Transport Phenomena in Biological Systems
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Lecture - 16
Unsteady-state Diffusion - continued

Welcome back. Let us resume the solution to the problem. There is a lot of intense working in the last class to convert the partial differential equation into an ordinary differential equation which can be solved more easily. That is one of the ways of solving a partial differential equation, if you recall from your mathematics classes.

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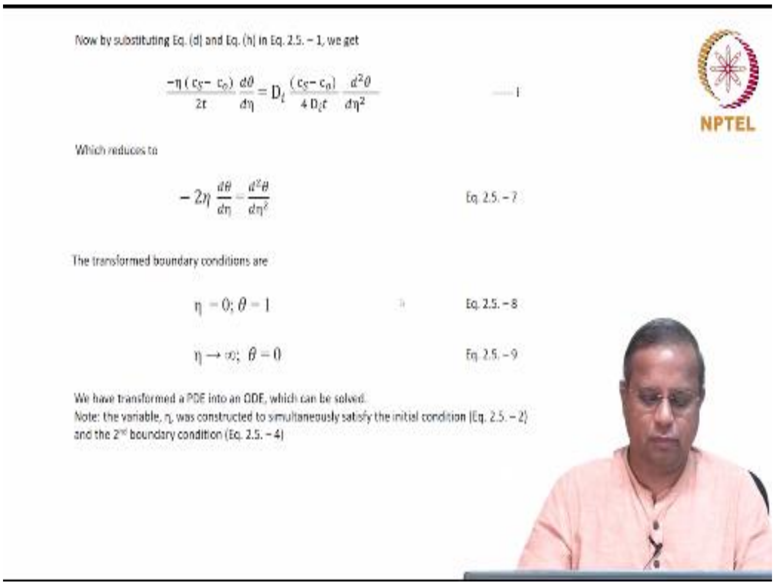

So, this was the converted differential equation, the ordinary differential equation.

$$-2\eta \frac{d\theta}{d\eta} = \frac{d^2\theta}{d\eta^2} \qquad (2.5\text{-}7)$$

The boundary conditions get transformed to

$$\eta = 0; \ \theta = 1 \qquad (2.5\text{-}8)$$

$$\eta \rightarrow \infty; \ \theta = 0 \qquad (2.5\text{-}9)$$

With the converted boundary conditions in terms of the non-dimensional parameters. We want to solve it in terms of non-dimensional parameter so that the solution becomes applicable in general.

This is the, the problem that we are considering, the sorption of a surface modifying agent from the liquid onto a surface, we are interested in the concentration profiles of the surface modifying agent or the SMA in the liquid at various points in time.

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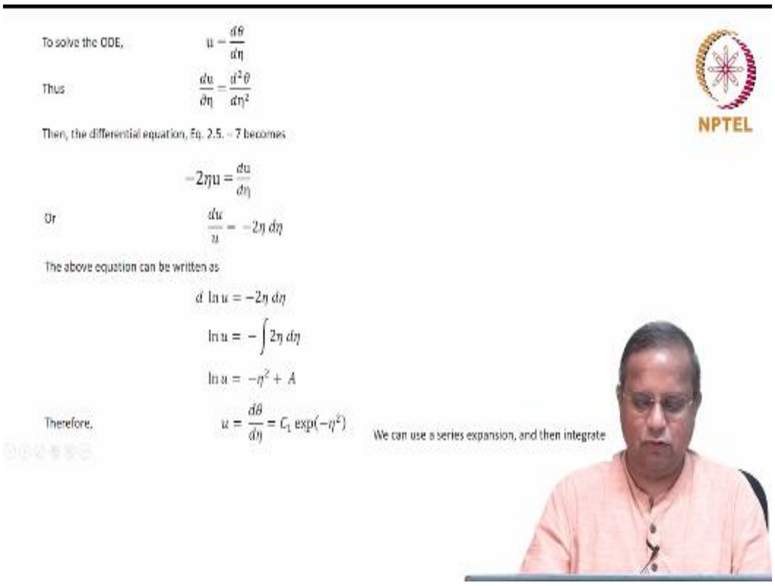

To solve this ODE, let us put u = $\frac{d\theta}{d\eta}$. If it is ODE, you know how to solve this, is one of the ways of doing it;

$$\frac{du}{\partial\eta} = \frac{d^2\theta}{d\eta^2}$$

Therefore, Eq. 2.5-7 becomes

$$-2\eta u = \frac{du}{d\eta}$$

Recognising that the above equation can be written as

$$\frac{du}{u} = d\ \ln u - 2\eta\, d\eta$$

$$\ln u = -\int 2\eta\, d\eta$$

$$\ln\ u\ =\ -\ \eta^2\ +\ A$$

Therefore

$$u = \frac{d\theta}{d\eta} = C_1 \exp(-\eta^2)$$

This cannot be integrated analytically, except by series expansion

$$e^{-\eta^2} = 1 - \frac{\eta^2}{1!} + \frac{\eta^4}{2!} - \frac{\eta^6}{3!} + \ldots$$

So we got the solution of u. One of the ways of doing the solution is that you could use a series expansion for this, okay. You all know what a series expansion for an exponential function is. So series expansion converts it into additive terms. Then, integration is quite straightforward. You do not have this complication here.

$$e^{-\eta^2} = 1 - \frac{\eta^2}{1!} + \frac{\eta^4}{2!} - \frac{\eta^6}{3!} + \ldots$$

which, when integrated, yields

$$\int e^{-\eta^2} d\eta = \eta - \frac{\eta^3}{3\times 1!} + \frac{\eta^5}{5\times 2!} - \frac{\eta^7}{7\times 3!} + \ldots + C$$

So that is one way of doing it. I am going to show you two ways of doing it. And the second way becomes a lot more general or it is nice to know the second way also. You see that quite often. It leads to it leads you to a particular function that is used a lot of times they are a function and so on. So, let me show you this.

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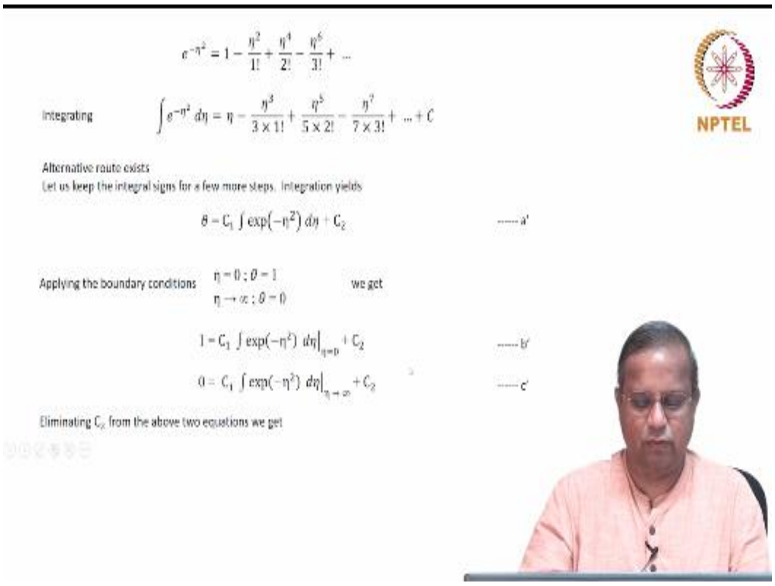

And I am more interested in this alternative route. So, this give you a solution. This certainly gives you a solution, series expansion solution. However, there is an alternative route that exists. To do that, I am going to go back a few steps. And we will keep the integral signed for some steps because it becomes clearer. So, if you go back a few steps, somewhere as shown below and start integrating that I mean and start processing that.

We can get at the solution through another route; let us keep the integral signs for a few more steps. Integration yields

$$\theta = C_1 \int \exp(-\eta^2)\, d\eta + C_2 \qquad (a')$$

Applying the boundary conditions

$$\eta = 0;\ \theta = 1$$

$$\eta \to \infty;\ \theta = 0$$

we get

$$1 = C_1 \int \exp(-\eta^2)\, d\eta\Big|_{\eta=0} + C_2 \qquad (b')$$

$$0 = C_1 \int \exp(-\eta^2)\, d\eta\Big|_{\eta\to\infty} + C_2 \qquad (c')$$

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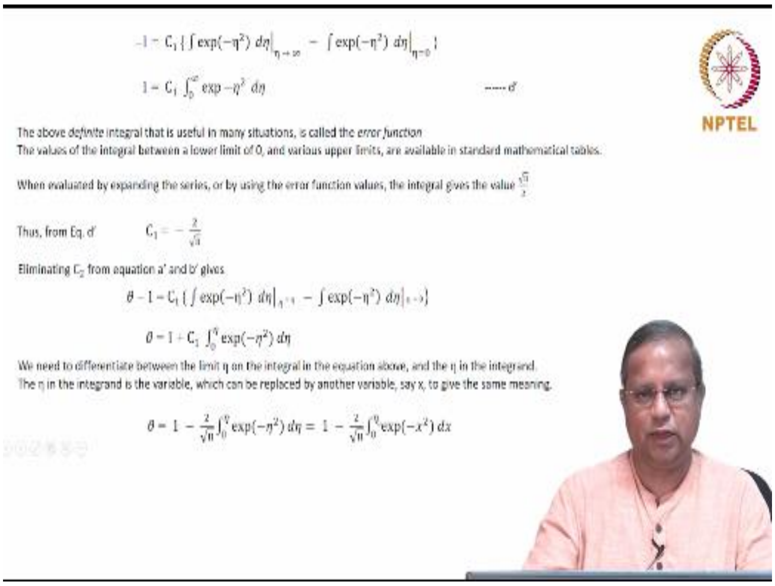

Now from here, if you eliminate C_2 subtract one equation from the other, I am subtracting the first b` from c`. If I do that, I get

Eliminating C_2 from the above two equations, we get

$$-1 = C_1\left\{\int \exp(-\eta^2)\, d\eta\Big|_{\eta\to\infty} - \int \exp(-\eta^2)\, d\eta\Big|_{\eta=0}\right\}$$

$$= C_1\int_0^{\infty} \exp(-\eta^2)\, d\eta \qquad (d')$$

Since a series expansion provides

$$\exp(-\eta^2) = 1 - \eta^2 + \frac{\eta^4}{2!} - \frac{\eta^6}{3!} + \ldots$$

You can write it as a definite integral. Then you know there is a sign change here, because integral of zero to infinity. So, infinity minus that and there is a negative there. So, you get that. And the above definite integral is of a standard form, okay. That is the reason why we wanted to keep the integral and see. This integral is called an error function.

And the values of the integral between the lower limit of zero and various upper limits are available in error function tables that are found in mathematical handbooks and of some of your mathematical textbooks even. You have the various values of this error function. It is the value of the area under the curve from zero(lower limit) onwards.

And when evaluated by expanding the series or by using the error function.

$$\exp(-\eta^2) = 1 - \eta^2 + \frac{\eta^4}{2!} - \frac{\eta^6}{3!} + \ldots$$

the series expansion can be substituted into the integral for evaluation. The above *definite* integral, which is useful in many situations, is called the *error function*. The values of the integral between a lower limit of 0, and various upper limits, are available in standard mathematical tables. When the expression is evaluated by expanding the series, or by using the error function values, the value $\frac{\sqrt{\pi}}{2}$ is got.

Thus, from Eq. (d′)

$$C_1 = -\frac{2}{\sqrt{\pi}}$$

To make this equation consistent and applicable in general,

Eliminating C_2 from equation (a′) and (b′) gives

$$\theta - 1 = C_1 \left\{ \int \exp(-\eta^2)\, d\eta \Big|_{\eta=\eta} - \int \exp(-\eta^2)\, d\eta \Big|_{\eta=0} \right\}$$

$$\theta = 1 + C_1 \int_0^{\eta} \exp(-\eta^2)\, d\eta$$

We need to differentiate between η in the limit on the integral in the equation above, and the η in the integrand. The η in the integrand is a variable, which can be replaced by another variable, say *x*, to give the same meaning. Thus

$$\theta = 1 - \frac{2}{\sqrt{\pi}} \int_0^{\eta} \exp(-\eta^2)\, d\eta = 1 - \frac{2}{\sqrt{\pi}} \int_0^{\eta} \exp(-x^2)\, dx$$

or

$$\theta = 1 - \operatorname{erf}(\eta)$$

$$\theta = \operatorname{erfc}(\eta)$$

We have replaced this variable η by the variable x to avoid the confusion with the limit η.

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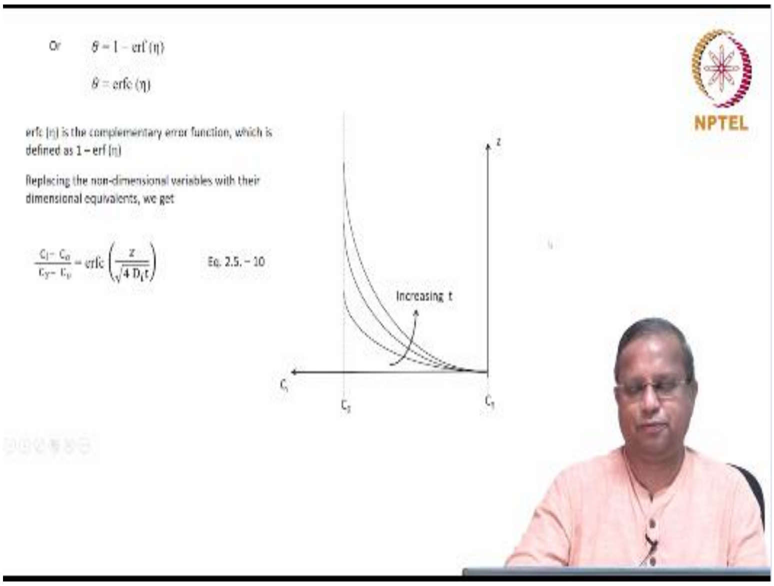

And this is nothing but the error function of x. That we mentioned here.

$$\theta = 1 - \text{erf}(\eta)$$

$$\theta = \text{erfc}(\eta)$$

where erfc (η) is the complementary error function which is defined as 1 – erf (η). Replacing the non-dimensional variables with their dimensional equivalents, we get

Now we can replace the non-dimensional variables by the actual variables for our case. Therefore, this θ was nothing but $(c_i - c_0)/(c_s - c_0)$. And this is the complimentary error function of $[z/\sqrt{4Dit}]$, which is at η. If you plot this on our earlier graph, remember I showed you this plot without these lines earlier. This is the concentration axis C_i in the solution. This is the z axis, z equals zero here. And at various times you get various profiles and as time increases, the profile shifts from here to here to here. Note how do you read this? This is the z axis. This is the concentration axis. So high on the concentration axis means a large value of concentration. So somewhere here, it reaches the highest concentration at a certain low time.

And then it drops to 0 at z equals 0. At a different time, which is beyond the initial time, then this one becomes like this. At a third time, which is beyond the first two times, it becomes like this and so on so forth. The time from where it starts decreasing goes on increasing on the z axis scale.

$$\frac{c_i - c_o}{c_s - c_o} = \text{erfc}\left(\frac{z}{\sqrt{4D_i\ t}}\right) \qquad (2.5\text{-}10)$$

Thus, c_i will vary as shown in Fig. 2.5-1.

The flux

$$\vec{J}_i^* = -D_i \left.\frac{\partial c_i}{\partial z}\right|_{z=0} = -D_i\ (c_s - c_o)\left.\frac{\partial\theta}{\partial z}\right|_{z=0}$$

$$= -D_i\ (c_s - c_o)\left.\frac{d\theta}{d\eta}\frac{\partial\eta}{\partial z}\right|_{z=0}$$

$$\vec{J}_i^* = \frac{-D_i\ (c_s - c_o)}{\sqrt{4D_i\ t}}\left.\frac{d\theta}{d\eta}\right|_{\eta=0} \qquad (2.5\text{-}11)$$

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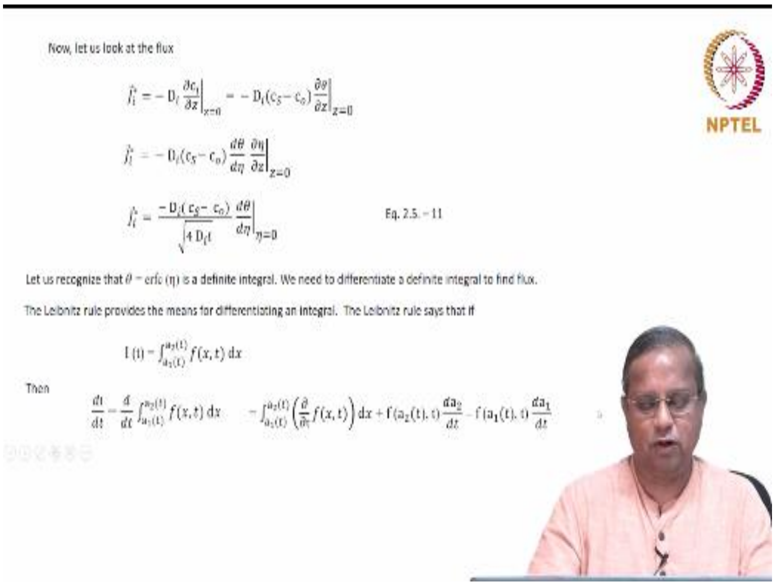

Now let us look at the flux which is what we need. Flux is again diffusive. There is no motion of the liquid. There is therefore, the SMA flux is only diffusive. Therefore, you could use Fick's first law to get it J^*_i

$$\frac{c_i - c_o}{c_s - c_o} = \operatorname{erfc}\left(\frac{z}{\sqrt{4D_i \; t}}\right) \qquad (2.5\text{-}10)$$

Thus, c_i will vary as shown in Fig. 2.5-1.

The flux

$$\vec{J}_i^* = -D_i \left.\frac{\partial c_i}{\partial z}\right|_{z=0} = -D_i \;(c_s - c_o)\left.\frac{\partial \theta}{\partial z}\right|_{z=0}$$

$$= -D_i \;(c_s - c_o)\left.\frac{d\theta}{d\eta}\frac{\partial \eta}{\partial z}\right|_{z=0}$$

$$\vec{J}_i^* = \frac{-D_i \;(c_s - c_o)}{\sqrt{4D_i \; t}}\left.\frac{d\theta}{d\eta}\right|_{\eta=0} \qquad (2.5\text{-}11)$$

And this is nothing but as we already seen, but the complementary error function of η and that is a different integral.

And now we need to differentiate the θ we need to differentiate with respect to η and therefore, we are differentiating a definite integral and that is what we need to do to find flux. So this is another aspect which is not trivial. This is a different concept altogether. We are differentiating an integral.

However, if you recall your math course you would recall the Leibnitz rule which provides us with a way of differentiating an integral. So, this can be found, this is what the Leibnitz rule says.

The Leibnitz rule provides the means for differentiating an integral. It says that if

$$I(t) = \int_{a_1(t)}^{a_2(t)} f(x,t)\, dx$$

So, this is what our Leibnitz rule tells us.

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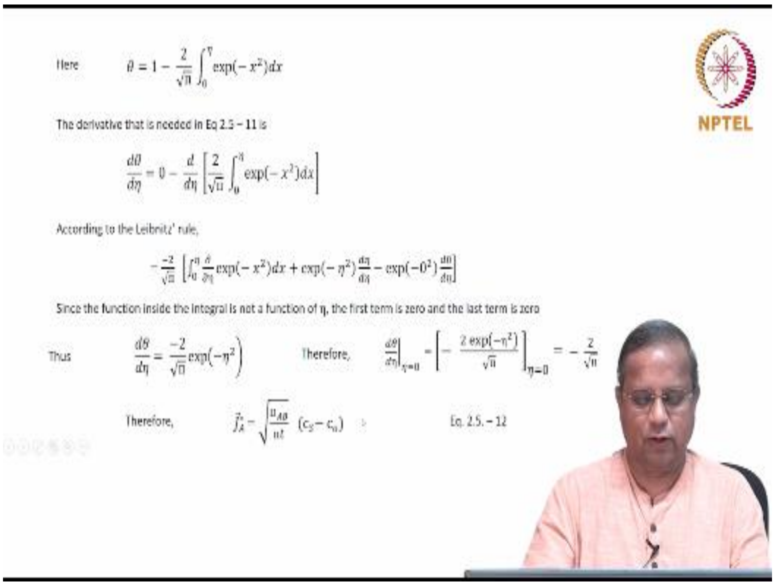

$$\frac{dI}{dt} = \frac{d}{dt}\int_{a_1(t)}^{a_2(t)} f(x,t)\, dx$$

$$= \int_{a_1(t)}^{a_2(t)} \left(\frac{\partial}{\partial t} f(x,t) \right) dx + f(a_2(t),t)\frac{da_2}{dt} - f(a_1(t),t)\frac{da_1}{dt}$$

Thus, in this case, since

$$\theta = 1 - \frac{2}{\sqrt{\pi}} \int_0^{\eta} \exp(-x^2)\, dx$$

the derivative that is needed in Eq. 2.5-11 is

$$\frac{d\theta}{d\eta} = 0 - \frac{d}{d\eta}\left[\frac{2}{\sqrt{\pi}} \int_0^{\eta} \exp(-x^2)\, dx \right]$$

According to the Leibnitz rule

$$\frac{d\theta}{d\eta} = \frac{-2}{\sqrt{\pi}}\left[\int_0^{\eta} \frac{\partial}{\partial\eta}\exp(-x^2)dx + \exp(-\eta^2)\frac{d\eta}{d\eta} - \exp(-0^2)\frac{d0}{d\eta}\right]$$

Since the function inside the integral is not a function of η, the first term is zero, and the last term is zero. Thus

$$\frac{d\theta}{d\eta} = \frac{-2}{\sqrt{\pi}}\exp(-\eta^2)$$

At $\eta = 0$

$$\left.\frac{d\theta}{d\eta}\right|_{\eta=0} = \left[-\frac{2\exp(-\eta^2)}{\sqrt{\pi}}\right]_{\eta=0} = -\frac{2}{\sqrt{\pi}}$$

Therefore, the flux

$$\vec{J}_A^* = \sqrt{\frac{D_{AB}}{\pi t}}(c_s - c_o) \qquad (2.5\text{-}12)$$

D_{AB} is nothing but D_i itself. This is sometimes used in a binary system. We do not have to worry about this too much. I am going to use this D_{AB} , D_i, $D_{i\ effective}$ in the same sense and you think is that it is a slightly different situation, therefore I call it $D_{i\ effective}$ and so on. So, all these are interchangeably used in this course. So please do not get confused. So D_{AB} is the same as D_i in equation 2.5-12. So, we got an expression for the flux that was required when the surface modifying agent is being adsorbed onto a surface from a stationary liquid.

This had quite a bit of intense mathematics, but that is required as a part of this course. And that was a prerequisite. The mathematics, engineering mathematics was a prerequisite for this course. But do not worry about it. I have given you every single step here. In most books, you do not have these individual steps, therefore it is difficult to follow. And that kind of puts off many students.

That is the reason why I have spent time to show you most of these steps till a certain basal point. Beyond that you need to work out yourself. Okay. Let us stop here. And when we meet in the next class, we will take things forward. See you then.