Diffusion in Multicomponent Solids
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Lecture No. 20
Instantaneous Planar Source

Welcome back. Now that we have been introduced to Laplace transform and derived Laplace transforms for some of the important functions, let us try to make use of those in solving diffusion equation. The solution for steady state conditions we have already seen. In next few lasses will try to solve diffusion equation for non-steady state condition.

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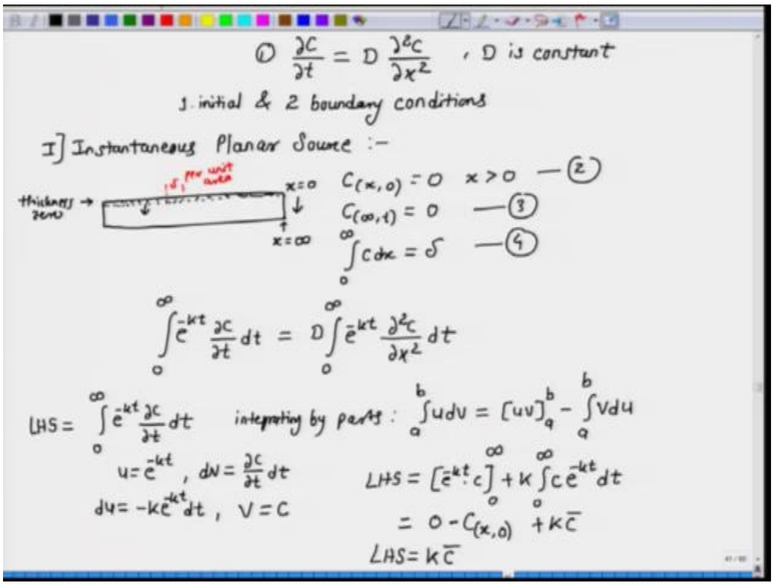

The diffusion equation that we are talking about is:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad (1)$$

Basically when we write this equation, we are assuming that D is constant. Now this equation is first order in time t and second order in distance x, which means we need one initial condition and two boundary conditions to solve these equations. We will see how we can solve this equation for different initial and boundary conditions.

Let us start with the solution for instantaneous planar source. This is an important boundary condition that is encountered in some of the applications. For example, in semiconductor industry, the doping of silicon is carried out by diffusion process right. The silicon semiconductor is first deposited with the thin layer of dopant on the top surface this is the deposition step. And then this assembly is heated at an elevated temperature at which the dopant now starts diffusing into silicon.

Now, it is very important to control the concentration at the desired depth. So, we need to know at a given time that a given concentration plane has penetrated to what depth or at a given distance what is the concentration of dopant and for this, we need the solution based on this diffusion equation..

This is the instantaneous planar source, what is the initial condition here? To start with there is no dopant in the silicon or if we are considering the diffusion of let us say material B in A. Initially A is pure, the initial concentration of B in A is 0 and that is 0 everywhere except on the top surface. The surface layer which is deposited is extremely small.

For the purpose of solution, we assume that this thickness of the layer is 0. Our initial condition becomes:

$$C(x,0) = 0, \qquad At\ x > 0 \qquad (2)$$

In this case our $x = 0$ is on the surface and the x is increasing with the depth downwards, then what are the boundary conditions?

Typically, width is large compared to the distance to which B C can diffuse in A at a given temperature and time, which means B will never diffuse all the way and reach the other surface. So, the other surface still remain pure at any time. Mathematically we say that:

$$C(\infty,t) = 0 \qquad (3)$$

at any time, the concentration is original concentration which was 0. Our x equal to infinity is the other surface.

What is the second boundary condition? Initially we deposited some quantity of material B. let us assume that the quantity that was deposited per unit area is δ per unit cross sectional area. And after that we are not adding or removing any material right and this is a unidirectional diffusion.

So, at any given time, the total quantity if we look through the entire thickness of A, it should remain constant equal to delta δ. We can express this as:

$$\int_0^\infty C dx = \delta \qquad (4)$$

We have equation (1) based on the initial condition (2) and the boundary conditions (3) and (4).

Now we will make use of Laplace transform to solve this. To do that, if we multiply both sides of equation one with $e^{-kt}$and integrate within the limits of time equal to 0 to infinity:

$$\int_0^\infty e^{-kt} \frac{\partial C}{\partial t} dt = D \int_0^\infty e^{-kt} \frac{\partial^2 C}{\partial x^2} dt$$

Now let us try to solve each side one by one. If you first look at the left-hand side LHS, this integral we can solve by the method of integration by parts. If we integrate by parts, what is the formula for integration by parts?

$$\int_a^b u dv = [uv]_a^b - \int_a^b v du$$

We have to select u and dv appropriately from this integral. If we write:

$$u = e^{-kt}, \quad dv = \frac{\partial C}{\partial t} dt$$

$$du = -ke^{-kt} dt, \quad v = C$$

Now, we substitute in the integration by part for u and v, your LHS becomes:

$$LHS = [e^{-kt} C]_0^\infty + k \int_0^\infty C e^{-kt} dt = 0 - C(x, 0) + k \int_0^\infty C e^{-kt} dt$$

This integral looks familiar, what is this? It is the Laplace transform of function C? Let us denote that by $\bar{C}$.

Now, we know the initial   conditions C at x at $t = 0$ equals 0. LHS   comes out to be :

$$LHS = k\bar{C}$$

$\bar{C}$ is the Laplace transform of function C.

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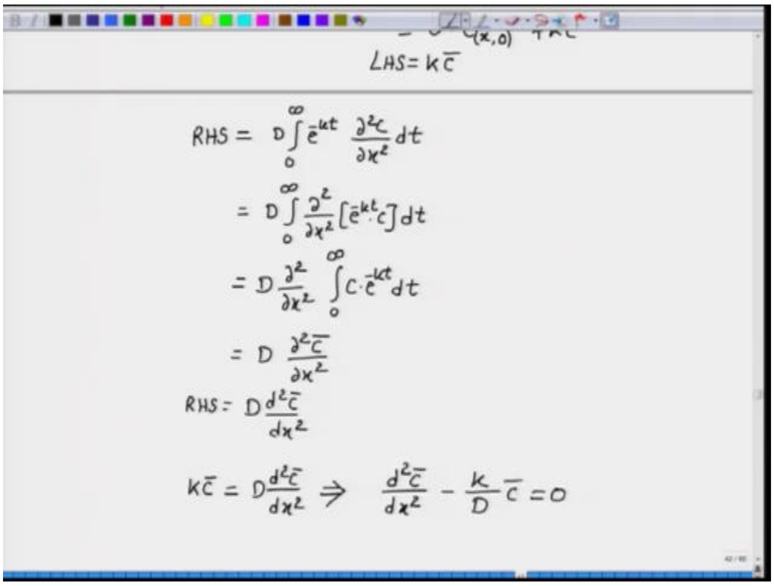

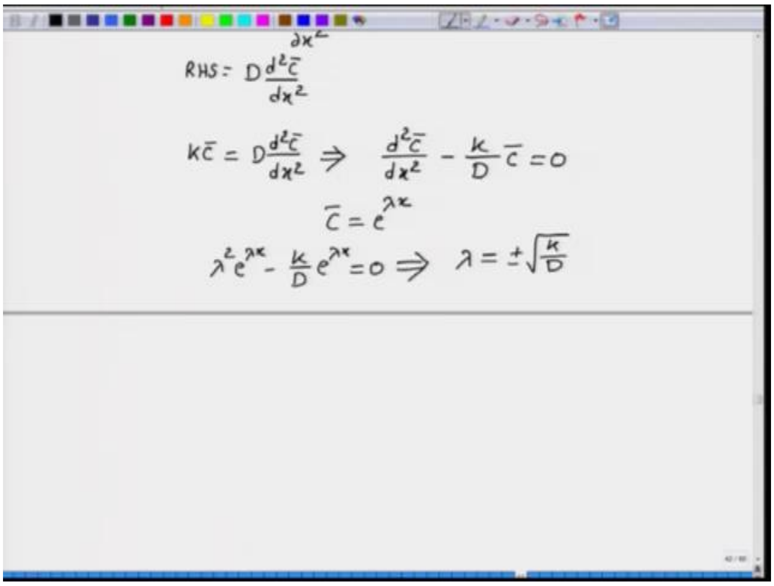

Now let us take the second side RHS, RHS in this case is:

$$RHS = D\int_0^\infty e^{-kt}\frac{\partial^2 C}{\partial x^2}dt$$

Now, e^{-kt} is not a function of x. We can take it inside the partial differential here that becomes:

$$RHS = D\int_0^\infty e^{-kt}\frac{\partial^2 C}{\partial x^2}dt = D\int_0^\infty \frac{\partial^2}{\partial x^2}(Ce^{-kt})dt$$

And next, we can change the order of integral and differentiation. This becomes:

$$RHS = \frac{\partial^2}{\partial x^2}\int_0^\infty (Ce^{-kt})dt$$

Again, we encounter the integral for Laplace transform of C as this integral is nothing but the Laplace transform of C, which we denote as $\bar{C}$. So this equals to:

$$RHS = D\frac{\partial^2 \bar{C}}{\partial x^2}$$

Now, we know this Laplace transform is the integral with respect to t and so this is a definite integral. $\bar{C}$ is independent of t or $\bar{C}$ is not a function of t now. We can replace this partial differential with ordinary differential we can write after substituting for RHS and LHS as:

$$k\bar{C} = D\frac{\partial^2 \bar{C}}{\partial x^2} \quad or \quad k\bar{C} = D\frac{d^2 \bar{C}}{dx^2}$$

On rearranging:

$$\frac{d^2 \bar{C}}{dx^2} - \frac{k\bar{C}}{D} = 0$$

This is interesting. We had a partial differential equation in x and t and Laplace transform has helped us to transform it to an ordinary differential equation in x. Now, we know the general solution for this equation. Let us take $\bar{C}$ equal to:

$$\bar{C} = e^{\lambda x}$$

If we substitute for second derivative of $\bar{C}$ we get:

$$\lambda^2 e^{\lambda x} - \frac{ke^{\lambda x}}{D} = 0$$

This gives the value of λ as:

$$\lambda = \pm\sqrt{\frac{k}{D}}$$

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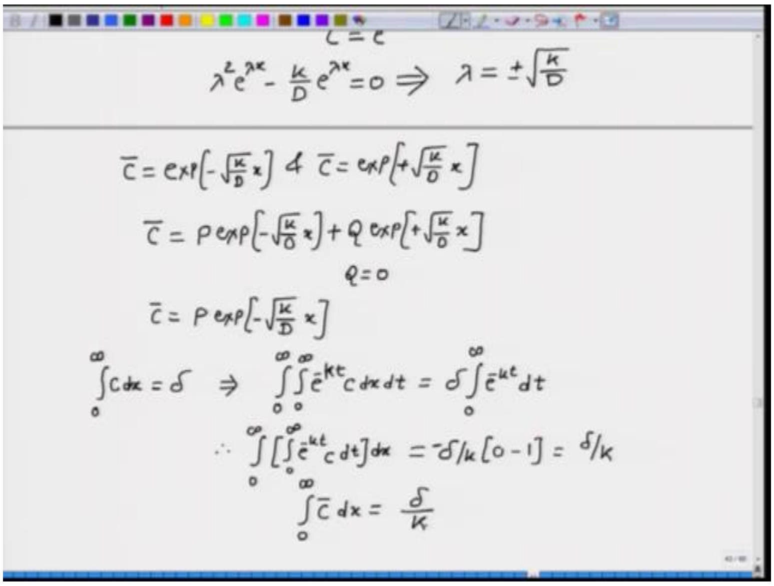

Now, we have two solutions here:

$$\bar{C} = exp\left(-\sqrt{\frac{k}{D}}x\right) \quad and \quad \bar{C} = exp\left(\sqrt{\frac{k}{D}}x\right)$$

And we know the linear combination of solutions is also a solution. So we can write the solution as:

$$\bar{C} = Pexp\left(-\sqrt{\frac{k}{D}}x\right) + Qexp\left(\sqrt{\frac{k}{D}}x\right)$$

Now, we need to find out the values of these constants P and Q. We can determine one of them straight away, based on looking at our boundary conditions. Now what happens here, if x tends to ∞, the first term will tend to 0, but the second term will tend to infinity then. But we want that even at x equal to infinity, we should have a well-behaved solution for concentration. So if we need to get any physically meaningful solution, Q has to be 0.

Q is 0 here, we are left with only the first term:

$$\bar{C} = Pexp\left(-\sqrt{\frac{k}{D}}x\right)$$

And to find a value of P, we now use our second boundary condition, what was that?

$$\int_0^\infty C dx = \delta$$

Again, we take Laplace transform on both sides:

$$\int_0^\infty \int_0^\infty e^{-kt} C dx dt = \delta \int_0^\infty e^{-kt} dt$$

C is a constant, so we can take it outside of integral. And if we change the order of integration, on the left-hand side, we have:

$$\int_0^\infty \left[\int_0^\infty e^{-kt} C dt \right] dx = \int_0^\infty \left[\int_0^\infty e^{-kt} C dt \right] dx = \delta \int_0^\infty e^{-kt} dt = -\frac{\delta}{k}[0-1] = \frac{\delta}{k}$$

Or:

$$\int_0^\infty \left[\int_0^\infty e^{-kt} C dt \right] dx = \frac{\delta}{k}$$

As the inside integral on the left hand side is the Laplace transform of $\bar{C}$, so we have:

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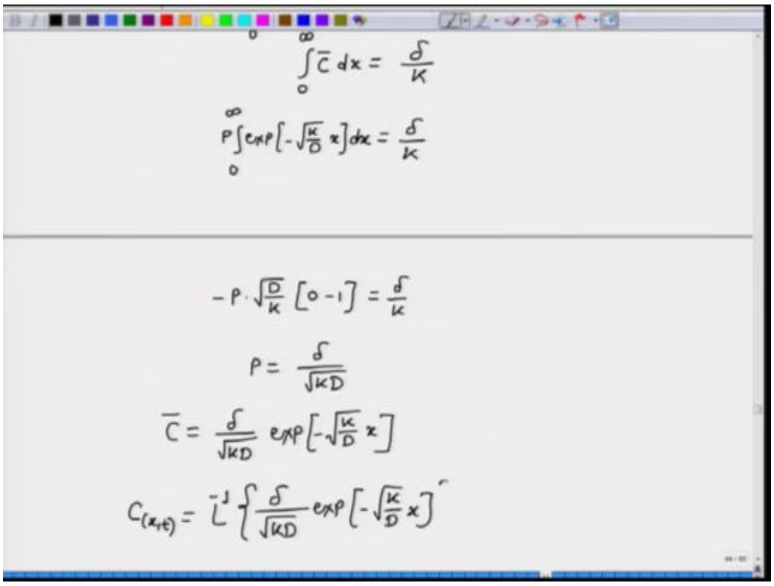

$$\int_{0}^{\infty} \bar{C} dx = \frac{\delta}{k}$$

Now we know the equation for $\bar{C}$, and we substitute for $\bar{C}$ from here. We get:

$$P \int_{0}^{\infty} exp\left(-\sqrt{\frac{k}{D}}x\right) dx = \frac{\delta}{k}$$

As P is a constant, it is taken outside integral. And :

$$-P\sqrt{\frac{D}{k}}[0-1] = \frac{\delta}{k}$$

and we get the value of P as:

$$P = \frac{\delta}{\sqrt{kD}}$$

So, the solution becomes:

$$\bar{C} = \frac{\delta}{\sqrt{kD}} exp\left(-\sqrt{\frac{k}{D}}x\right)$$

Hence we found the solution for $\bar{C}$ and $\bar{C}$ is a Laplace transform of C. To get back to C, we need to take inverse Laplace:

$$C(x,t) = L^{-1}\left\{\frac{\delta}{\sqrt{kD}} exp\left(-\sqrt{\frac{k}{D}}x\right)\right\}$$

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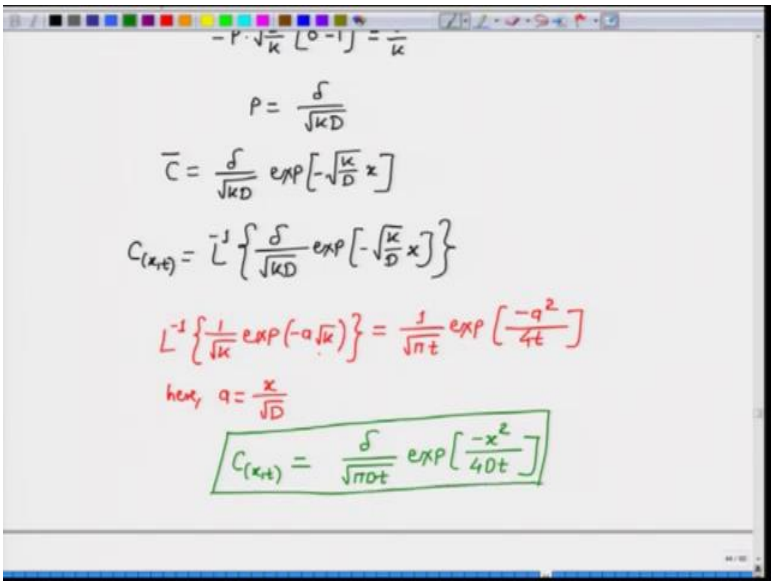

Now, we have studied before that:

$$L^{-1}\left\{\frac{1}{\sqrt{k}}exp\left(-\frac{a}{\sqrt{k}}\right)\right\} = \frac{1}{\sqrt{\pi t}}exp\left[-\frac{a^2}{4t}\right]$$

where a is a constant. We can compare our solution for $\bar{C}$ with this function on left side here. If we do that it is the value of a here is:

$$a = \frac{x}{\sqrt{D}}$$

So, we get the solution for C as:

$$C(x,t) = \frac{\delta}{\sqrt{\pi Dt}}exp\left[-\frac{x^2}{4Dt}\right]$$

and this is the solution for diffusion equation for instantaneous planar source condition. This is an important solution. As I said it is very important during the doping of semiconductors, so that is where we need to refer to this solution. The process of diffusing this dopant into the silicon hip or any other semi-conductor is called drive in. And if you need to know how much the given concentration plane has penetrated at a given time, we need to refer to the solution.

Now, here we assumed D is constant and this assumption is very close to reality in such cases for example, the dopant concentration is typically very small in ppm. At that small concentration we can assume D is constant okay. Where is another use, another example of the application of this particular equation is in the field of diffusion itself.

You guys have heard of tracer diffusion experiments right. This equation is also used for measuring the diffusion coefficients, particularly the impurity diffusion coefficient of, let us say B in A.

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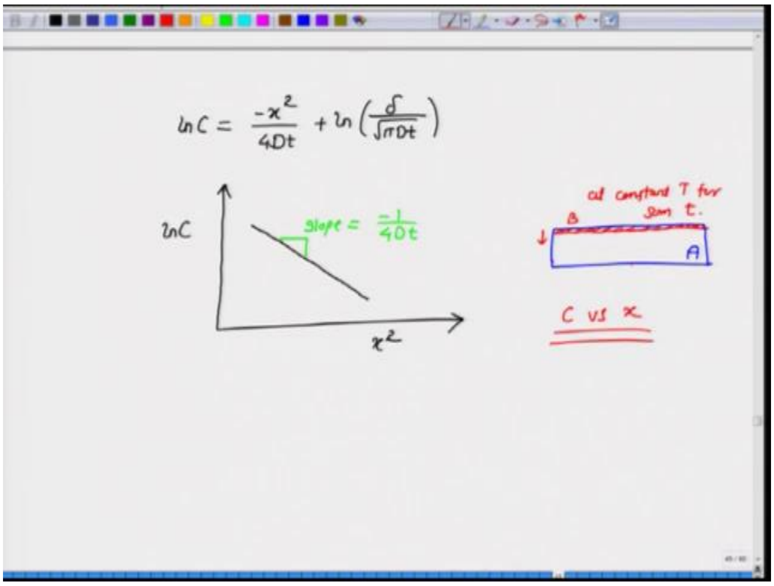

How is it done? Let us see first mathematically, then I will explain the experimental aspects. If we take logarithm on both side of previous equation for $C(x,t)$ we will get:

$$\ln C = -\frac{x^2}{4Dt} + ln\left(\frac{\delta}{\sqrt{\pi Dt}}\right)$$

This is a simpler form which tells me if I plot $\ln C$ against x^2, what should be the nature of the plot, it should be a straight line. And, what should be the slope?

$$Slope = -\frac{1}{4Dt}$$

This gives me idea of how I can measure the diffusivity term D let us say for impurity diffusion of B in A. For this, we can have a similar assembly as described before. If we want to measure B in A, I take the substrate of A and deposit a very thin layer of B on the surface and this assembly is heated so that B is allowed to diffuse into A isothermally. This is done at constant temperature. Then after the diffusion experiment stops, I can plot the concentration as a function of x. And then if I plot $\ln C$ versus x^2 I should get a straight line. Again, this is an impurity coefficient of B in pure A that means that it is the diffusion coefficient for extremely dilute solution of B in A. Again, the concentrations that we are dealing with here are very small and we can assume D as a constant within the small concentration range that is encountered here, which is close to reality.

Now experimentally, there is a little challenge, although this looks very simple mathematically but measuring concentration at that small scale of values is not possible right with the typical concentration measurement setups that we have, like WDS or EDX. We cannot directly measure this concentration and to measure the concentration gradient, we need to measure them with very good accuracy.

So, what is done is to use radioactive isotopes of B in this case. Instead of depositing the normal B, radioactive isotope of B is deposited and the experiment is carried out. Then they measure the intensity of radiation on the surface and the intensity of radiation is related to the concentration and to get the profile of intensity versus depth, we can remove the layer by polishing.

And every time we remove small layer, we measure the intensity, again we remove the small layer on the surface measure the intensity and that is how we experimentally obtain this profiles. This is one important solution that we studied, which is very useful in many applications. Now let us try to see how the profiles actually develop.

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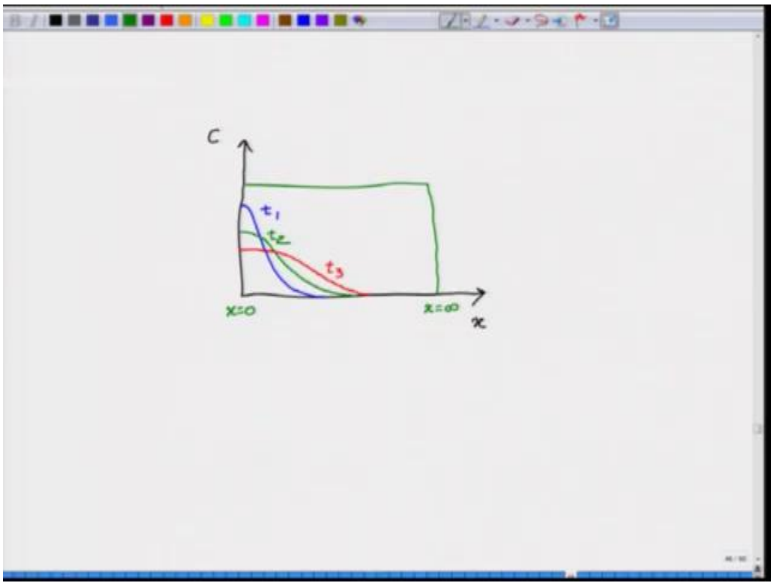

If we try to plot C versus x based on the solution that we have seen and this is our block of B originally left end is x equal to 0 and we call the other end as $x = \infty$. Again, although this block is finite the other end we call as $x = \infty$ because in the given time the diffusant has not penetrated all the way up to the other side. As long as that is true this infinite boundary condition will be satisfied and this solution can be applied.

But if we select the thickness for the given time such that the diffusant penetrates all the way up to the other end then we cannot use that solution okay. In this case if we draw the profiles at different times, let us say at some time t_1 we will see that, it will be something like this. For some other time, as the time progresses, the diffusant spreads into the material.

Now obviously, the concentration on the surface will keep dropping. This is how the C versus x plots will look like for this instantaneous planar source solution.

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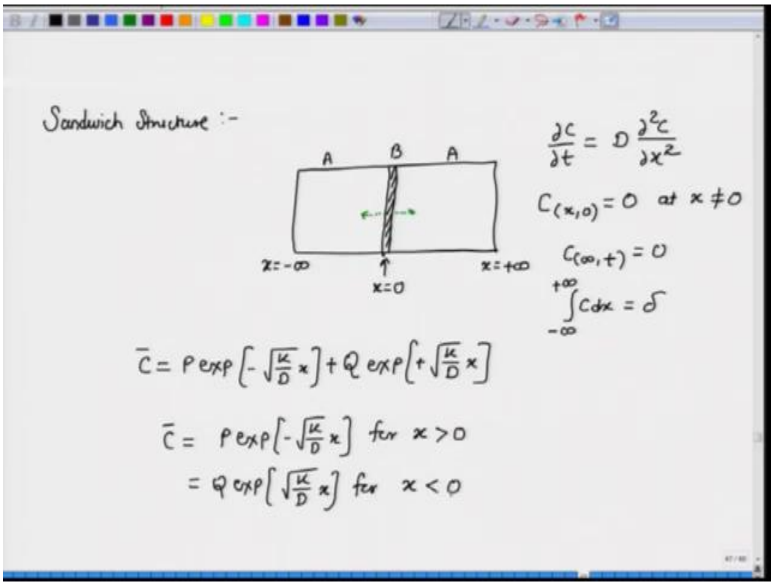

Now let us look a case where , instead of the instantaneous planar source of B in A what I am doing is I am sandwiching can instantaneous planar source of B in two infinite blocks of A, infinite in the sense again that the diffusion does not penetrate to the other end during the diffusion time.

Now, we are solving the same equation, but the boundary conditions will be a little bit different at the initial condition. Initially we have for time $t = 0$ at any x:

$$C(x, 0) = 0 \quad at\ x \neq 0$$

Boundary condition:

$$C(\infty, t) = 0$$

and then the total amount of B, which is basically:

$$\int_{-\infty}^{\infty} C dx = \delta$$

Unlike the previous case, now the diffusant is diffusing in both the directions. Earlier it was on the surface and it diffused in only one direction, now here it is diffusing in both directions. We can follow the Laplace transform procedure and we will get to the similar type of solution:

$$\bar{C} = Pexp\left(-\sqrt{\frac{k}{D}}x\right) + Qexp\left(\sqrt{\frac{k}{D}}x\right)$$

In the previous case, we had only positive values of x, but here we have negative as well as positive right. If we look at the solution and at the boundary condition, we will see that when x has a negative value, the first term becomes ∞ at $x = -\infty$. So, for negative values of x, the first part should not be there.

Similarly, for positive values of x, the second part should not be there. So we can write:

$$\bar{C} = Pexp\left(-\sqrt{\frac{k}{D}}x\right) \quad for\ x > 0$$

$$\bar{C} = Qexp\left(\sqrt{\frac{k}{D}}x\right) \quad for\ x < 0$$

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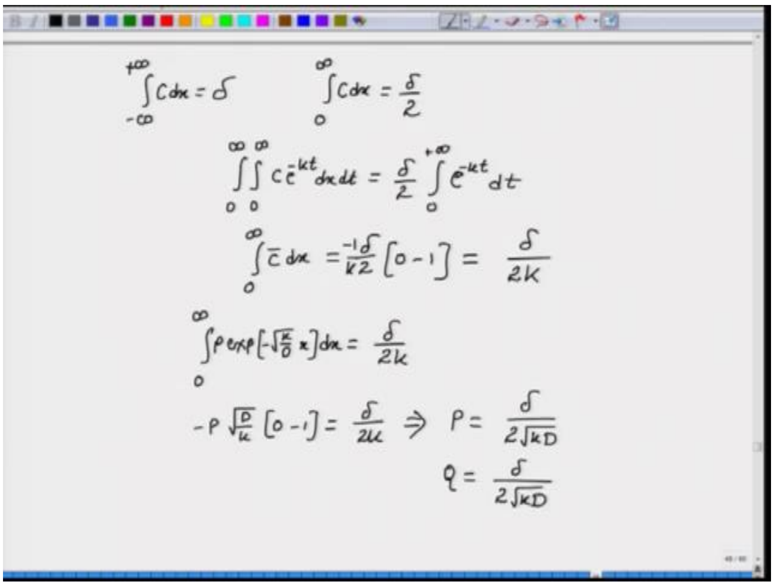

Now, we need to find these constants P and Q, we will use our second boundary condition, which is:

$$\int_{-\infty}^{\infty} Cdx = \delta$$

If we look at our system, on both side we have pure A and the diffusivity is constant. It is a unidirectional diffusion, which means, the solution will be symmetric about x equal to 0.

That means, at any given instant out of the total amount δ of B which is diffusing inside the two blocks of A, half of it will be on left and half of it would have diffused on the right. Which means we can split this integral as:

$$\int_0^\infty C dx = \frac{\delta}{2}$$

If we take Laplace transform again on both sides:

$$\int_0^\infty \int_0^\infty C e^{-kt} dx dt = \frac{\delta}{2} \int_0^\infty e^{-kt} dt$$

and if we rearrange we will find the Laplace transform of C appears.

$$\int_0^\infty \bar{C} dx = -\frac{\delta}{2k}[0-1] = \frac{\delta}{2k}$$

And if we substitute for $\bar{C}$ for positive value of x we get:

$$\int_0^\infty P exp\left(-\sqrt{\frac{k}{D}}x\right) dx = \frac{\delta}{2k}$$

This comes out to be:

$$-P\sqrt{\frac{D}{k}}[0-1] = \frac{\delta}{2k}$$

or P is equal to:

$$P = \frac{\delta}{2\sqrt{kD}}$$

Now with a similar treatment on the left-hand side, we can show the Q will also be same.

$$Q = \frac{\delta}{2\sqrt{kD}}$$

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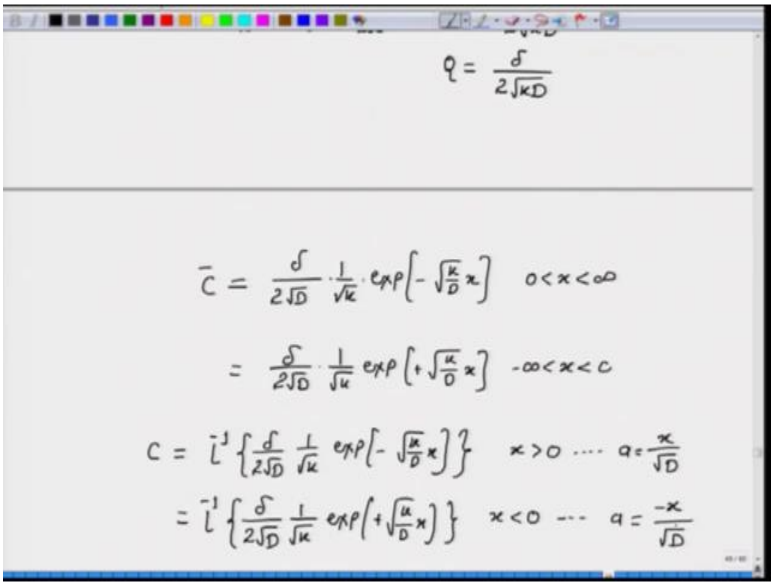

Our $\bar{C}$ will be:

$$\bar{C} = \frac{\delta}{2\sqrt{kD}} exp\left(-\sqrt{\frac{k}{D}}x\right) \qquad 0 < x < \infty$$

And

$$\bar{C} = \frac{\delta}{2\sqrt{kD}} exp\left(\sqrt{\frac{k}{D}}x\right) \qquad -\infty < x < 0$$

Again we can compare with the Laplace transform that we know.

C will be:

$$C = L^{-1}\left\{\frac{\delta}{2\sqrt{kD}} exp\left(-\sqrt{\frac{k}{D}}x\right)\right\} \quad for\ x > 0, \quad a = \frac{x}{\sqrt{D}}$$

and equal to:

$$C = L^{-1}\left\{\frac{\delta}{2\sqrt{kD}} exp\left(\sqrt{\frac{k}{D}}x\right)\right\} \quad for\ x < 0, \quad a = \frac{-x}{\sqrt{D}}$$

If we compare with our formula that we saw earlier, we will see in the first case $a = \frac{x}{\sqrt{D}}$.

Whereas, in the second case $a = \frac{-x}{\sqrt{D}}$, but it should not matter because inside the exponential a appears as a square right.

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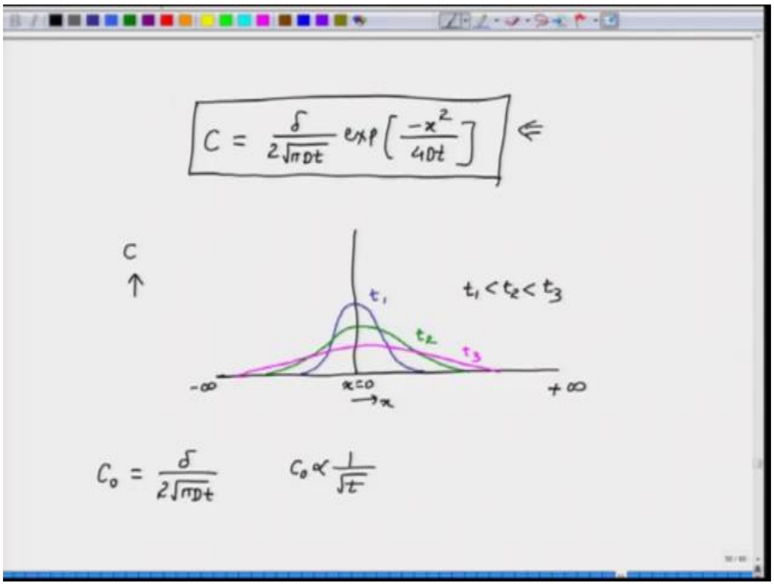

For both the cases we have the solution:

$$C = \frac{\delta}{2\sqrt{\pi D t}} exp\left(\frac{-x^2}{4Dt}\right)$$

This is the solution when we an infinitesimally small in thickness planar source sandwiched between two blocks of A.

If we plot this, on the Y axis is concentration, X axis is x. Obviously, the solution is symmetric because D is constant and we will see something like these curves. This is a typical Gaussian type of solution and $t_1 < t_2 < t_3$. With time we can see the peak of the profile is decreasing and the peak is at x=0. And the width of the profile is increasing that means the penetration depth is increasing with time, but the peak is decreasing. The diffusant is spreading into the material. This is obvious because the total amount δ is constant as it is spreading inside, the peak value has to decrease. How do you find the peak value here? It is at x=0.

If you substitute x=0 in previous equation:

$$C_o = \frac{\delta}{2\sqrt{\pi D t}}$$

So it is $\frac{1}{\sqrt{t}}$ and concentration at x=0 should decrease with time.

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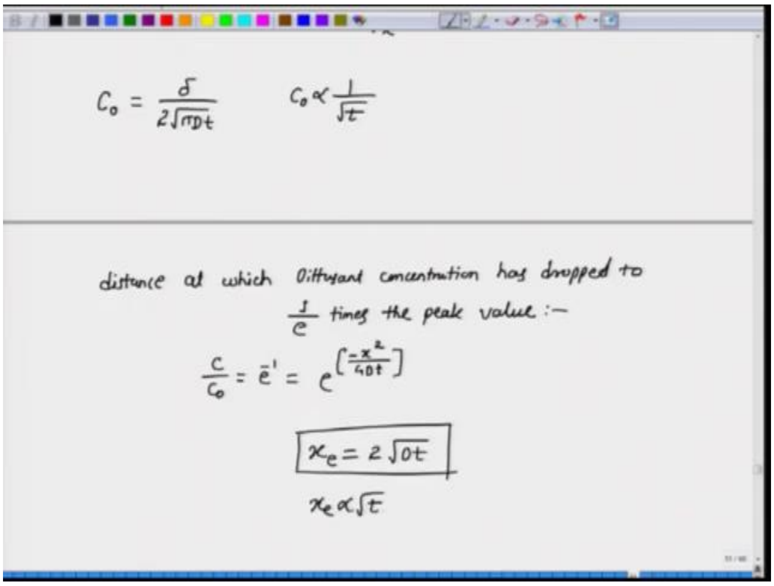

Also if we try to find the distance at which diffusant concentration has dropped to $\frac{1}{e}$ times the peak value:

$$\frac{C}{C_o} = e^{-1}$$

and from this equation:

$$C = \frac{\delta}{2\sqrt{\pi D t}} exp\left(\frac{-x^2}{4Dt}\right)$$

We can say:

$$\frac{C}{C_o} = \exp(-1) = exp\left(\frac{-x^2}{4Dt}\right)$$

What we get?

$$\frac{x^2}{4Dt} = 1$$

Let us define:

$$x_e = 2\sqrt{Dt}$$

So, if you follow this plane at which concentration is $\frac{1}{e}$ times the maximum concentration, it is moving as a function of square root of time. That means the diffusant is spreading inside, at the same time the maximum concentration is decreasing. We will stop here for today. Next class we will go over solutions for other boundary conditions. Thank you.