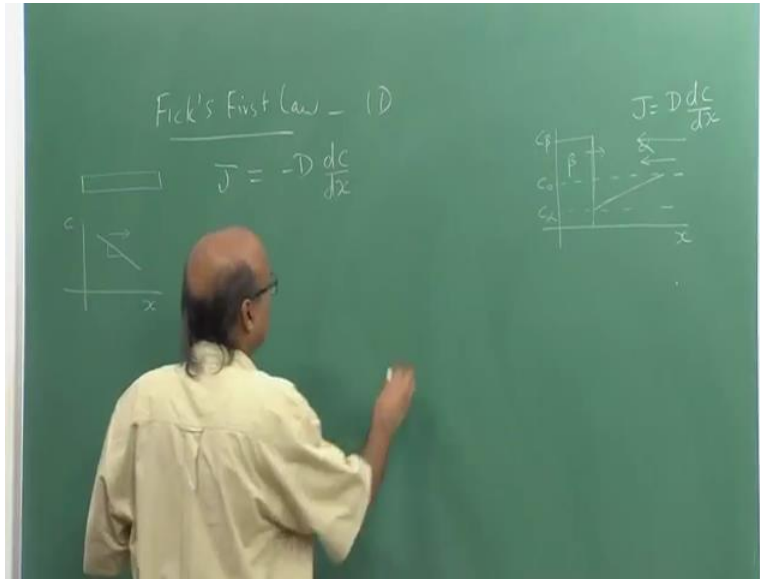


Heat Treatment and Surface Hardening (Part-1)
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Lecture Number 38
Diffusion in Solids - 3

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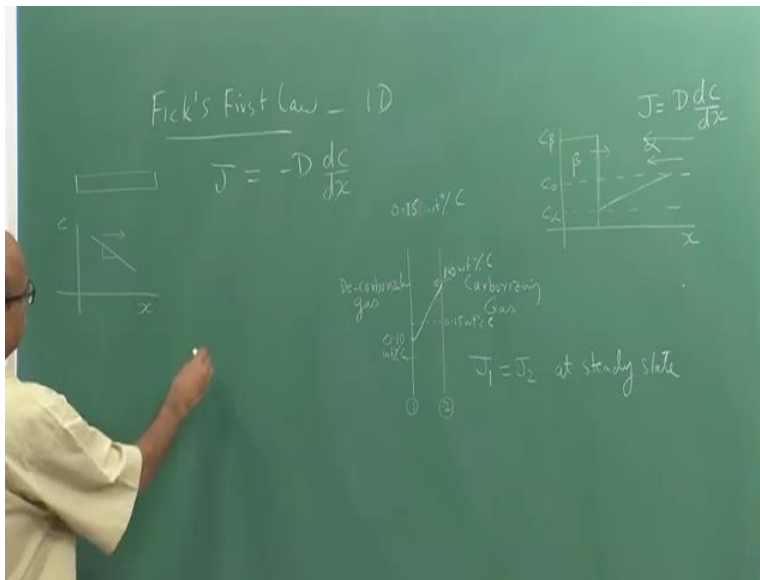


So, in the last lecture we had looked at Fick's First law and just a restated again the Fick's first law of diffusion in one dimension can be written as the flux of the atom in a concentration gradient is given by $J = -D \frac{dc}{dx}$. The $\frac{dc}{dx}$ is the concentration gradient D is a diffusion coefficient J is the flux of atoms for so for instance if I had a concentration in a bar of solute atoms in this fashion, then the slope of this line is $\frac{dc}{dx}$ and this will indicate this particular relationship of Fick's first law will indicate that flux of solute atoms would take place from higher concentration to lower concentration.

We had seen this relationship in another context in the lectures on diffusional growth. So, just to recall we had this situation where there was a beta precipitate growing in an alpha matrix. So, beta precipitate has a concentration of c_β concentration far away from the beta into the alpha you c_α not while the equilibrium concentration at the given temperature of alpha is c_α . So, here inside alpha beta is growing in this direction and inside alpha thus the concentration of the solute atoms given by this line.

Here we had assumed that this was a linear relationship for simplicity. In this context there was a flux of solute atoms in this direction and which we had written as this flux as D times dc by dx . Note that we had not written any negative sign here as it is written in the Fick's first law because we had simply written that this is the magnitude of the flux and the flux was clearly from a higher concentration to a lower concentration. And this flux then was related to the velocity of the alpha beta interface that was growing into the alpha.

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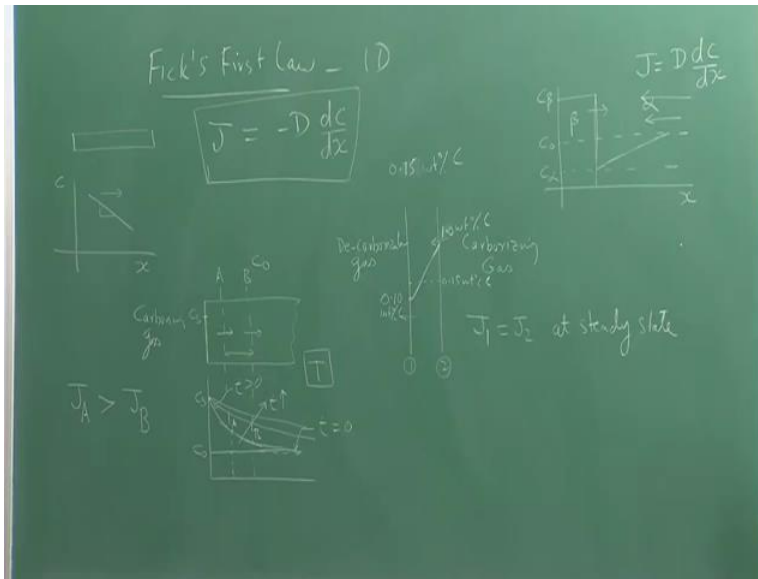


Consider another situation suppose I had a thin miles still sheet of 0.1 weight percent carbon or zero point let me make it 0.15 weight percent carbon. And let say I have a decarburizing gas on this side of the miles steel sheet such that the concentration on the carbon on the surface of the sheet is kept at 0.1 weight percent carbon.

On this side on this surface of the sheet we have a carburizing gas, such that the surface concentration is fixed at zero as as 1.0 weight percent carbon. And we had a sheet which we started out 0.15 weight percent carbon. Very clearly carbon will be depleted on the left hand side, because of the smaller concentration of carbon on the left hand side while on the right hand side the sheet will be enriched with carbon because of the higher surface concentration of 1 weight percent that is fixed on the surface.

But eventually when the steady state is reached then the concentration in this mild steel sheet will be given by this straight line. So, here it is 1 weight percent here it is 0.1 weight percent. So, there is a continuous flux of carbon going in to the sheet from the right hand surface and the continuous flux out. And both of these fluxes at steady state are constant and hence the profile of the carbon concentration inside this thin sheet would be given by this linear line.

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So, if I look at flux at the two surfaces, at surface 1 at surface 2, then at steady state J_1 is equal to J_2 . Now consider another situation where I have a long rod or let say of mild steel, again of some concentration c_0 . Now I this surface of this rod is exposed to a carburizing gas such that the surface concentration is maintained at c_s . So if I plot how the carbon concentration varies at different times.

So, this is my fixed surface concentration at time t equal to zero. The carbon contain in this mild steel sheet is simply c_0 everywhere. So, the this is the situation, this is the concentration profile at t equal to zero. But we had put keeping this at some high temperature, so that carbon atoms can diffuse after some time the, the concentration profile would become something like this. So, this is at some time t greater than zero.

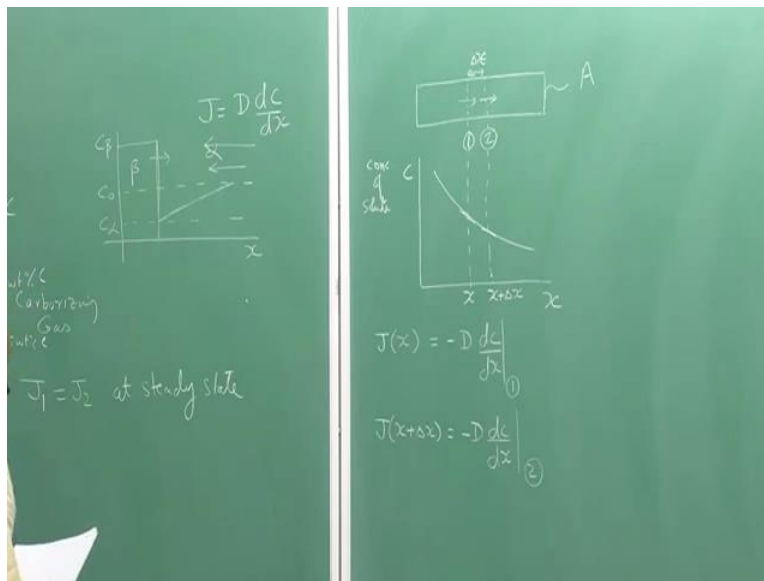
Now, if I look at the fluxes at the flux is at different locations in this material, so if I look at the flux of carbon atoms on this plane A and plane B. so, there is a flux of carbon atoms going into

this and the flux going across the two planes A and B. So, if I look at what is the flux at A and what is a flux at B. So, flux at A J_A is given by would be related to the slope at point A of the curve flux at B would be related to the slope at point B of the flux and very clearly the slope at A is larger than the at B, and if I look at the Fick's first law it will tell me, because D being constant at both A and, B J_A would be greater than J_B .

Very clearly if I look this element in this region of the material, the more carbon atoms entering this region then the number of carbon atoms leaving this region because there is a higher flux entering the region as compared to the flux of carbon atoms leaving this region. So, there is going to be a buildup of carbon atoms as the function of time and slowly as time increases these profiles would keep becoming like this with increasing carbon contain at various locations.

Clearly there is a time dependence in this diffusion and we should try to see how we can quantitatively assess this time diffusion and how this concentration profiles will change with increasing time.

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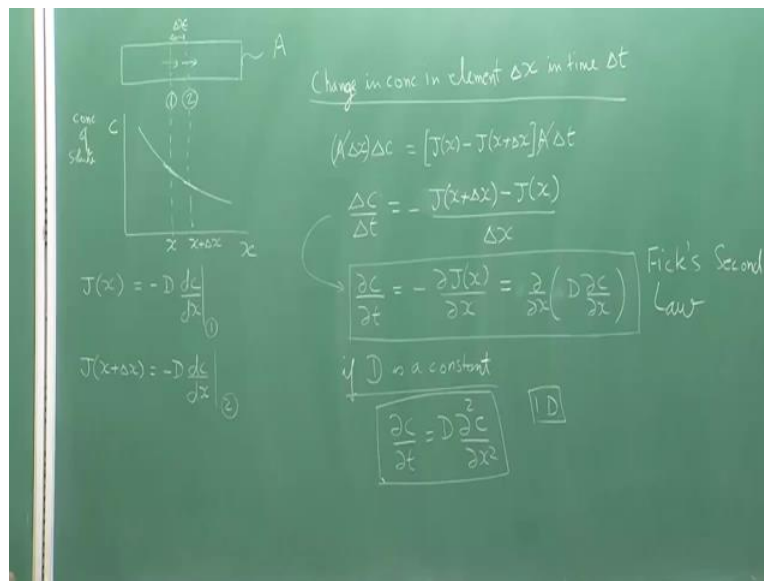
So, let us consider the situation in this manner, rod whose area of cross section is A and if I look at the concentration profile of the solute atoms in this rod, so concentration of solute given by c as a function of distance this profile is not no longer a straight line as we did not taking but as a curve.

And let us consider a small region a small element in this rod where we will analyze how the concentration is going to change in this region as a function of time. So, let us consider this as plane 1 and consider this as plane 2 and these two planes are located at plane 1 is located at x plane 2 is located at $x + \Delta x$. So, small increment Δx , so we are looking at a small element Δx and the area of the cross section of this element is A .

So, what is the flux at across the plane 1. So, number of atoms diffusing across plane 1 per unit area per unit time. So, let me write this flux at this directly comes from Fick's First law which tells me that the flux would should be minus D times the concentration gradient at plane 1 dc by dx . So, therefore flux at plane 1 would be minus D the diffusion coefficient dc by dx the slope of the concentration profile at plane 1.

Similarly I can analyze what is the flux of solute atoms across plane 2 that is j at $x + \Delta x$, well again from Fick's First law this is minus D dc by dx at plane 2. So, I have dc by dx there is a slope given by this line and a tangent here gives me the slope at plane 2 of the concentration profile.

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Now let us see the change in concentration in the element Δx in a small interval of time Δt . So, what is the change in concentration of Δx inside this element after time Δt .

Suppose the change in concentration is Δc , if I so this concentration is number of solute atoms or moles of solute atoms per unit volume. So, let me multiply these Δc by the volume by this element and the volume of this element is simply A times Δx , A is the area of cross section and Δx is the length of the element. So, this is the total change in the concentration in time Δt . This should be equal to the rate at which solute atoms are entering this minus the rate at which the solute atoms are leaving this element from plane 2 multiplied by the area of cross section multiplied by the time elapsed that is Δt .

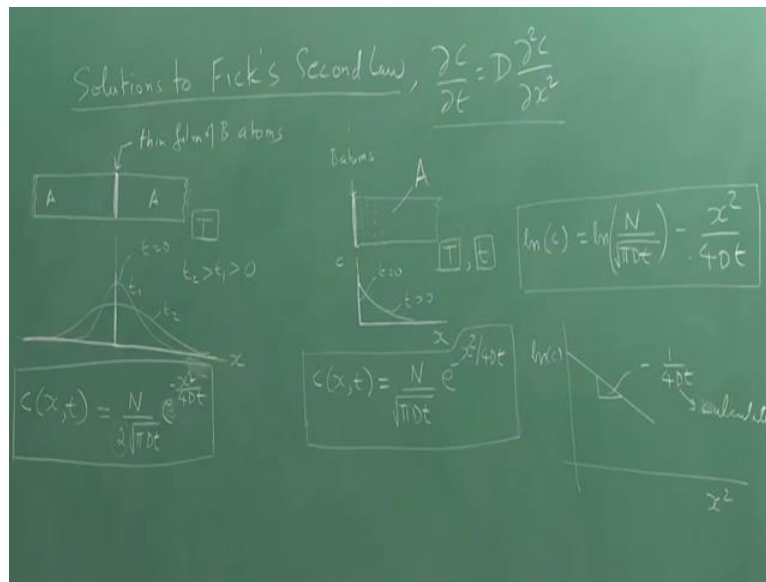
So, J_x minus $J_{x+\Delta x}$, this is the net flux per unit area per unit time, so A multiplied by area and multiplied by time Δt . So, this represents on the right hand sides that again the change in concentration after time Δt . So, both so both of these sides, so left hand side also represents the same thing on the right hand side is also is also representing the same thing. I can delete this area of cross section and rewrite this equation as Δc upon Δt equals and let me rewrite this, I interchange these two terms and put a minus sign outside as J_x plus Δx minus $J_{x+\Delta x}$ divided by Δx .

Now in the limit of Δt and Δx both becoming in infinite decimal, this relationship can simply be written as in terms of partial derivatives $\frac{\partial c}{\partial t}$ equals minus $\frac{\partial J_x}{\partial x}$. This is J from the Fick's first law is simply minus $D \frac{\partial c}{\partial x}$ I substitute that and this would become minus $\frac{\partial}{\partial x}$ times minus $D \frac{\partial c}{\partial x}$. Since, both of them are we have a sign minus inside and outside I can just remove the negative signs everything is positive now.

So, this expression that we have is this is a differential equation which describes the change in concentration as a function of both distance and time x and t . This relationship is also called as Fick's Second law. This is written in one dimensions one can generalize this 2 - 3 dimensions as well. If the diffusion coefficient D is a constant which in many situations we can assume then Fick's second law can be written as essentially we take the diffusion coefficient out of the differential and it can be written as $\frac{\partial c}{\partial t}$ is equal to $D \frac{\partial^2 c}{\partial x^2}$. So, this is Fick's second law in 1 dimension.

So, the solutions to this Fick's second law we would be able to solve problems like this as to how the concentration profile would vary as a function of time. So, therefore the next step is let us explore the solutions to this particular differential equation.

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So, let us look at solutions to Fick's second law which $\frac{\partial c}{\partial t}$ is equal to D the diffusion coefficient times $\frac{\partial^2 c}{\partial x^2}$. Let us consider a following situation, suppose I had a thin film of B atoms sandwiched between two rods of long rods of A atom. So, I have a thin film of B atoms and out here I have atoms in on this side also I have A atoms forming some crystal structure.

And if I look at the concentration profile of B and clearly at a time t equal to zero, this is by concentration profile. However after some time t_1 let say this profile would have become something like this provided the temperature was high enough for appreciable diffusion to take place.

So, this could be at time t_1 , even of some more larger time this profile would become broader as B atoms spread on both sides of the thin film. So, here it is t_2 greater than t_1 greater than t_1 greater than zero. So, as time is spreading B atoms are diffusing. To this kind of a problem we can apply Fick's second law and solve the differential equation and the solution to this differential equation is given as.

Suppose in this thin film I had 10 atoms so B per unit area then these concentration profiles as a function of time and distance is given by the following solution of the Fick's second law. So, $c(x,t)$ as the function of x and t is given by $\frac{N}{\sqrt{4Dt}}$ times $e^{-\frac{x^2}{4Dt}}$.

minus x^2 upon $4Dt$. So, this is the solution, this is one of the solutions of the Fick's second law for a situation like this.

So, as this is giving me now the concentration profile as a function of both distance and time you can verify that this is actually indeed the solution to the differential equation is by substituting the solution back into the differential equation which means that you on left hand side you will compute by taking the derivative with respect to time right hand side you will take the second derivative of concentration c with respect to the distance x and both the left hand side and right hand side must be equated for verifying the solutions.

If can also have a situation like this that I have a long rod and at the end of this rod I plate I coat of thin film of B atoms and this is all pure A, then at time t equal to zero. This is by concentration profile of b and that at later time by profile is going to become something like this eventually it will should flatten out.

So, this is at t equal to zero this is at some time t greater than zero. The solution to this is very similar to this, since now the diffusion of B atom will only take place on one side where here diffusion of B atoms are taking place on both the sides this factor of 2 would not be present in the solution otherwise the solution will remain the same.

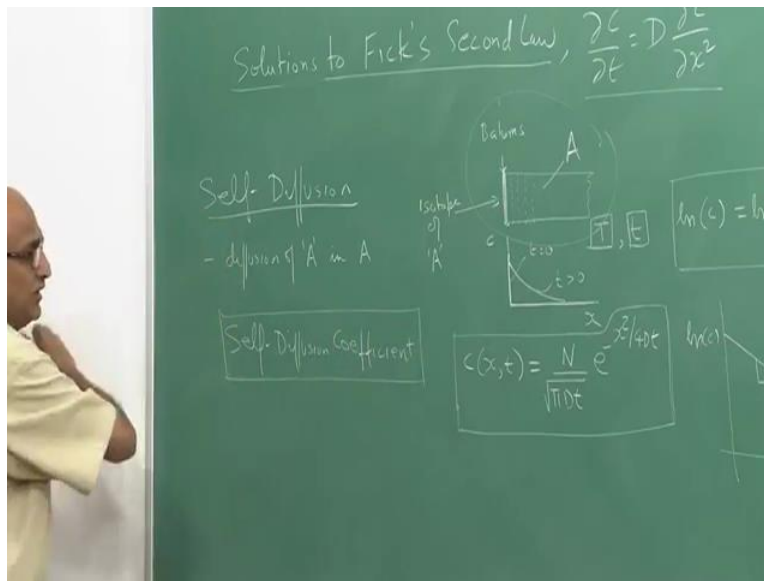
And hence the solution to this is simply $c(x,t)$ is equal to N divided by square root $\pi D t$, $e^{-x^2/4Dt}$ to power minus x^2 upon $4Dt$. But this also suggest a simple way of experimentally estimating the diffusion coefficient D . How can we do that, well we can do that A in the in the following manner that we create a situation like this we perhaps electroplate B atoms at 1 end of a rod, then we keep this rod at some temperature T at which some appreciable diffusion can takes place for a certain amount of time t .

After that at different distances we slice the material and measure the concentration of B at different distances x . So, I will have a data concentration versus distance for a given temperature and a given time that should follow this relationship. So how should we do this suppose I take natural log of both sides, so this will give me $\ln c$ equal $\ln N$ divided by under root $\pi D t$ minus $x^2/4Dt$, so, taking natural logs on both sides.

This suggests that the log of the concentration should linearly vary with the square of the distance. So, if I would plot that experimental data in the form of $\log c$ versus x square, I should get a relationship I should get a straight line like this. The slope of the line clearly would be minus 1 upon 4 d t from this slope I can find out I can measure or calculate the diffusion coefficient.

And in fact I can then estimate diffusion coefficient for different temperatures as well as different types. So, I can also study how the diffusion coefficient D varies with temperature in fact it will vary with temperature and we would be discussing this in a subsequent lecture that how the diffusion coefficient D varies with temperature. And finally there is one important concept that I can bring in and which is the concept of self-diffusion coefficient or simply self-diffusion.

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So, what is self diffusion well it is simply 5 A atoms I want to find out how fast A atoms diffuse in A atoms. So, diffusion of A in A, here so far we able looking at diffusion of B in A here I am saying diffusion of A atoms in the structure of A. So, what do we do we use the similar setup to measure except that instead of B atoms I would put in isotope I will the plate I will produce a thin film plated on the end of it an isotope of A would be plated.

And this isotope of A would be dragged and measured, what is the concentration of the A isotopes at different distances after an experiment has been done for a specific temperature and time with that one can then obtain what is called the self-diffusion coefficient, with this I stopped here and will continue with the next lecture.