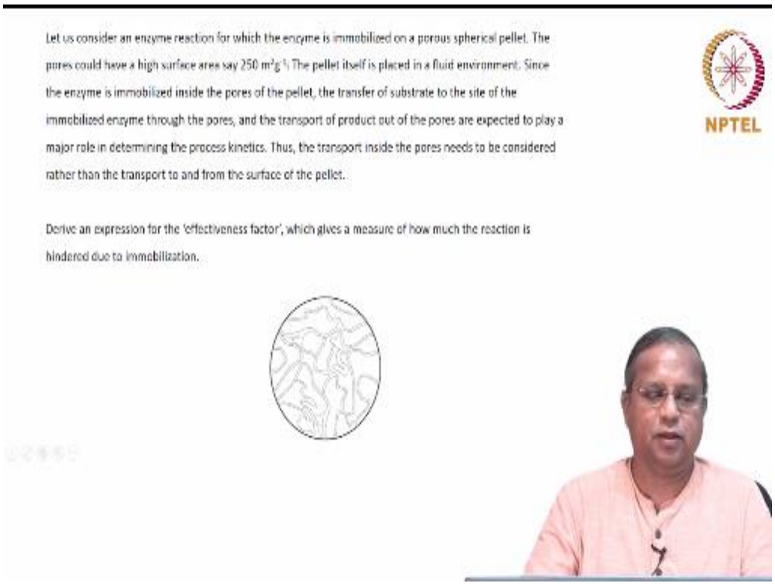

Let us consider an enzyme reaction for which the enzyme is immobilized on a porous spherical pellet. The pores could have a high surface area say 250 m^2g^{-1}. The pellet itself is placed in a fluid environment. Since the enzyme is immobilized inside the pores of the pellet, the transfer of substrate to the site of the immobilized enzyme through the pores, and the transport of product out of the pores are expected to play a major role in determining the process kinetics. Thus, the transport inside the pores needs to be considered rather than the transport to and from the surface of the pellet.

Derive an expression for the 'effectiveness factor', which gives a measure of how much the reaction is hindered due to immobilization.

So to do that to understand this let us consider doing this problem. Let us consider an enzyme reaction for which the enzyme is immobilized on a porous spherical pellet. The pores could have a high surface area that is say approximately 250 m^2/g is very standard in these situations, high huge surface area, one gram of the substance has 250 m^2.

The pellet itself is placed in a fluid environment. Since the enzyme is immobilized inside the pores of the pellet, the transfer of substance to the site of the immobilized enzyme through the pores and the transport of product out of the pores are expected to play a major role in determining process kinetics, okay. So the substrate needs to get to the place of the enzyme, it is in the pores, it needs to get there.

And then there the reaction happens. It gets converted to a product. It needs to get out, the product needs to get out of the pores back to the surface and so on so forth. So both those are expected to play a role here. Thus, the transport inside the pores needs to be considered rather than the transport to and fro from the surface of the pellet. We are interested in the transport inside the pores.

We are not so much worried about how the transport, it is in a fluid environment and the substrate is in the fluid and how it transfers from the bulk of the fluid to the surface is not much of our interest. The other process, **how it goes from the surface through the pores to the site of the enzyme that is more our interest here**.

What you are asked to do is derive an expression for something called an effectiveness factor which gives a measure of how much the reaction is hindered due to immobilization, okay. Suppose you had the enzyme free in a fluid, how quickly it reacts. That there is a certain process kinetics associated with, the process speed associated with it. By immobilizing that on to the pores in the in a certain pellet here, how much does it get hindered?

By how much does the process rate decrease is a very important thing to know while working with immobilized enzymes okay. So this is a, this is a direct application. Very many different applications immobilized enzymes are used in so many different processes by processes across the world to produce products with billions of dollars a year and so on so forth.

And therefore, this is all depend on whatever we are going to look at in this particular analysis. In fact, people need to analyze this and then understand this and then design the various aspects of their bio reactors to optimize their production. Okay, let us start looking at this.

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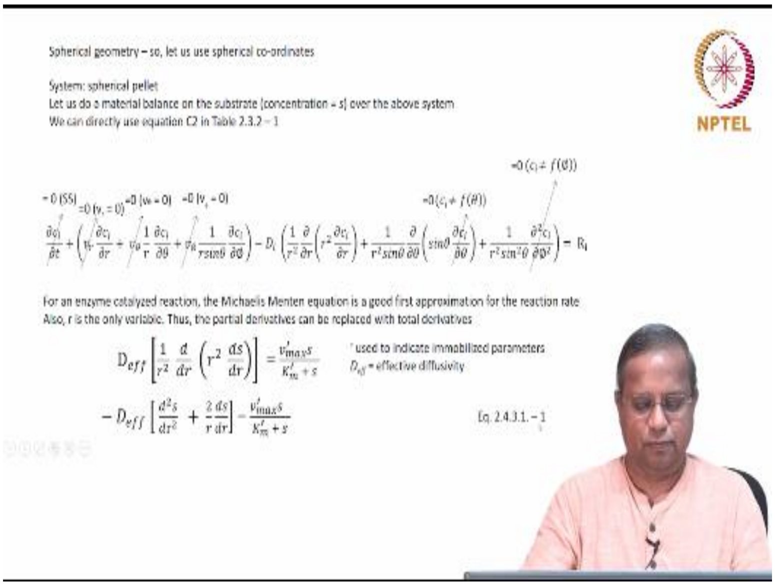

Spherical geometry – so, let us use spherical co-ordinates

System: spherical pellet
Let us do a material balance on the substrate (concentration = s) over the above system
We can directly use equation C2 in Table 2.3.2 – 1

$$\overset{=0\,(SS)}{\cancel{\frac{\partial c_i}{\partial t}}}+\left(\overset{=0\,(v_r=0)}{\cancel{v_r\frac{\partial c_i}{\partial r}}}+\overset{=0\,(v_\theta=0)}{\cancel{v_\theta\frac{1}{r}\frac{\partial c_i}{\partial \theta}}}+\overset{=0\,(v_\phi=0)}{\cancel{v_\phi\frac{1}{r\sin\theta}\frac{\partial c_i}{\partial \phi}}}\right)-D_i\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c_i}{\partial r}\right)+\overset{=0\,(c_i\neq f(\theta))}{\cancel{\frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial c_i}{\partial \theta}\right)}}+\overset{=0\,(c_i\neq f(\phi))}{\cancel{\frac{1}{r^2\sin^2\theta}\frac{\partial^2 c_i}{\partial \phi^2}}}\right)=R_i$$

For an enzyme catalyzed reaction, the Michaelis Menten equation is a good first approximation for the reaction rate
Also, r is the only variable. Thus, the partial derivatives can be replaced with total derivatives

$$D_{eff}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{ds}{dr}\right)\right]=\frac{v'_{max}s}{K'_m+s}$$

' used to indicate immobilized parameters
D_{eff} = effective diffusivity

$$-D_{eff}\left[\frac{d^2s}{dr^2}+\frac{2}{r}\frac{ds}{dr}\right]=\frac{v'_{max}s}{K'_m+s}$$

Eq. 2.4.3.1. – 1

Spherical geometry therefore, we will use spherical coordinates. In this case, we are interested in the processes that happen inside the sphere into which the enzyme is immobilized itself. We are not worried about what happens outside. This system, therefore is a spherical pellet, and let us do a material balance on the substrate. The concentration of the substrate is **s** over this system.

You know what to do now. We go to, it is a spherical coordinate system. Go to table 2.3.2-1 to do the material balance. Pick out equation C2 because the concentration, total concentration and the diffusivity are constants. And that is the reason why we are picking C2 over C1. And if you do that, we have already seen this equation earlier. Let us not go, let me not go through term by term again.

So this is the equation C2, which is the material balance equation and we are doing the material balance on the substrate here, okay. So the c_i is nothing but **s** as we know. No c_i, the concentration of the substrate in the liquid is s, is some s. Let us see how we are going to do that. It is going to be c_i or s we will see. I think we switch to s and see.

So if you look at the terms that are relevant here, it is a steady state analysis. That is what we have decided to do. Most processes are at steady state for most of the time okay except for batch processes. The steady state analysis can be used to make sense of many different situations. The therefore this goes to 0. There is no variation with respect to time.

There is no bulk fluid motion. There is no convective fluid motion that is and therefore v_r, v_θ, v_φ are 0. This of course remains. There is angular symmetry and therefore there is no variation with θ. θ is this angle. There is no variation with φ which is this angle. And of course, there is a reaction that is happening here, okay. So the only difference between the earlier case in the growth factor, and this case is this **reaction term** R_i, okay.

For the enzyme catalyzed reaction, the Michaelis Menten equation is a very good first approximation, we all know this from the various courses that we have done. And also r is the only variable and therefore, we can replace the partial derivatives with the total derivatives. So if we do that, we get, I am going to replace the i with the effective for the pores and so on so forth. Of course, I am using v'_{max} and k'_m in the place of v_{max} and k_{max}. That is only because when we immobilize things, the parameter when we immobilize enzymes, the parameters could change or they normally change. And therefore, the v_{max} in solution may not be equal to the v_{max} when it is immobilized. And therefore, to differentiate that I am using this ' here. D_{eff} is the effective diffusivity. And if I expand this, it is not equal to zero. So I cannot take this to be constant and so on. Therefore, I will have to expand this.

You do the differentiation, term by term using the product rule. And then there is $\frac{1}{r^2}$ term. So sum of those terms will cancel and finally, you will get this. So please work things out, pause the video here work things out if you are not clear, okay. Each one of these mathematical steps that I have shown, I have tried to make them as detailed as possible. But you will have to draw a line somewhere.

$$-D_{\text{eff}}\left[\frac{d^2 s}{dr^2}+\frac{2}{r}\frac{ds}{dr}\right]=\frac{v'_{\max}s}{K'_m+s} \qquad (2.4.3.1\text{-}1)$$

If you feel uncomfortable, then stop and work step by step. I am sure if you do that, you will feel lot more comfortable. You do not have to take things at face value. No, you know exactly how things come about and that you know, that improves the confidence significantly. It is no longer some black box kind of a thing. Let us call this equation 2.4.3.1-1.

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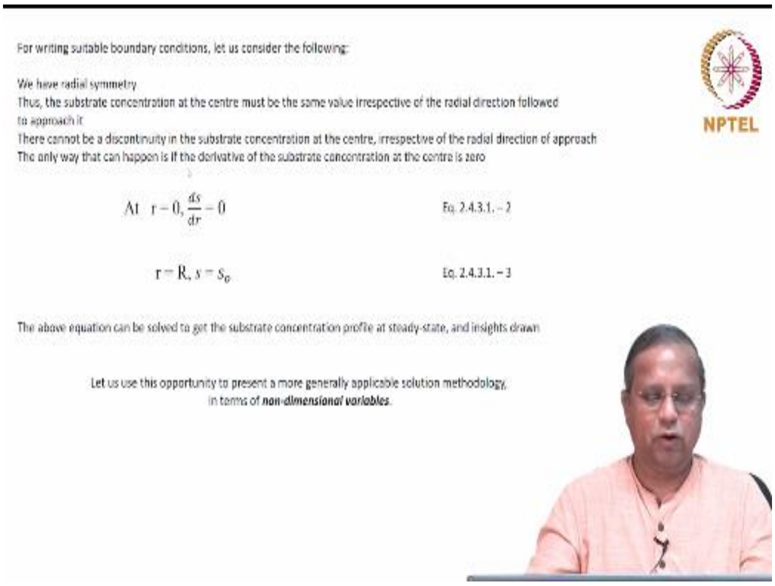

For writing suitable boundary conditions, let us consider the following:

We have radial symmetry

Thus, the substrate concentration at the centre must be the same value irrespective of the radial direction followed to approach it

There cannot be a discontinuity in the substrate concentration at the centre, irrespective of the radial direction of approach

The only way that can happen is if the derivative of the substrate concentration at the centre is zero

$$\text{At} \quad r = 0, \frac{ds}{dr} = 0 \qquad \text{Eq. 2.4.3.1.} - 2$$

$$r = R, s = s_0 \qquad \text{Eq. 2.4.3.1.} - 3$$

The above equation can be solved to get the substrate concentration profile at steady-state, and insights drawn

Let us use this opportunity to present a more generally applicable solution methodology, in terms of ***non-dimensional variables***.

For writing the boundary conditions, let us consider the following. We have radial symmetry, okay. And when we model something that has to reflect some key aspects of reality. Otherwise, there is no point right? The we have radial symmetry and therefore whether you approach using this radius, this radius, this radius, this radius, you should reach the same condition at the center, okay?

So that is physical reality. It is a single pellet. How you traverse and because there is spherical symmetry, the concentration of something at the center has to be the same irrespective of the direction of traversing. So the substrate concentration at the center must be the same value irrespective of the radial direction followed to approach it. And this is physical, this is mandated by physical reality.

So in other words there cannot be a discontinuity. If you approach here it is some s and if you approach here it is some s’ that cannot be the case. Therefore, there cannot be a discontinuity in the substrate concentration at the center irrespective of the radial direction of approach. And the only way in which this can happen is that the concentration at the center either goes through a maximum or a minimum of the profile, okay.

In this case it will be a minimum because there is a continuous decrease, it could be a maximum. I mean mathematically speaking, the derivative needs to go to zero. Physically speaking the concentration needs to be either a maximum or a minimum at that point for reality to be valid, okay? So the only way this can happen is that if the derivative of the substrate concentration at the center is zero.

Think about this. If you are unclear about this, send me an email. We will discuss more and I will try to clarify this better. Therefore, at r equals R, the derivative of the substrate concentration with respect to radius has to be zero. This of course, is the condition for the maxima as you all know or one of the conditions for the maxima or minima, extrema let us say.

Boundary conditions:

At $$r = 0, \frac{ds}{dr} = 0 \qquad (2.4.3.1\text{-}2)$$

$$r = R,\ S = S_o \qquad (2.4.3.1\text{-}3)$$

And the above equation which is this needs to be solved with those boundary conditions to get at the particular solution. If you do that we will get the variation of the substrate concentration with radius.

And that is what we are after. What we are going to do is I am going to use this opportunity to introduce to you a slightly different way of solving which makes the solution a lot more general by the way we get the solution itself okay. We are going to use something called non-dimensional parameter. So whether it is a pellet of this size, or a pellet of this size, or a pellet of this size, it does not make a difference in the solution that we get.

The solution is better in general for any size just by looking at it. You do not have even have to substitute various things and see. Just by looking at it that becomes valid. And that can be achieved by the use of non-dimensional variables. We look at non-dimensional variables from a slightly different context later in the course. But let me introduce the non-dimensional variables.

As the name implies non-dimensional variables do not have a dimension, okay. So there is a non-dimensional variable for distance. There is a non-dimensional variable for other things and so on so forth. Okay, let us look at this. Before solving this, we are going to convert the equation in terms of non-dimensional variables and solve it. And thereby the solution becomes general.

We just have to finally substitute the actual values of a system to get the particular solution that is all. And the solution in terms of the non-dimensional variables themselves is applicable in general. It is not dependent on the particular radius and things like that.

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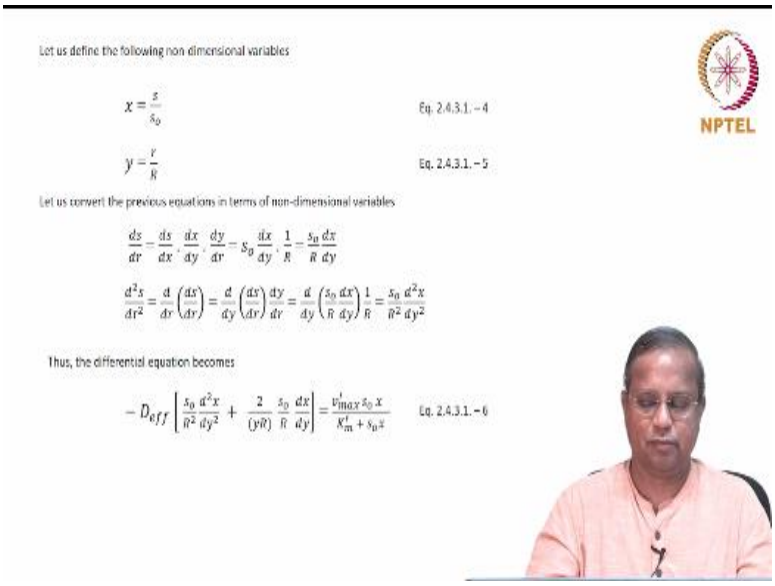

Let us define the following non dimensional variables

$$x = \frac{s}{s_0} \qquad \text{Eq. 2.4.3.1.-4}$$

$$y = \frac{r}{R} \qquad \text{Eq. 2.4.3.1.-5}$$

Let us convert the previous equations in terms of non-dimensional variables

$$\frac{ds}{dr} = \frac{ds}{dx} \cdot \frac{dx}{dy} \cdot \frac{dy}{dr} = s_0 \frac{dx}{dy} \cdot \frac{1}{R} = \frac{s_0}{R}\frac{dx}{dy}$$

$$\frac{d^2s}{dr^2} = \frac{d}{dr}\left(\frac{ds}{dr}\right) = \frac{d}{dy}\left(\frac{ds}{dr}\right)\frac{dy}{dr} = \frac{d}{dy}\left(\frac{s_0}{R}\frac{dx}{dy}\right)\frac{1}{R} = \frac{s_0}{R^2}\frac{d^2x}{dy^2}$$

Thus, the differential equation becomes

$$-D_{eff}\left|\frac{s_0}{R^2}\frac{d^2x}{dy^2} + \frac{2}{(yR)}\frac{s_0}{R}\frac{dx}{dy}\right| = \frac{v'_{max}s_0 x}{K'_m + s_0 x} \qquad \text{Eq. 2.4.3.1.-6}$$

Let us define the needed non-dimensional variables as

$$x = \frac{s}{s_o} \qquad (2.4.3.1\text{-}4)$$

$$y = \frac{r}{R} \qquad (2.4.3.1\text{-}5)$$

Now we will have to convert the previous equations in terms of our non-dimensional variables, okay. This is going to take some work and so please be with me. So this is what we are trying to do. We are trying to write the earlier equations in terms of x and y which are non-dimensional variables and lot of math is coming up. So what is $\frac{ds}{dr}$ in terms of our non-dimensional variables? That is one of the things that we have earlier. So this is the standard, this you recall from your earliest math course, engineering mathematics course

$$\frac{ds}{dr} = \frac{ds}{dx} \cdot \frac{dx}{dy} \cdot \frac{dy}{dr} = s_o \frac{dx}{dy} \cdot \frac{1}{R} = \frac{s_o}{R} \frac{dx}{dy}$$

$$\frac{d^2 s}{dr^2} = \frac{d}{dr}\left(\frac{ds}{dr}\right) = \frac{d}{dy}\left(\frac{ds}{dr}\right)\frac{dy}{dr} = \frac{d}{dy}\left(\frac{s_o}{R}\frac{dx}{dy}\right)\frac{1}{R} = \frac{s_o}{R^2}\frac{d^2 x}{dy^2}$$

Thus, the differential equation becomes

$$-D_{\text{eff}}\left[\frac{s_o}{R^2}\frac{d^2 x}{dy^2} + \frac{2}{(yR)}\frac{s_o}{R}\frac{dx}{dy}\right] = \frac{v'_{\max} s_o x}{K'_m + s_o x} \qquad (2.4.3.1\text{-}6)$$

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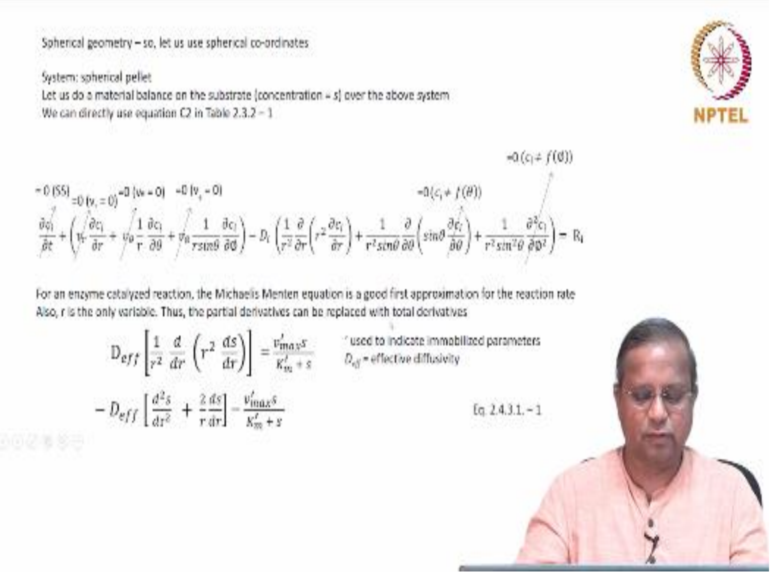

Spherical geometry – so, let us use spherical co-ordinates

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We can directly use equation C2 in Table 2.3.2 – 1

$$\overset{=0\,(SS)}{\frac{\partial c_i}{\partial t}} + \left(\overset{=0\,(v_r=0)}{v_r}\frac{\partial c_i}{\partial r} + \overset{=0\,(v_\theta=0)}{v_\theta}\frac{1}{r}\frac{\partial c_i}{\partial \theta} + \overset{=0\,(v_\phi=0)}{v_\phi}\frac{1}{r\sin\theta}\frac{\partial c_i}{\partial \phi}\right) - D_i\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c_i}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\,\overset{=0\,(c_i\neq f(\theta))}{\frac{\partial c_i}{\partial \theta}}\right) + \frac{1}{r^2\sin^2\theta}\overset{=0\,(c_i\neq f(\phi))}{\frac{\partial^2 c_i}{\partial \phi^2}}\right) = R_i$$

For an enzyme catalyzed reaction, the Michaelis Menten equation is a good first approximation for the reaction rate
Also, r is the only variable. Thus, the partial derivatives can be replaced with total derivatives

$$D_{eff}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{ds}{dr}\right)\right] = \frac{v'_{max}s}{K'_m + s}$$

' used to indicate immobilized parameters
D_{eff} = effective diffusivity

$$-D_{eff}\left[\frac{d^2 s}{dr^2} + \frac{2}{r}\frac{ds}{dr}\right] = \frac{v'_{max}s}{K'_m + s} \qquad \text{Eq. 2.4.3.1.} - 1$$

Stop the video if you are not comfortable with this. Go back, substitute the various things. Convince yourself that this is indeed the case, okay? Then restart the video.

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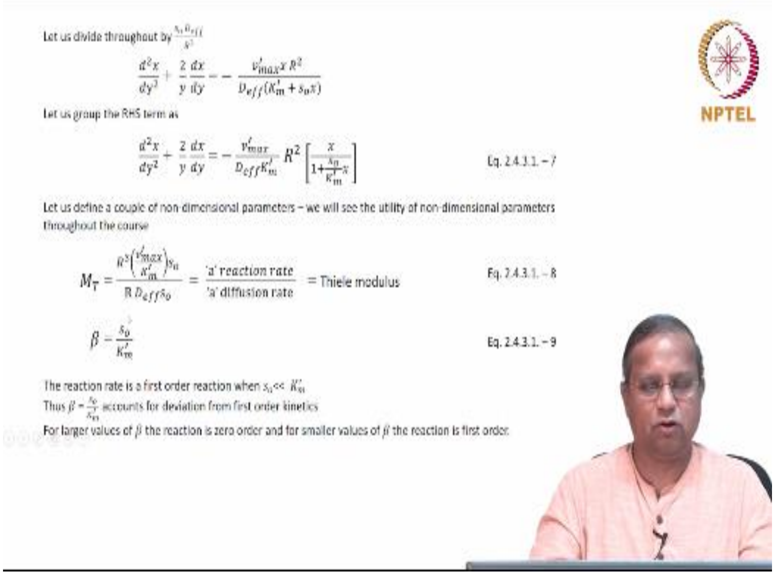

Let us divide throughout by $\frac{s_0 D_{eff}}{R^2}$

$$\frac{d^2 x}{dy^2} + \frac{2}{y}\frac{dx}{dy} = -\frac{v'_{max} x R^2}{D_{eff}(K'_m + s_0 x)}$$

Let us group the RHS term as

$$\frac{d^2 x}{dy^2} + \frac{2}{y}\frac{dx}{dy} = -\frac{v'_{max}}{D_{eff}K'_m}R^2\left[\frac{x}{1+\frac{s_0}{K'_m}x}\right] \qquad \text{Eq. 2.4.3.1.} - 7$$

Let us define a couple of non-dimensional parameters – we will see the utility of non-dimensional parameters throughout the course

$$M_T = \frac{R^2\left(\frac{v'_{max}}{K'_m}\right)s_0}{R\, D_{eff} s_0} = \frac{\text{'a' reaction rate}}{\text{'a' diffusion rate}} = \text{Thiele modulus} \qquad \text{Eq. 2.4.3.1.} - 8$$

$$\beta = \frac{s_0}{K'_m} \qquad \text{Eq. 2.4.3.1.} - 9$$

The reaction rate is a first order reaction when $s_0 << K'_m$
Thus $\beta = \frac{s_0}{K'_m}$ accounts for deviation from first order kinetics
For larger values of β the reaction is zero order and for smaller values of β the reaction is first order

Thus, the differential equation becomes

$$-D_{\text{eff}}\left[\frac{s_o}{R^2}\frac{d^2x}{dy^2}+\frac{2}{(yR)}\frac{s_o}{R}\frac{dx}{dy}\right]=\frac{v'_{\max}s_o x}{K'_m+s_o x} \qquad (2.4.3.1\text{-}6)$$

Dividing throughout by $\frac{s_o D_{\text{eff}}}{R^2}$, we get

$$\frac{d^2x}{dy^2}+\frac{2}{y}\frac{dx}{dy}=-\frac{v'_{\max}xR^2}{D_{\text{eff}}(K'_m+s_o x)}$$

or

$$\frac{d^2x}{dy^2}+\frac{2}{y}\frac{dx}{dy}=-\frac{v'_{\max}}{D_{\text{eff}}K'_m}R^2\left[\frac{x}{1+\frac{s_o}{K'_m}x}\right] \qquad (2.4.3.1\text{-}7)$$

Similar to non-dimensional quantities mentioned earlier in this section, one can think of non-dimensional parameters, which are useful for analysis, as will become apparent later. Let us define some non-dimensional parameters, as follows:

. So we have this. Now we have it of a form that you are comfortable with or you are already familiar with from your mathematics courses. Before we proceed further, remember we are looking at the effect of this factor. Therefore, let us do something here.

Now let us define a couple of non-dimensional parameters. And we will talk about the utility of them much more later. We will talk about it a little bit now also at the end of this. Let us define something called a **Thiele modulus**, which is designated as capital **M_T as a reaction rate divided by a diffusion rate**, okay.

Remember, this is an immobilized situation. In the free situation of course, the rates are going to be much higher, because the immobilized situation is limited by the transport of both the reactant and the product, reactant to the site of the reaction and product away from the site of the reaction. And therefore, we would like to compare the pure reaction rate with a pure diffusion rate.

$$M_T = \frac{R^3\left(\frac{v'_{\max}}{K'_m}\right)s_o}{R\,D_{\text{eff}}\,s_o} = \frac{'a'\text{ reaction rate}}{'a'\text{ diffusion rate}} = \text{Thiele modulus} \qquad (2.4.3.1\text{-}8)$$

$$\beta = \frac{s_o}{K'_m} \qquad (2.4.3.1\text{-}9)$$

When $s_o << K'_m$, the reaction rate is of first order. Thus, $\beta = \frac{s_o}{K'_m}$ accounts for deviation from first order kinetics. For larger values of β, the reaction is of zero order, and for smaller values of β, the reaction is of first order.

Therefore, this is called a Thiele modulus. This is a standard modulus that is used if you look at heterogeneous reactions. And therefore, let us define this Thiele modulus for our situation. The reaction rate is first order when s_0 is much less than k'_m. You know this. So you take a look at the Michaelis Menten equation and recall this situation. And that is being reflected by this β here. And that is the reason why we have taken s_0/k'_m as different parameter here β, which accounts for the deviation from the first order kinetics. You can view that as providing as with how much it deviates from the first order kinetics. For large values of β of course, the reaction is zero order, it does not depend on the concentration at all. And for small values of β, the reaction is first order because it is going to depend on s_0.

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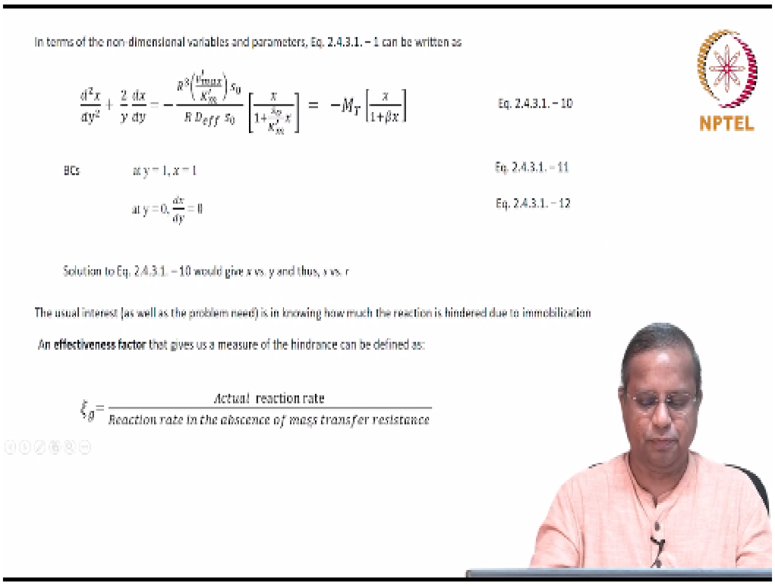


In terms of the non-dimensional variables and parameters, Eq. 2.4.3.1. – 1 can be written as

$$\frac{d^2x}{dy^2} + \frac{2}{y}\frac{dx}{dy} = -\frac{R^3\left(\frac{v'_{max}}{K'_m}\right)s_0}{R\,D_{eff}\,s_0}\left[\frac{x}{1+\frac{s_0}{K'_m}x}\right] = -M_T\left[\frac{x}{1+\beta x}\right] \qquad \text{Eq. 2.4.3.1.} - 10$$

BCs at $y = 1, x = 1$ Eq. 2.4.3.1. – 11

at $y = 0, \frac{dx}{dy} = 0$ Eq. 2.4.3.1. – 12

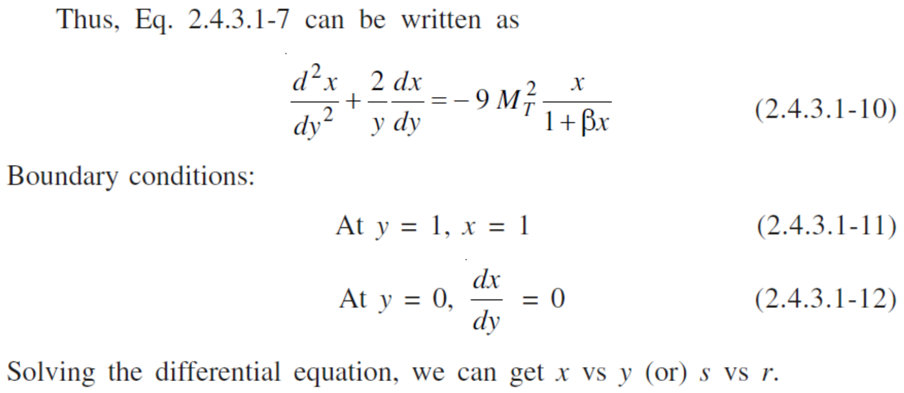
Solution to Eq. 2.4.3.1. – 10 would give x vs. y and thus, s vs. r

The usual interest (as well as the problem need) is in knowing how much the reaction is hindered due to immobilization

An **effectiveness factor** that gives us a measure of the hindrance can be defined as:

$$\xi_g = \frac{Actual\ \ reaction\ rate}{Reaction\ rate\ in\ the\ abscence\ of\ mass\ transfer\ resistance}$$

Okay. In terms of these non-dimensional variables and parameters, you could write the equation that we had earlier as



Thus, Eq. 2.4.3.1-7 can be written as

$$\frac{d^2x}{dy^2}+\frac{2}{y}\frac{dx}{dy}=-9\,M_T^2\,\frac{x}{1+\beta x} \qquad (2.4.3.1\text{-}10)$$

Boundary conditions:

$$\text{At } y = 1,\ x = 1 \qquad (2.4.3.1\text{-}11)$$

$$\text{At } y = 0,\ \frac{dx}{dy} = 0 \qquad (2.4.3.1\text{-}12)$$

Solving the differential equation, we can get x vs y (or) s vs r.

And the boundary conditions are, you know earlier we saw the boundary conditions that at the surface the concentration is the concentration of the liquid and at the center the derivative must be zero, right for continuity.

Therefore, we have completely converted our differential equation as well as the boundary condition in terms of the non-dimensional variables, x and y. Recall what x and y are. If you are unclear, go back and check and then it will be clear to you. Just number the equations for the boundary conditions. Now if I substitute this solution, or rather the solution of this equation of this differential equation would give us the variation of x with y.

And we know what x is we know what y is, and therefore, it will give us the variation of s with r. I am going to leave it at that I am not going to take it forward. You can solve it. You can plot x versus y and then you can use some typical values of the radius of the pellet and so on so forth substrate concentration. See how things vary. Please do that.

That will give you an insight. The usual interest, as well as the problem need is knowing how much the reaction is hindered due to immobilization. And that is the effectiveness factor. So the effectiveness factor is a measure that gives us the hindrance. And we are going to define the effectiveness factor as the actual reaction rate and with all these hindrances, what the reaction rate is divided by the reaction rate in the absence of mass transfer resistance.

Suppose there has been no mass transfer resistance, hypothetical situation there is no mass transfer resistance. What happened? What is the rate at that thing that would be the maximum. And the actual reaction rate is what actually happens with all the processes, the diffusion, the mass transfer and so on so forth included. So what is the ratio? How much is it getting hindered by because of the mobilization is given by this effectiveness factor.

So let us get an expression for the effectiveness factor. That is what is needed in the problem. Let us do that.

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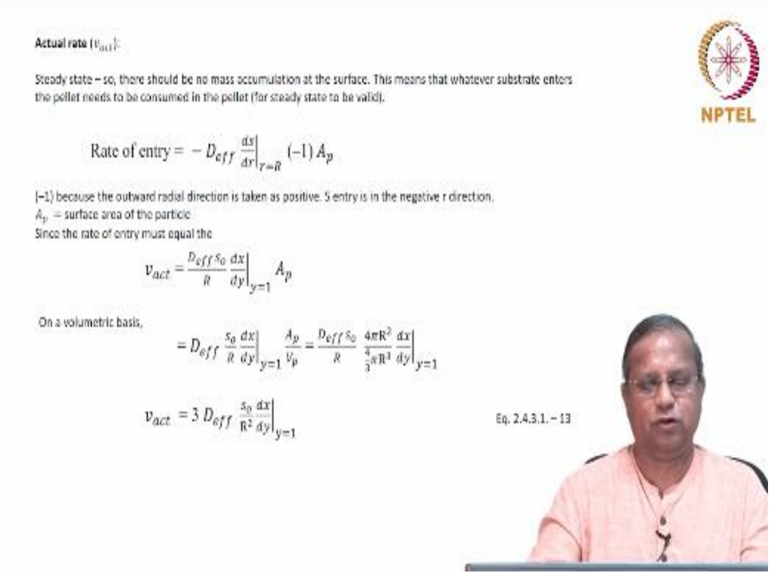


Actual rate (v_{act}):

Steady state – so, there should be no mass accumulation at the surface. This means that whatever substrate enters the pellet needs to be consumed in the pellet (for steady state to be valid).

$$\text{Rate of entry} = -D_{eff} \left.\frac{ds}{dr}\right|_{r=R} (-1) A_p$$

(−1) because the outward radial direction is taken as positive. S entry is in the negative r direction.
A_p = surface area of the particle
Since the rate of entry must equal the

$$v_{act} = \frac{D_{eff} s_0}{R} \left.\frac{dx}{dy}\right|_{y=1} A_p$$

On a volumetric basis,

$$= D_{eff} \frac{s_0}{R} \left.\frac{dx}{dy}\right|_{y=1} \frac{A_p}{V_p} = \frac{D_{eff} s_0}{R} \frac{4\pi R^2}{\frac{4}{3}\pi R^3} \left.\frac{dx}{dy}\right|_{y=1}$$

$$v_{act} = 3\, D_{eff} \frac{s_0}{R^2} \left.\frac{dx}{dy}\right|_{y=1} \qquad \text{Eq. 2.4.3.1.} - 13$$

So the actual rate I am calling it v_{act} is to find that out. Let us consider this. This is a steady state situation okay. Steady state means at a certain point of interest, the variables of interest should not change with time okay. Therefore, there should be no mass accumulation at the surface of the pellet. If it accumulates it is changing with time.

If the substrate accumulates or mass accumulates at the surface, mass at the surface is changing with time. That is not allowed at steady state. And therefore, there should be no mass accumulation at the surface. This in turn means that whatever substrate is entering the surface needs to be consumed in the pellet for the steady state to be valid. If that is not happening, the steady state is no longer valid, okay.

So if we look at the rate of entry through diffusion as given by Fick’s first law. We multiply it by the surface area of the particle A_p to get the diffusion rate from the flux rate. And in spherical geometry if you recall, the positive r direction is from the inside to the outside.

Here the substrate is entering from the outside to the inside, okay. Just in the negative r direction. And therefore, we include a **-1** here to indicate that direction. So the rate of entry is Fick's first law at r equals R times A_p times -1. Yeah -1 because the outward radial direction is taken as positive, S entry is in the negative r direction.

We are usually more interested in determining how much the reaction is hindered due to immobilisation. To find this out, let us define an effectiveness factor that gives us a measure of the hindrance, and evaluate the same.

An effectiveness factor can be defined as

$$\xi_g = \frac{\text{Actual reaction rate}}{\text{Reaction rate in the absence of mass transfer resistance}}$$

Actual rate v_{act}: At steady state, there should be no accumulation of substrate or product at the surface. Thus, whatever substrate enters, needs to be consumed in the pellet for steady state to be valid.

$$\text{Rate of entry} = -\,D_{\text{eff}}\left.\frac{ds}{dr}\right|_{r=R}(-1)A_p$$

Since the by steady state requirement, the rate of entry must equal the rate at which it is being consumed in the pellet. The actual rate must equal the rate of entry, as given here. The negative and negative cancel out. I have written it in terms of the non-dimensional variables, times A_p must equal the actual rate, the rate at which it is getting consumed inside the pellet.

Rate of entry = $\mathbf{D_{eff}\frac{ds}{dr}\big|_{r=R}\,A_p}$

Now, to write it in terms of volumetric basis, we divide it by the volume here. We get the volume or moles per time basis we divide it by the volume to get the volume. And that both are I mean the A_p is the surface area of the sphere. V_p is the volume of the sphere. Surface area of the sphere is $4\pi R^2$. Volume is $(4/3)\pi R^3$. And therefore, your actual rate turns out to be,

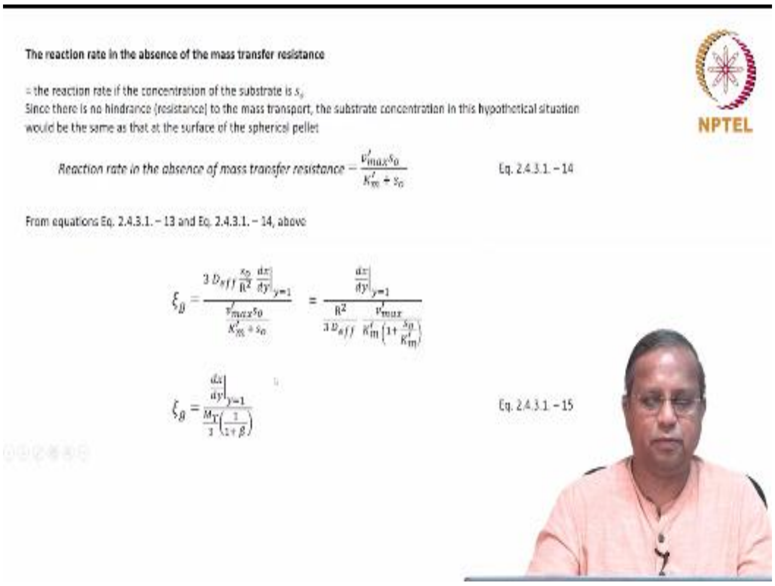
On a volumetric basis

$$v_{\text{act}} = D_{\text{eff}}\frac{s_o}{R}\left.\frac{dx}{dy}\right|_{y=1}\frac{A_p}{V_p} = \frac{D_{\text{eff}}\,s_o}{R}\,\frac{4\pi R^2}{\frac{4}{3}\pi R^3}\left.\frac{dx}{dy}\right|_{y=1}$$

$$v_{\text{act}} = 3\,D_{\text{eff}}\,\frac{s_o}{R^2}\left.\frac{dx}{dy}\right|_{y=1} \qquad (2.4.3.1\text{-}13)$$

Okay, we have been at it for a while. This is a slightly involved thing, it does not matter. Let us spend some time on this. One of the lectures being a little longer is fine. If you want you can take a break. You can pause it, come back, take a look.

(Refer Slide Time: 30:05)



The reaction rate in the absence of the mass transfer resistance

= the reaction rate if the concentration of the substrate is s_o

Since there is no hindrance (resistance) to the mass transport, the substrate concentration in this hypothetical situation would be the same as that at the surface of the spherical pellet

$$\text{Reaction rate in the absence of mass transfer resistance} = \frac{v'_{max} s_o}{K'_m + s_o} \qquad \text{Eq. 2.4.3.1.} - 14$$

From equations Eq. 2.4.3.1. – 13 and Eq. 2.4.3.1. – 14, above

$$\xi_\beta = \frac{3 D_{eff} \frac{s_o}{R^2} \left.\frac{dx}{dy}\right|_{y=1}}{\frac{v'_{max} s_o}{K'_m + s_o}} = \frac{\left.\frac{dx}{dy}\right|_{y=1}}{\frac{R^2}{3 D_{eff}} \frac{v'_{max}}{K'_m \left(1 + \frac{s_o}{K'_m}\right)}}$$

$$\xi_\beta = \frac{\left.\frac{dx}{dy}\right|_{y=1}}{\frac{M_T}{3}\left(\frac{1}{1+\beta}\right)} \qquad \text{Eq. 2.4.3.1} - 15$$

The reaction rate in the absence of the mass transfer resistance is the reaction rate if the concentration of the substrate is s_o. Since there is no hindrance (resistance) to the mass transport, the substrate concentration in this hypothetical situation would be the same as that at the surface of the spherical pellet.

$$\text{Reaction rate in the absence of mass transfer resistance} = \frac{v'_{\max} s_o}{K'_m + s_o} \qquad (2.4.3.1\text{-}14)$$

If there is no mass transfer resistance, then the entire insight would have a concentration of s_0 of the substrate. That is not happening here. And or that is the situation that we are looking at as this situation a hypothetical situation that arises in the absence of mass transfer resistance. Since there is no hindrance or resistance to mass transport, the substrate concentration in this hypothetical situation would be the same as that at the surface of the pellet as I just mentioned.

The Michaelis Menten rate with the substrate concentration being the surface substrate concentration. And from these two equations, we get the effectiveness factor which is the actual rate divided by the reaction rate in the absence of the mass transfer resistance. The actual rate is this. The reaction rate and the absence of mass transfer resistance is this. The entire enzyme, the entire pellet being at s_0.

Thus, from the previous two equations

$$\xi_g = \frac{3\,D_{\mathrm{eff}}\,\dfrac{s_o}{R^2}\left.\dfrac{dx}{dy}\right|_{y=1}}{\dfrac{v'_{\max}\,s_o}{K'_m + s_o}}$$

$$= \frac{\left.\dfrac{dx}{dy}\right|_{y=1}}{\dfrac{R^2}{3\,D_{\mathrm{eff}}}\,\dfrac{v'_{\max}}{K'_m\left(1+\dfrac{s_o}{K'_m}\right)}}$$

$$= \frac{\left.\dfrac{dx}{dy}\right|_{y=1}}{3M_T^2\left(\dfrac{1}{1+\beta}\right)} \qquad (2.4.3.1\text{-}15)$$

So we have the effectiveness factor, we needed an expression for the effectiveness factor is $\frac{dx}{dy}$ at y equals 1 divided by this is nothing but your Thiele modulus M_T apart from this 3 here. We will call this equation 2.4.3.1-15. I think this is what we are looking for in the problem here. The effectiveness factor in this given situation. Here we had a spherical geometry with reaction happening. I hope you got an idea as to how to apply these material balance expressions to arrive at very useful insights into the system and thereby use those insights for design and operation later.

Let us stop here for this class. When we come back, we will take things forward. See you then.