Diffusion in Multicomponent solids
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Lecture 16
Diffusion Equation and Solution to Steady State Diffusion

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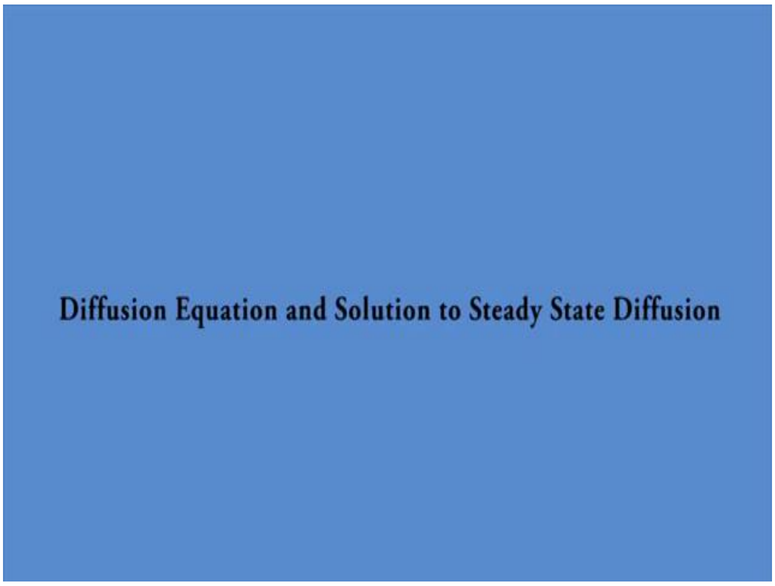

Diffusion Equation and Solution to Steady State Diffusion

Welcome to the sixteenth lecture in the open course on diffusion in multi-component solids. In this lecture, we will derive continuity equation which along with Fick's law establishes dependence of concentration on time and distance coordinate. We will also solve diffusion equation for steady state diffusion condition in this lecture.

Now, we have gone through Fick's law and also the application of Fick's law in multi-component systems. We saw that we need at least $(n-1)^2$ interdiffusion coefficients to describe diffusion in n component system. It means if we have a ternary system, we need 4 interdiffusion coefficients, for quaternary we need 9 and on. And they are again all functions of composition. Let us come back to binary system, so in binary system we showed that we need only one interdiffusion coefficient. The diffusion flux of both the components is described based on only one interdiffusion coefficients and this interdiffusion coefficient again varies with composition.

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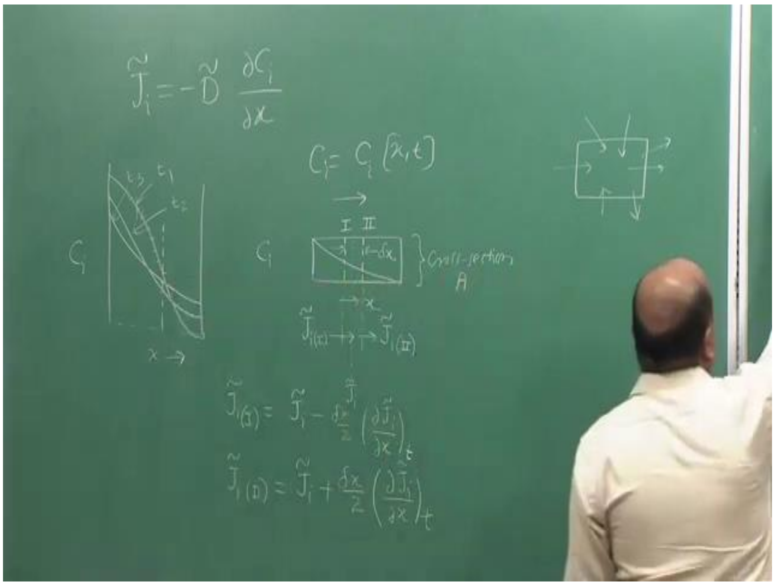

If we write Fick's law for binary system:

$$\tilde{J}_i = -\tilde{D}\frac{\partial C_i}{\partial x}$$

Tilde sign here denotes that we are talking about interdiffusion or inter mixing or diffusion along the strong concentration gradients. $\tilde{J}_i$ is the interdiffusion flux of i is equal to $-\tilde{D}$ times the gradient of concentration of i with respect to the distance coordinate $\frac{\partial C_i}{\partial x}$. Now we know that the concentration varies as a function of distance coordinate as well as time.

If we consider a particular diffusion zone and at some time t_1 if this is the concentration profile, then after some time t_3 we might see the profile like this. So the concentration is continuously evolving at t_1, t_2 and t_3. At any particular time, let us say at t_1, C_i is varying as a function of x but if you consider at any particular x, C_i is also varying as a function of time. So:

$$C_i = C_i(x,t)$$

And that is the reason we are using the partial differentiation sign here. Now you will see one of the limitations of Fick's law here that it talks about concentration variation with respect to x but it is not explicitly talking about concentration variation with time. If you want to predict the evolution of concentration this equation alone cannot be used. That is one of the limitations of Fick's law. But anyway that does not mean that Fick's law is not applicable when C is varying as a function of time. In fact at any given time you can apply Fick's law at any given plane along this concentration profile.

Now there is one more thing $\widetilde{D}$ is a function of composition and since composition varies with x and t so diffusion coefficient in this equation is also varying with x and t. $\widetilde{D}$ is not constant, it is not independent of composition but it varies with composition and since composition varies with x and t, $\widetilde{D}$varies with x and t. That has to be taken into account whenever we solve the equations for predicting evolution of concentration profiles.

Now, how do we overcome this? Or take into account the variation of concentration with time also? In order to take into account the variation with time we use what is called as principle of conservation of species. Consider a box into which there is a species i entering from some directions and there is also species leaving from other directions. It is a simple equation the rate of inflow minus rate of outflow will give me the rate of accumulation of component i inside this box.

I am making one assumption here, what is that? I am assuming that there is no production or loss of component i within this box. One example where this can happen is if there is a radioactive decay of component i. You might lose some of the species of i. When this happens you have to take into account the rate of production or loss also. Let us assume that there is no production or loss of component i and let us consider the case of unidirectional diffusion. I am considering here the situation where, I have a specimen along which there is some concentration gradient and the diffusion is occurring. The diffusion is unidirectional, let us call this plus x direction. I consider a small volume element which is bound by two vertical planes which are perpendicular to the diffusion direction, let us call them plane 1 and plane 2. And the cross sectional area of this specimen is, let us say it is A. We know since the concentration gradient here is negative, this way the diffusion flux is from left to right. Let us say at plane 1 the flux is $\tilde{J}_{i(I)}$ and this is at given time t. And at plane 2 the flux is denoted as $\tilde{J}_{i(II)}$. Width of this volume element is let us say δx. Exactly at the centre of this, I consider one more plane and the flux there is denoted as $\tilde{J}_i$.

If δx is very small, I can express $\tilde{J}_{i(I)}$ and $\tilde{J}_{i(II)}$in terms of $\tilde{J}_i$ and the gradient of flux with respect to x. I can write:

$$\tilde{J}_{i(I)} = \tilde{J}_i - \frac{\delta x}{2}\left(\frac{\partial \tilde{J}_i}{\partial x}\right)_t$$

$$\tilde{J}_{i(II)} = \tilde{J}_i + \frac{\delta x}{2}\left(\frac{\partial \tilde{J}_i}{\partial x}\right)_t$$

Now, the flux at plane 1 is basically the incoming flux or the inflow into the volume element δx. And the flux at plane 2 is the outflow basically rate of outflow per unit time per unit area that is the unit of flux. Inflow minus outflow will give me the accumulation.

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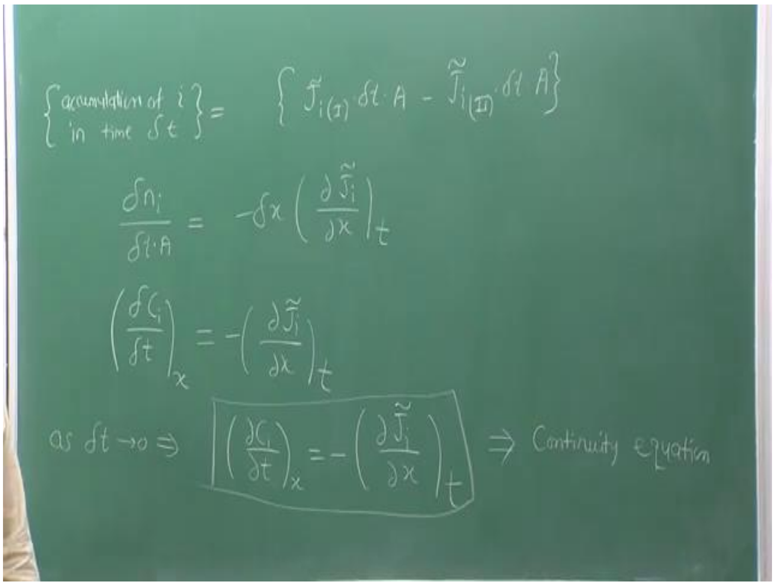

$$\begin{Bmatrix}\text{accumulation of } i \\ \text{in time } \delta t\end{Bmatrix} = \left\{\tilde{J}_{i(I)} \cdot \delta t \cdot A - \tilde{J}_{i(II)} \cdot \delta t\, A\right\}$$

$$\frac{\delta n_i}{\delta t \cdot A} = -\delta x \left(\frac{\partial \tilde{J}_i}{\partial x}\right)_t$$

$$\left(\frac{\delta C_i}{\delta t}\right)_x = -\left(\frac{\partial \tilde{J}_i}{\partial x}\right)_t$$

$$\text{as } \delta t \to 0 \Rightarrow \boxed{\left(\frac{\partial C_i}{\partial t}\right)_x = -\left(\frac{\partial \tilde{J}_i}{\partial x}\right)_t} \Rightarrow \text{Continuity equation}$$

If I write this equation accumulation of i in small time interval δt it should be equal to inflow minus outflow or

$$\{accumulation\ of\ i\ in\ time\ \delta t\} = \{\tilde{J}_{i(I)}\delta tA - \tilde{J}_{i(II)}\delta tA\}$$

Where inflow is the first term. I write accumulation of i in time δt as $\frac{\delta n_i}{\delta tA}$. And if I substitute for $\tilde{J}_{i(I)}$ and $\tilde{J}_{i(II)}$ from above, I get:

$$\frac{\delta n_i}{\delta tA} = -\delta x\left(\frac{\partial \tilde{J}_i}{\partial x}\right)_t$$

And $A\delta x$ is nothing but the volume of the element that I am considering.

δn_i by volume is just nothing but the concentration in the units that we usually use, i.e., moles per centimetre cube or number of atoms per centimetre cube according to the unit in which n_i is expressed. So LHS becomes $\frac{\delta c_i}{\delta t}$ and this I am considering at location x. So:

$$\left(\frac{\delta C_i}{\delta t}\right)_x = -\left(\frac{\partial \tilde{J}_i}{\partial x}\right)_t$$

And if I consider a very small time interval that is as $\delta t \to 0$, I can replace this with again the partial derivative of C_i with respect to t:

$$\left(\frac{\partial C_i}{\partial t}\right)_x = -\left(\frac{\partial \tilde{J}_i}{\partial x}\right)_t$$

And this is the so-called conservation equation or continuity equation. Now this gives me C_i as a function of both t and x. This is the fundamental equation, the continuity equation. Now remember again while deriving this I assume that there is no production or loss of the species i. Typically, in the diffusion in solid that we consider, especially, when the diffusion is defect mediated like for example through vacancies, there may be production of excess vacancies or loss of vacancies to the sink. And that might affect this term C_i here, because it affects the site fraction of species i. In that case we need to also consider the rate of production or rate of loss of the particular sites or vacancies.

For now, we are assuming that there is no production or loss of species i. Let us try to analyse the consequences of this equation.

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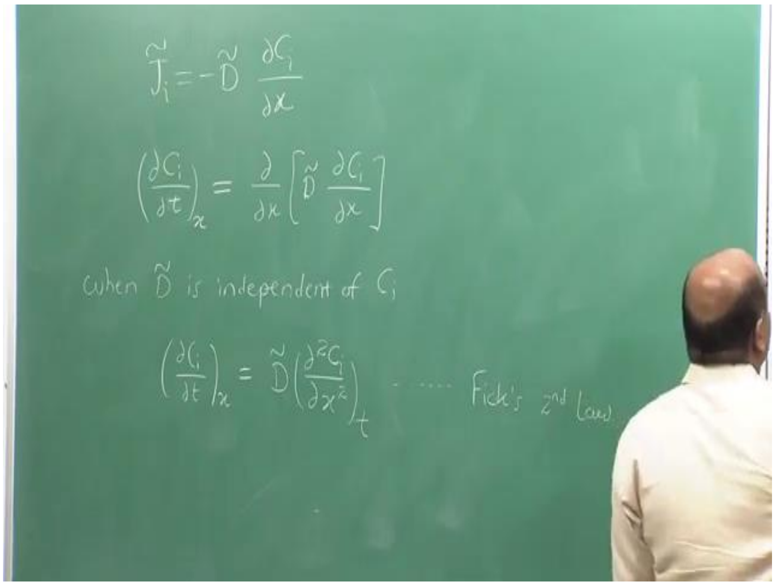

If I substitute Fick's law equation in the continuity equation I get:

$$\left(\frac{\partial C_i}{\partial t}\right)_x = \frac{\partial}{\partial x}\left(\widetilde{D}\,\frac{\partial C_i}{\partial x}\right)$$

Now remember again as I mentioned earlier $\widetilde{D}$ is a function of composition and since composition varies with x, $\widetilde{D}$ also varies with x. you cannot straight away take this out as a constant. Only when $\widetilde{D}$ is constant or $\widetilde{D}$ is independent of C_i we can write:

$$\left(\frac{\partial C_i}{\partial t}\right)_x = \widetilde{D}\left(\frac{\partial^2 C_i}{\partial x^2}\right)_t$$

And this is commonly known as Fick's second law. It is not exactly appropriate to mention this as Fick's second law, but it is popularly known as because the fundamental equation is Fick's law equation:

$$\tilde{J}_i = -\widetilde{D}\frac{\partial C_i}{\partial x}$$

And the continuity equation is simply the principle of conservation. One more thing this continuity equation is valid only in stationary frame of reference.

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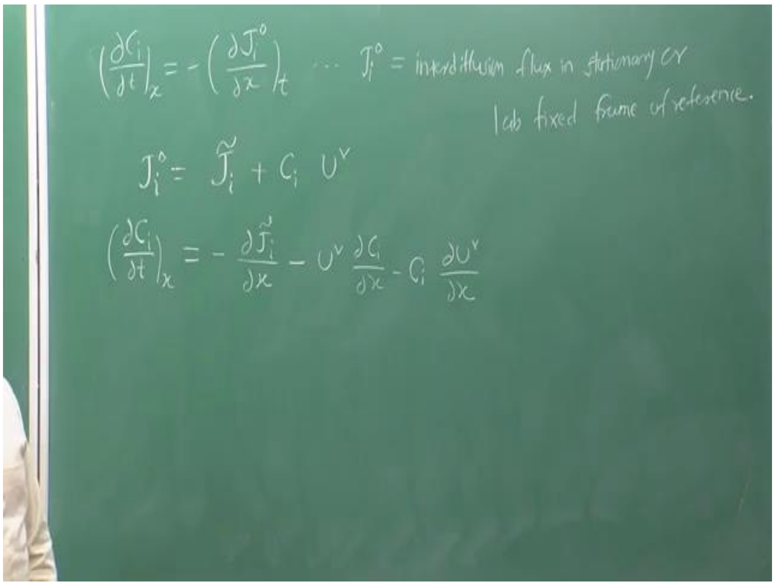

$$\left(\frac{\partial C_i}{\partial t}\right)_x = -\left(\frac{\partial J_i^0}{\partial x}\right)_t \quad \ldots \quad J_i^0 = \text{interdiffusion flux in stationary or}$$

lab fixed frame of reference.

$$J_i^0 = \tilde{J}_i + C_i\, \upsilon^v$$

$$\left(\frac{\partial C_i}{\partial t}\right)_x = -\frac{\partial \tilde{J}_i}{\partial x} - \upsilon^v\frac{\partial C_i}{\partial x} - C_i\frac{\partial \upsilon^v}{\partial x}$$

I should more accurately write the continuity equation as:

$$\left(\frac{\partial C_i}{\partial t}\right)_x = -\left(\frac{\partial J_i^o}{\partial x}\right)_t$$

where J_i^o is the interdiffusion flux in stationary or which is also referred to as lab-fixed frame. Now, based upon our previous discussion when I wrote this, what is the assumption that I have made here? What is the frame of reference that we usually use when we write the above equation? That it is in volume fixed frame. And if I am substituting the flux in volume fixed frame as the flux in stationary frame of reference, what is the assumption that I am making.

Student: Volume fixed frame is equal to lab-fixed frame

Professor: Right. Volume fixed frame is coinciding with the lab fixed frame, that is when the velocity of volume fixed frame, U^v is 0. Only then this can happen. Otherwise, we know:

$$J_i^o = \tilde{J}_i + C_i U^v$$

$\tilde{J}_i$ is in volume fixed frame. When I substitute this original equation becomes:

$$\left(\frac{\partial C_i}{\partial t}\right)_x = -\frac{\partial \tilde{J}_i}{\partial x} - U^v \frac{\partial C_i}{\partial x} - C_i \frac{\partial U^v}{\partial x}$$

If I want to write the diffusion equation in terms of fluxes in volume fixed frame, I also need to consider the velocity of the volume fixed frame. And only when U^v is 0, I get the original form of continuity equation in the stationary frame because in that case the stationary frame and volume fixed frame coincide. And as I said this happens when the partial molar volumes are assumed constant, in other words when there is no net volume change occurring because of diffusion.

If the partial molar volumes are functions of composition, then with diffusion there will be a change in volume. There will be net contraction or expansion of the diffusion zone. Obviously, when there is an expansion or contraction you can visualize that along with the diffusive flow or the Fickian flux, there will also be a net mass flow because of the expansion or contraction. That you need to consider when you write the flux in lab fixed frame.

When I write this equation:

$$\left(\frac{\partial C_i}{\partial t}\right)_x = -\left(\frac{\partial J_i^o}{\partial x}\right)_t$$

I am assuming that my lab fixed frame is coinciding with volume fixed frame which in other words means the velocity of volume fixed frame, U^v is 0. Again, U^v also varies with x. U^v is not constant, it change as a function of x and t. We will talk about this in more detail later, but at this point just understand that continuity equation applies only in stationary fixed frame.

Now, with that assumption let us try to solve continuity equation. We should call it as diffusion equation. This is the basic diffusion equation which we should solve for different boundary values and initial conditions. You can see this is a partial differential equation of second order in x and first order in t. So, how many conditions are needed to solve these equations? We need one initial condition, the condition in time and two boundary conditions, condition in x, in order to solve this partial differential equation. Let us try to solve these equations for different boundary and initial conditions in next few classes.

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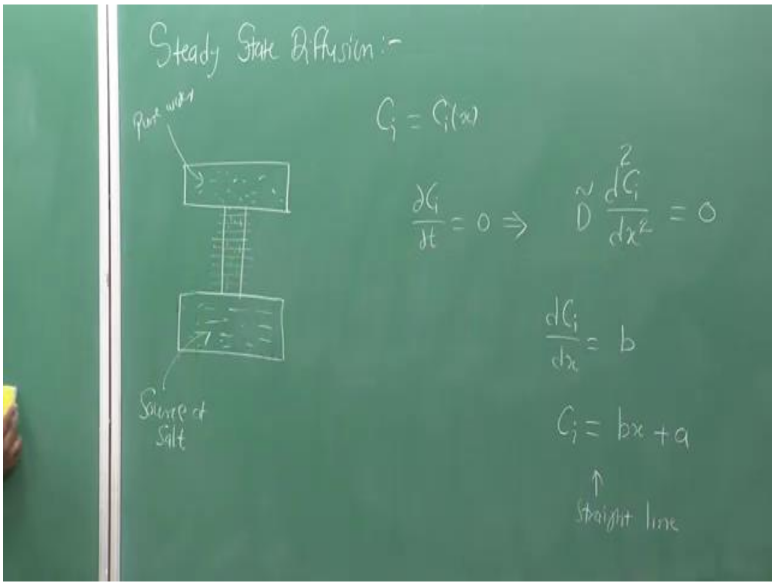

Let us start with the very simple case which is known as steady state diffusion. What is a steady state?

Professor: Right. The diffusion is occurring but it is not causing any change in concentration at any given position. And the classic example is the experiment done by Fick, remember. What he did he studied the diffusion of salt in water and he developed the steady state for that explained this in previous class.

And the way he conducted the experiment was a vertical tube through which salt was diffusing. The vertical tube contains solution of salt and water. At the bottom, this was basically the source of salt or has the saturated solution of salt in water. Its concentration was fixed which will not change because of diffusion, so this was almost an infinite source of salt. Similarly, top container had pure water which was a sink for salt. The water container was very large.

The addition of salt from bottom tube by diffusion into top will not cause significant change in the concentration. This remained pure water. So, C_i for salt of concentration was 0 here and it was fixed at the saturated concentration at the bottom. And through the middle tube the salt diffused through the solution from bottom to top and the steady state was developed. Steady state means at any given x position (x axis is vertical here), the concentration did not vary with time. Although, the concentration varies from bottom to top but at any given x it was fixed. Now, what should be the flux condition for this to happen? Think of the volume element that we used to derive continuity equation. The accumulation is equal to inflow minus outflow. So here there is no net accumulation or loss which means inflow should be equal to outflow. The flux should be constant at any given position for steady state to develop.

In this case C_i varies only as a function of x not as a function of t or:

$$C_i = C_i(x)$$

$$\frac{\partial C_i}{\partial t} = 0$$

which means from this diffusion equation we can write:

$$\widetilde{D}\frac{\partial^2 C_i}{\partial x^2} = 0, \qquad \frac{\partial^2 C_i}{\partial x^2} = 0$$

I am replacing the partial sign with ordinary derivative sign, because now C is only function of x, it is not a function of t because of the steady state. Now, you can easily solve the above equation.

$$\frac{dC_i}{dx} = b$$

b is a constant. If we solve this further we get:

$$C_i = bx + a$$

and this is an equation of straight line. When $\widetilde{D}$ is constant, the steady state profile that develops is a straight line. This is obvious from here itself, the second derivative is 0 which means the curvature is 0 which is basically the straight line.

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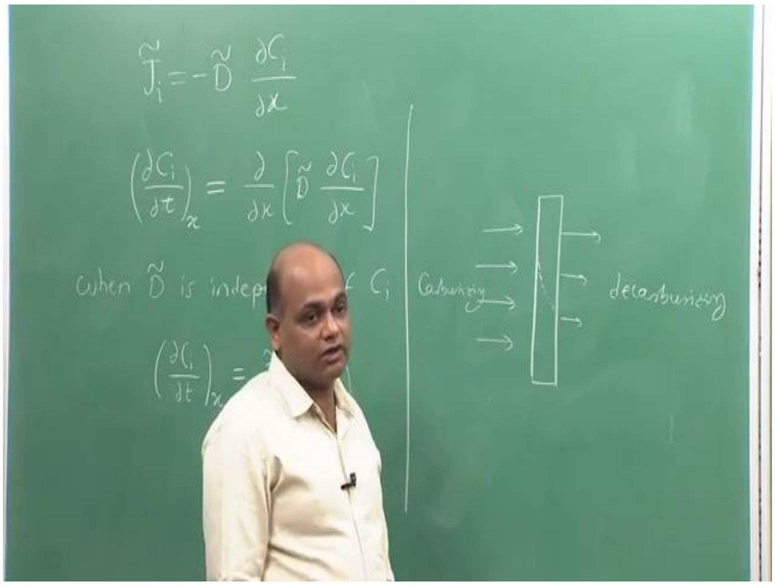

Another example of steady state, I can give here is consider a thin slab of low carbon steel. which is subjected to continuous carburizing on one side and decarburizing on the other side. Carburizing is addition of carbon onto the steel surface. Decarburizing means carbon is getting removed from the steel surface.

Now, if we maintain the right conditions, which are the carbon potentials at the two end are kept constant, there will be a continuous carburizing occurring from one side, continuous decarburizing occurring from the other side and in some time a steady state will be developed across the steel slab thickness. A profile like this will be developed. Now if I assume that diffusion coefficient is constant then I know it should be a straight line.

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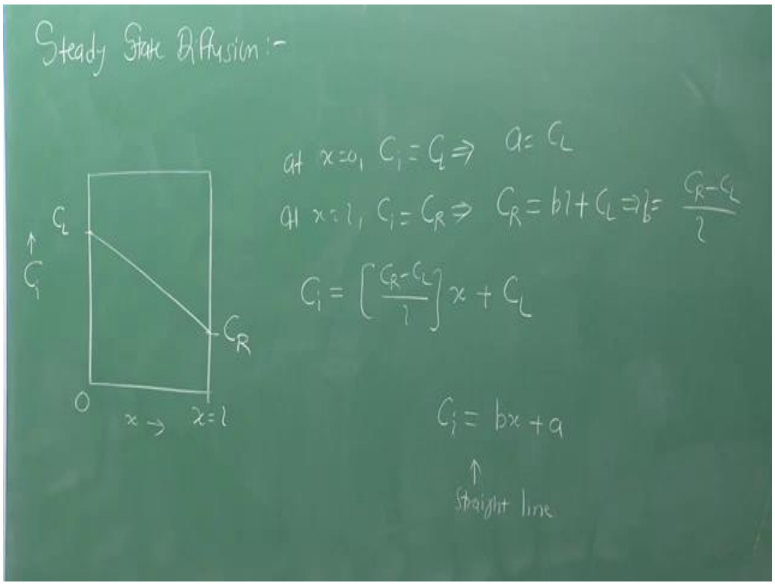

Let us draw the concentration profile here, I draw C_i versus x. x is from 0 to L, L is the thickness of the slab. And on left side concentration is C_L, C_R is the right side concentration and obviously right side is decarburizing. $C_R < C_L$ and I know a steady state will develop if the $\widetilde{D}$ is constant. And what should be that? We know at x equal to 0, $C_i = C_L$. This will give me:

$$At\ x = 0, \quad C_i = C_L \rightarrow a = C_L$$

$$At\ x = l, \quad C_i = C_R$$

$$C_R = bl + C_L \ \rightarrow b = \frac{C_R - C_L}{l}$$

$\frac{C_R - C_L}{l}$ is basically the slope of this straight line. We can write:

$$C_i = \left(\frac{C_R - C_L}{l}\right) x + C_L$$

This is the steady-state equation when $\widetilde{D}$ is constant. Now what happens if $\widetilde{D}$ is not constant which should be typically the case. If $\widetilde{D}$ is not constant, we cannot take simply $\widetilde{D}$ out.

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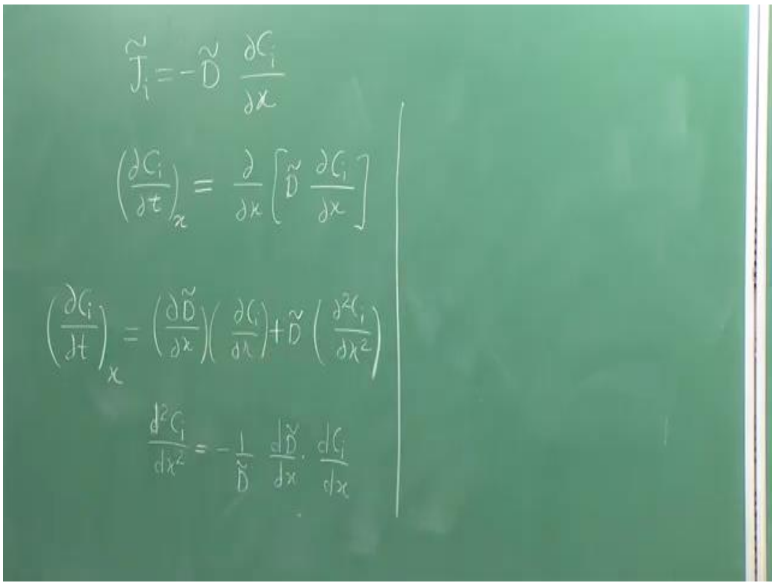

$$\tilde{J}_i = -\tilde{D}\frac{\partial C_i}{\partial x}$$

$$\left(\frac{\partial C_i}{\partial t}\right)_x = \frac{\partial}{\partial x}\left[\tilde{D}\frac{\partial C_i}{\partial x}\right]$$

$$\left(\frac{\partial C_i}{\partial t}\right)_x = \left(\frac{\partial \tilde{D}}{\partial x}\right)\left(\frac{\partial C_i}{\partial x}\right) + \tilde{D}\left(\frac{\partial^2 C_i}{\partial x^2}\right)$$

$$\frac{d^2 C_i}{dx^2} = -\frac{1}{\tilde{D}}\frac{d\tilde{D}}{dx}\cdot\frac{dC_i}{dx}$$

We can write:

$$\left(\frac{\partial C_i}{\partial t}\right)_x = \left(\frac{\partial \tilde{D}}{\partial x}\right)\left(\frac{\partial C_i}{\partial x}\right) + \tilde{D}\left(\frac{\partial^2 C_i}{\partial x^2}\right)$$

And when the steady state develops, we can replace dou with d and $\left(\frac{\partial C_i}{\partial t}\right)_x = 0$:

$$\frac{d^2 C_i}{dx^2} = -\frac{1}{\tilde{D}}\frac{d\tilde{D}}{dx}\frac{dC_i}{dx}$$

Now, we need to know $\tilde{D}$ as a function of x or in other words we need to know $\tilde{D}$ as a function of C_i. If $\tilde{D}$ varies with composition, we need to know how $\tilde{D}$ is varying with composition. Otherwise, we cannot solve this equation. We can qualitatively see how the profile will look like, will it be a straight line? Obviously not.

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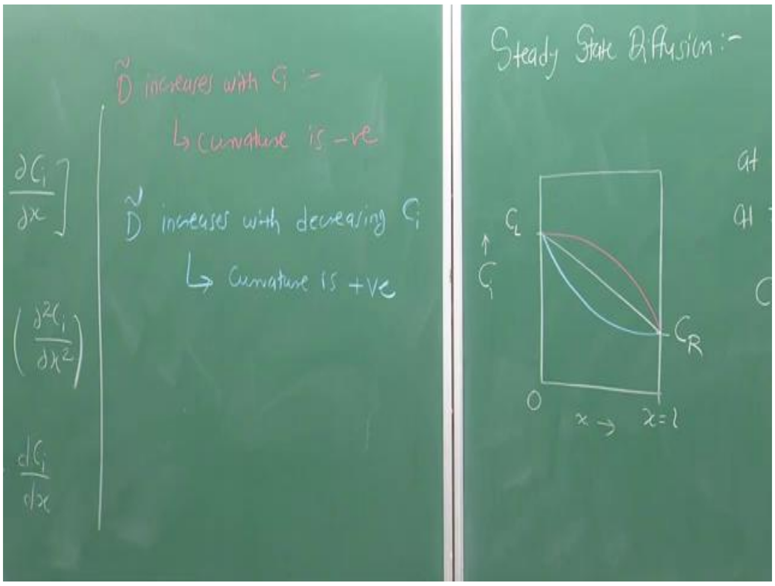

Suppose $\widetilde{D}$ increases with C_i, then what should happen? $\widetilde{D}$ is increasing with C_i and we know the concentration is decreasing from left to right. So, $\widetilde{D}$ is decreasing with x or this derivative $\frac{\partial \widetilde{D}}{\partial x}$ is negative. Now $\frac{\partial C_i}{\partial x}$ is here is negative because concentration is decreasing. So, the curvature in this case will be negative.

Qualitatively the concentration profile will look something like this, it will have a negative curvature. Oppositely if $\widetilde{D}$ decreases with increasing C_i, then the profile will develop positive curvature. Qualitatively, it will look like this, clear? Any question? This was about the steady state.

Now when concentration changes with time that is a non-steady state condition. We will solve this equation for different boundary conditions and initial conditions. We will like to assume $\widetilde{D}$ is constant then we can have analytical solution. So, we will assume $\widetilde{D}$ constant, so that we have an idea of how the concentration profiles will behave for different boundary conditions. Any doubt?

Student: In the curvature, would not there be a $\frac{1}{\widetilde{D}}$ effect as we have in the denominator $\widetilde{D}$.

Professor: But $\widetilde{D}$ is positive. For binary, $\widetilde{D}$ will always be positive. The magnitude obviously will be affected but the sign will not. Anything else? All right, thank you.