Diffusion in Multicomponent Solids
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Lecture-43

Last class we went over experimental techniques for the determination of self and impurity diffusion coefficients. Now, next few classes we will talk about interdiffusion. We will study some of the techniques which are used for determining interdiffusion coefficients. We will start with binary systems and will also see how the interdiffusion coefficients are determined in ternary and higher order multicomponent systems.

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Most commonly interdiffusion coefficients are determined using diffusion couple technique. In this, two alloys of different compositions are placed in contact with each other. They are held together by some kind of jig and this assembly is isothermally annealed at some temperature T at which we want to determine the interdiffusion coefficients. The annealing continues for the desired time so that good enough diffusion zone is developed which can be analysed for interdiffusion coefficients. At the end of the annealing, the diffusion couple is quenched from the annealing temperature. Quenching is essential in order to retain the concentration profiles and the microstructures that are developed at the desired temperature T. After quenching, the diffusion couple is cut parallel to the diffusion direction. One point has to be noted here is both the alloys are homogenous in the starting. Of course, they have different compositions, but each individual alloy block is homogeneous in composition itself.

And for the accurate determination of interdiffusion coefficients, we work with single phase alloys and single phase diffusion couples. It means even after diffusion, no second phase is developed within the interdiffusion zone. And both sides of the couple have same crystal structure or the same phase.

After sectioning, the surface is metallographically polished and the composition at each point is determined along the diffusion zone. Each composition point actually represents composition of the plane which is the plane going into the plane of board here. Determination of composition is typically done by electron probe micro analysis (EPMA) using wavelength dispersive spectroscopy (WDS) because it gives the most accurate micro composition. The experimental concentration profiles are further analysed for interdiffusion fluxes and interdiffusion coefficients.

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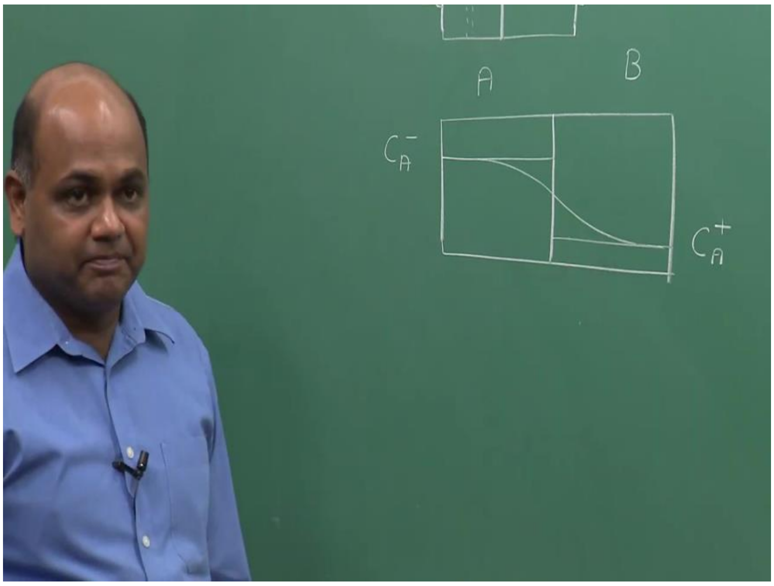

Suppose we started with two different alloys A and B. Let us first consider binary alloys. So, just one concentration variable is sufficient to define the composition of each individual alloy block. To start with let us say alloy A had composition C_A^- and alloy B had the composition C_A^+. After the diffusion annealing, there will be interdiffusion and a concentration gradient will be developed. Now, this composition profile as I said can be obtained by EPMA.

The first issue here is how do we locate this initial contact plane? Initial contact plane is the plane of contact before the diffusion started. Ideally, if there is a good diffusion bonding, that has occurred between the two alloy blocks, this plane will not be physically distinguishable in the diffusion zone.

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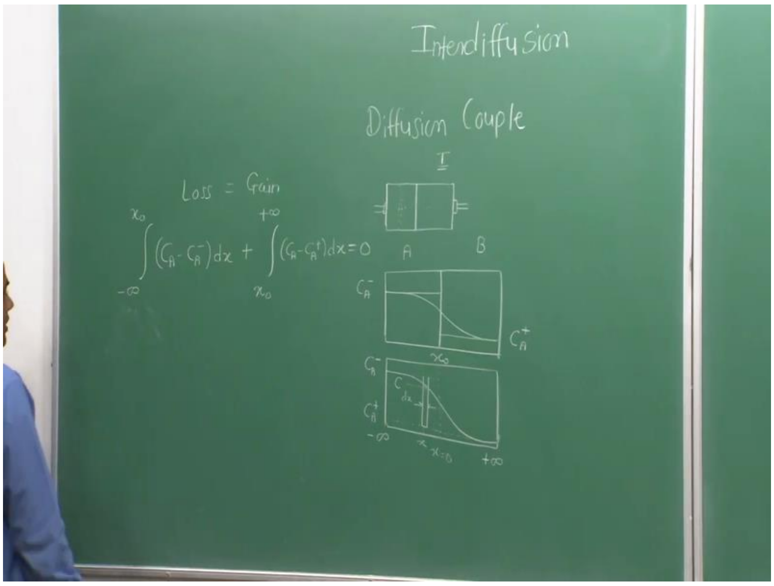

What we will see is only a concentration profile something like this. So, how do we identify this initial contact plane, where we assign $x = 0$ which is our plane of reference. It is first important to find out that initial contact plane. How do we go about this? The simplest way is, to do the mass balance. Because we know the loss of A on the left side of this initial contact plane should be equal to the gain in A on the right side of this initial contact plane. Whatever A has diffused from left should appear on right. That is the simple principle that we use.

If we consider a small volume element of width dx in the diffusion zone and if we consider unit cross sectional area, then the volume of this small element would be dx. We want to do the mass balance, loss on left side should be equal to gain on the right side. The loss in this case, if C represents the composition or concentration of A and x is the location of this volume element then the loss in this particular element would be $(C_A - C_A^-)dx$. And the loss will be from the left terminal all the way to the plane here $x = 0$. Let us call this x_o in terms of the coordinates that we have used for obtaining the profiles. If we integrate this from the left terminal alloy to the plane x_o, i.e. from $-\infty\ to\ x_o$ we will get the total loss..

Now, remember when we talk about diffusion couple, most of the time we are dealing with the infinite diffusion couple. For interdiffusion analysis infact, we want infinite boundary conditions to be obeyed. It means diffusion will not penetrate all the way through the two terminals of the two alloy blocks. In essence, we can treat the left terminal as $-\infty$ and the right terminal as $+\infty$. And at the two terminals, the original concentrations will be maintained. The original concentrations where C_A^- at $-\infty$ and C_A^+ at $+\infty$. If we consider any volume element the gain similarly on the other side would be $(C_A - C_A^+)dx$ from x_o to $+\infty$. And there summation should be equal to 0.

$$\int_{-\infty}^{x_o} (C_A - C_A^-)dx + \int_{x_o}^{+\infty} (C_A - C_A^+)dx = 0$$

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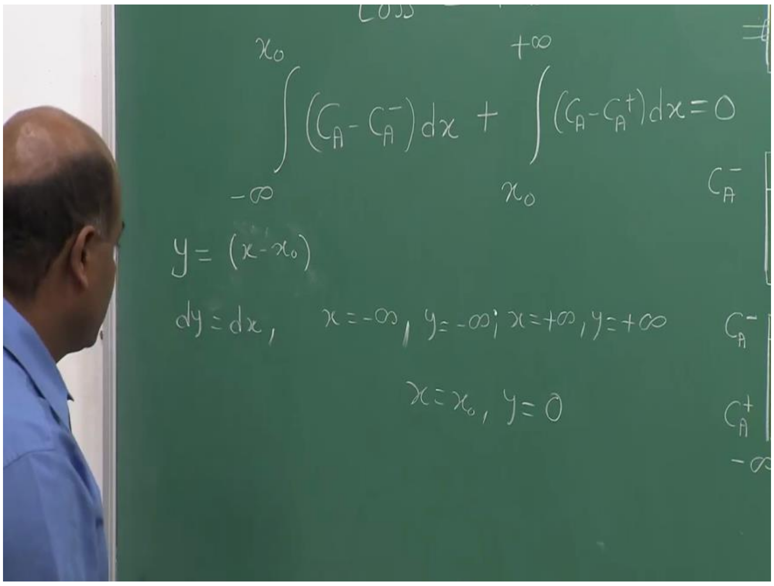

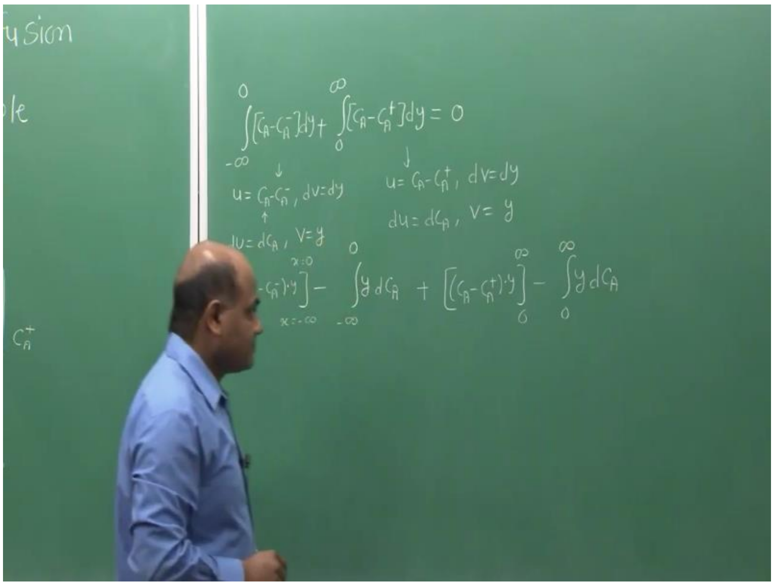

Now, if we replace:

$$y = (x - x_o)$$

we will get:

$$dy = dx\,, \quad At\; x = -\infty\,, \quad y = -\infty; \;\; At \quad x = +\infty, \quad y = +\infty$$

$$x = x_o, \quad y = 0$$

With this substitution we can write:

$$\int_{-\infty}^{0} (C_A - C_A^-)dy + \int_{0}^{+\infty} (C_A - C_A^+)dy = 0$$

To simplify this further, let us integrate by parts. For integration by parts, for the first integral, let us assume:

$$u = C_A - C_A^- \ , \quad dv = dy$$

Remember C_A here indicates C_A at the position x that is being considered. We have:

$$du = dC_A \quad , \ v = y$$

$$\int_{a}^{b} udv = [uv]_a^b - \int_{a}^{b} vdu$$

We will get the first integral as:

$$\int_{-\infty}^{0} (C_A - C_A^-)dy = [(C_A - C_A^-)y]_{-\infty}^{0} - \int_{-\infty}^{0} ydC_A$$

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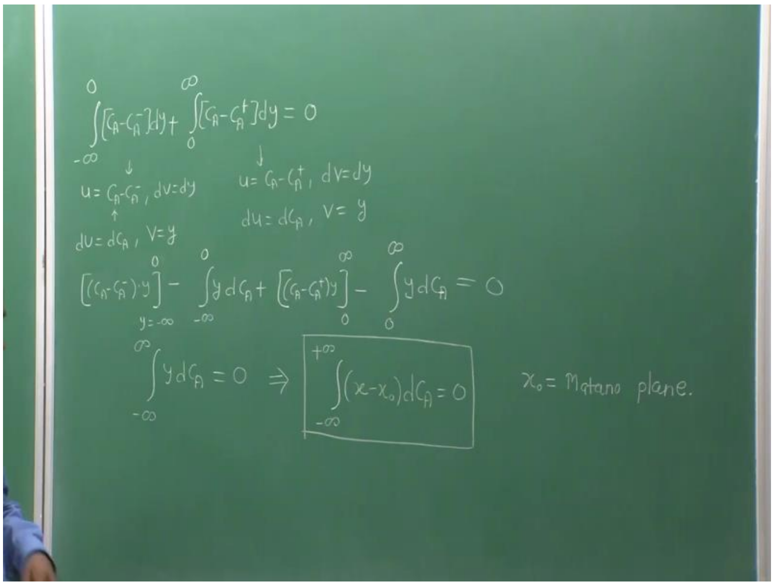

Similarly, for the second integral, we take:

$$u = C_A - C_A^+ \ , \qquad dv = dy$$

$$du = dC_A \quad , \quad v = y$$

Using the integration by parts we have:

$$\int_{x_o}^{+\infty} (C_A - C_A^+)dx = [(C_A - C_A^+)y]_0^{+\infty} - \int_0^{+\infty} ydC_A$$

Adding both the equation we get:

$$[(C_A - C_A^-)y]_{-\infty}^0 - \int_{-\infty}^0 ydC_A + [(C_A - C_A^+)y]_0^{+\infty} - \int_0^{+\infty} ydC_A = 0$$

At $y = -\infty$, $C_A = C_A^-$ and at $y = +\infty$, $C_A = C_A^+$. This will give:

$$\int_{-\infty}^0 ydC_A + \int_0^{+\infty} ydC_A = 0$$

Or

$$\int_{-\infty}^{+\infty} ydC_A = 0$$

If you substitute for y, we get:

$$\int_{-\infty}^{+\infty} (x - x_o)dC_A = 0$$

And this is the equation that we use for locating the initial contact plane here from the experimental concentration profile. This was proposed by Matano. This plane x_o is also referred to as Matano plane. Now, we need to know two points here. First, we obtained this equation independent of number of components. Which means, whether we are considering binary couple, ternary couple or quaternary couple, this should be applicable. But there is also other condition with it. We want to use Matano plane as the reference plane for finding out interdiffusion fluxes and interdiffusion coefficients. So. this plane has to be same for all the components. no matter which component we use for finding the location of Matano plane, we should get the same location. This is possible only if all the components have constant partial molar volumes. If the partial molar volume of the components is function of composition, then with diffusion there will be net expansion or shrinkage of the couple. And therefore, each individual component will yield different location of this plane. The second condition for this is that the partial molar volume should be independent of composition for each diffusing element.

So, we got the reference plane. Now, what next? We need to find the interdiffusion coefficient from here. How do we go about this?

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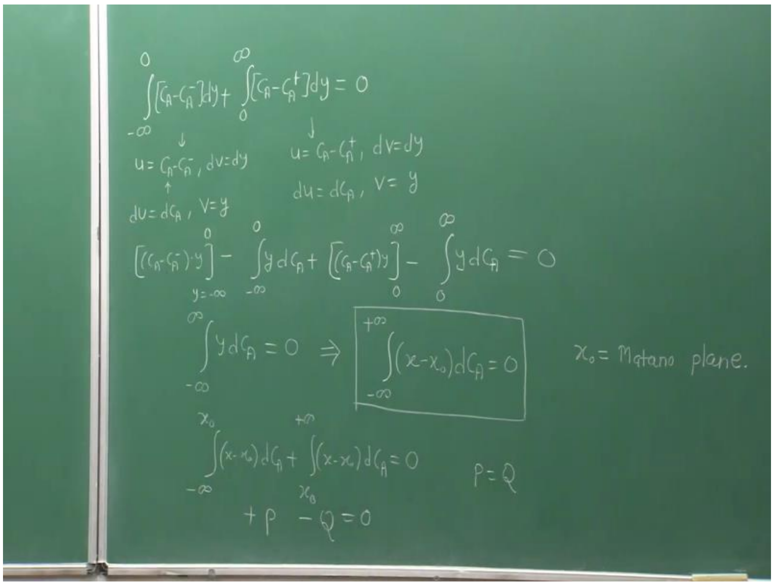


$$\int_{-\infty}^{0}[C_A-C_A^-]dy+\int_{0}^{\infty}[C_A-C_A^+]dy=0$$

$u=C_A-C_A^-,\ dv=dy$

$du=dC_A,\ v=y$

$u=C_A-C_A^+,\ dv=dy$

$du=dC_A,\ v=y$

$$\Big[(C_A-C_A^-)\cdot y\Big]_{y=-\infty}^{0}-\int_{-\infty}^{0}y\,dC_A+\Big[(C_A-C_A^+)y\Big]_{0}^{\infty}-\int_{0}^{\infty}y\,dC_A=0$$

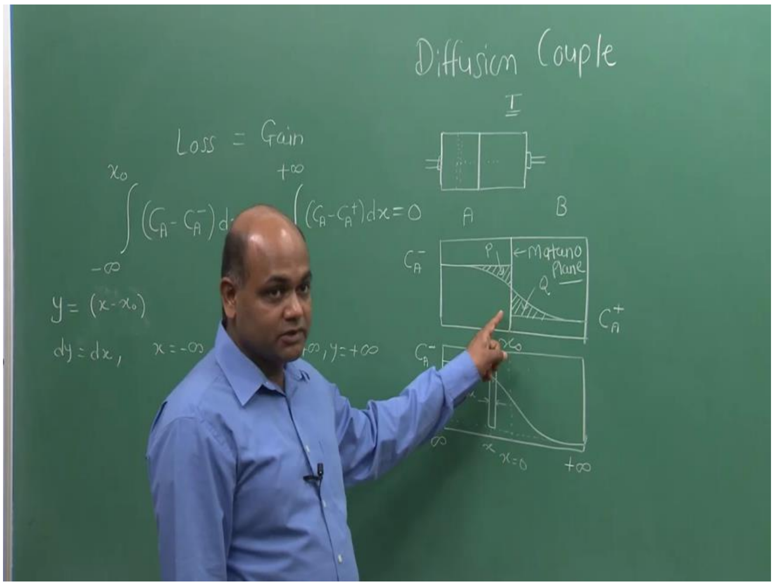
$$\int_{-\infty}^{\infty}y\,dC_A=0\Rightarrow\boxed{\int_{-\infty}^{+\infty}(x-x_o)dC_A=0}$$

x_o = Matano plane.

$$\int_{-\infty}^{x_o}(x-x_o)dC_A+\int_{x_o}^{+\infty}(x-x_o)dC_A=0$$

$$+P\quad -Q=0$$

$P=Q$



If we again write this equation, if we split this integral at x_o, we can write:

$$\int_{-\infty}^{x_o}(x-x_o)dC_A+\int_{x_o}^{+\infty}(x-x_o)dC_A=0$$

And this integral is nothing but the area under the curve plotted onto the plane x_o. If we look at this figure here, the integral from $-\infty$ to x_o, it is the area under the curve plotted on to this

x_o let us call this area P. What should be the sign for this area? Remember $x - x_o$ is negative on the left side and as we go from left to right dC_A is negative. So the sign should be positive.

This integral from x_o to $+\infty$ is the area under the curve again plotted on to the Matano plane. It represents this area Q. And the sign of the area would be $x - x_o$ is positive on the right side and dC_A is still negative, the sign would be negative.

$$P - Q = 0$$

It means area P on the left should be equal to area Q on the right. This is how we can locate the initial contact plane or which is also referred to as Matano plane. We have fixed the reference frame here with the assumption that partial molar volumes of all the individual components are independent of composition. Next, we need to find out the interdiffusion coefficient. That is our goal, main goal here.

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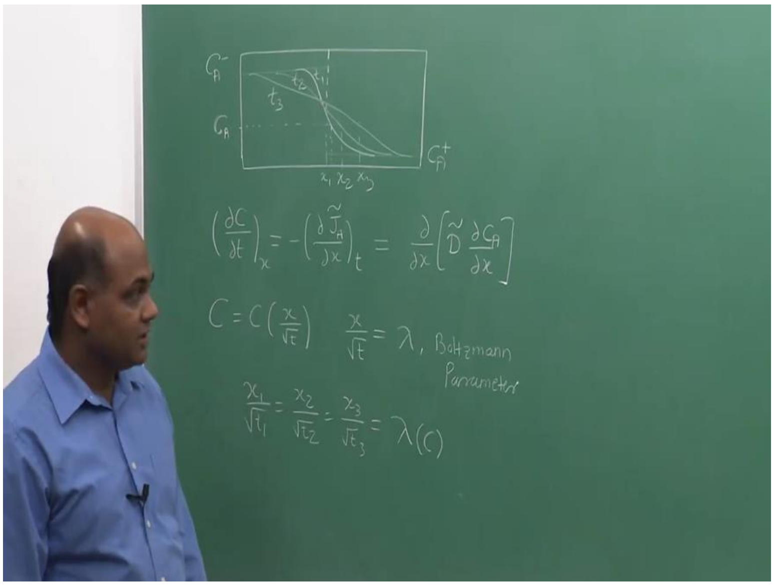

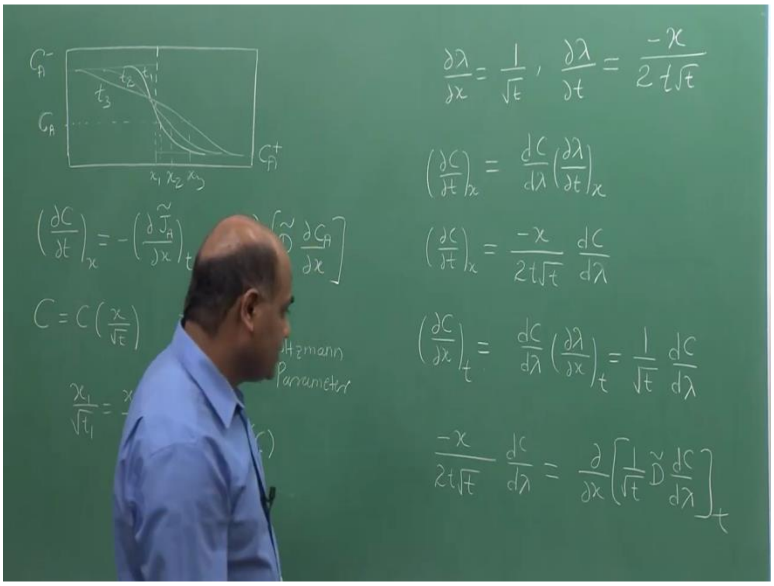

lLet us consider this concentration profile again. Here, we have C_A^- is concentration on left side, C_A^+ is concentration on the left terminal. And we know diffusion equation:

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

When we are considering the practical system, the interdiffusion coefficient $\widetilde{D}$ is function of composition. We have to write this right hand as:

$$\left(\frac{\partial C}{\partial t}\right)_x = -\left(\frac{\partial \tilde{J}}{\partial x}\right)_t = \frac{\partial}{\partial x}\left[\widetilde{D}\frac{\partial C}{\partial x}\right]$$

Since we are referring to component A, let us write:

$$\left(\frac{\partial C_A}{\partial t}\right)_x = -\left(\frac{\partial \tilde{J}_A}{\partial x}\right)_t = \frac{\partial}{\partial x}\left[\widetilde{D}\frac{\partial C_A}{\partial x}\right] \qquad (1)$$

Of course, we are referring to the binary interdiffusion here which needs only one interdiffusion coefficients for both component A and B. We need to solve this equation for $\widetilde{D}$ and $\widetilde{D}$ is varying with x. We will use the approach proposed by Boltzmann here. We know when $\widetilde{D}$ was constant, we have solved this equation analytically. C is a function of $\frac{x}{\sqrt{t}}$:

$$C = C\left(\frac{x}{\sqrt{t}}\right) \quad and \quad \frac{x}{\sqrt{t}} = \lambda$$

λ is known as Boltzmann parameter. Boltzmann proposed that this should also be true when $\widetilde{D}$ is varying with composition. This has been actually proved in practical diffusion couple, in practical systems that is   is a function of λ. What does that mean?

If we anneal the same diffusion couple at the same temperature for 3 different times, we will get different composition profiles like this and if you track any the position of particular composition plane, let us say C_A here for 3 different times in the diffusion zone, we can say:

$$\frac{x_1}{\sqrt{t_1}} = \frac{x_2}{\sqrt{t_2}} = \frac{x_3}{\sqrt{t_3}} = \lambda(C)$$

Where x_i is the position of the plane at time t_i. λ is constant for a given composition. We would transform this partial differential equation to ordinary differential equation using the Boltzmann transformation and by using this Boltzmann parameter λ. Let us see how we do that.

Since,

$$\lambda = \frac{x}{\sqrt{t}}$$

$$\frac{\partial \lambda}{\partial x} = \frac{1}{\sqrt{t}} \quad , \quad \frac{\partial \lambda}{\partial t} = -\frac{x}{2t\sqrt{t}}$$

Now, if we look at the left hand side of Eq. (1) we can write:

$$\left(\frac{\partial C}{\partial t}\right)_x = \frac{dC}{d\lambda}\left(\frac{\partial \lambda}{\partial t}\right)_x = -\frac{x}{2t\sqrt{t}}\frac{dC}{d\lambda}$$

Note, we are writing the derivative of C with respect to λ as ordinary derivative, because C is just a function of λ. Similarly,

$$\left(\frac{\partial C}{\partial x}\right)_t = \frac{dC}{d\lambda}\left(\frac{\partial \lambda}{\partial x}\right)_t = \frac{1}{\sqrt{t}}\frac{dC}{d\lambda}$$

And if we substitute in the diffusion equation here, we will get:

$$-\frac{x}{2t\sqrt{t}}\frac{dC}{d\lambda} = \frac{\partial}{\partial x}\left[\widetilde{D}\frac{1}{\sqrt{t}}\frac{dC}{d\lambda}\right]_t = \frac{d}{d\lambda}\left[\widetilde{D}\frac{1}{\sqrt{t}}\frac{dC}{d\lambda}\right]_t\frac{\partial \lambda}{\partial x}$$

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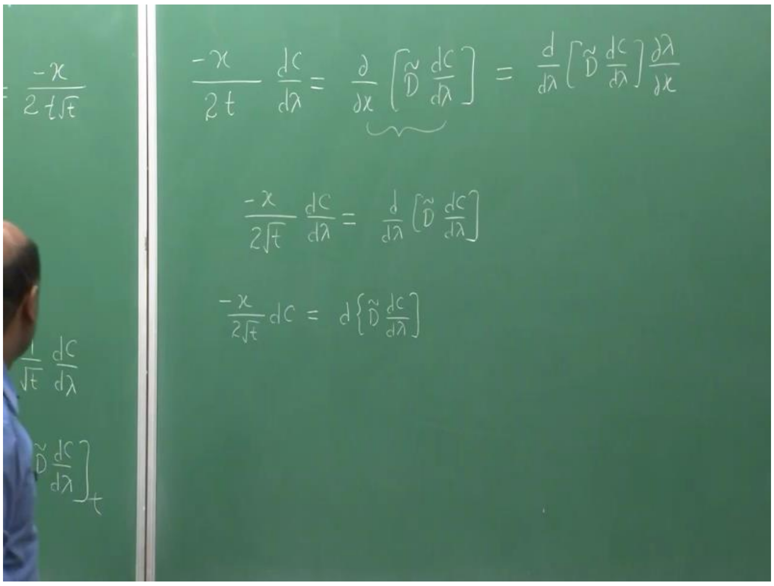

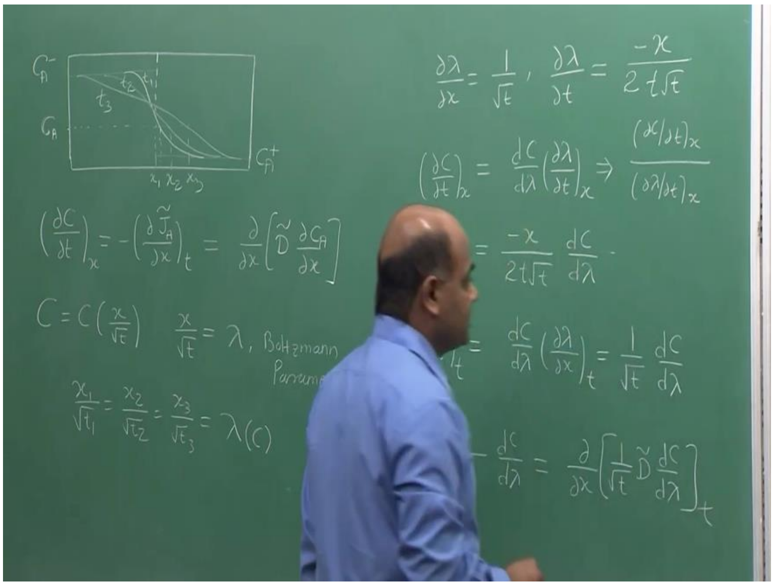

On simplifying and substituting for $\frac{\partial\lambda}{\partial x}$ we will get:

$$-\frac{x}{2\sqrt{t}}\frac{dC}{d\lambda} = \frac{d}{d\lambda}\left[\widetilde{D}\frac{dC}{d\lambda}\right]_t$$

as we can take if you take $\frac{1}{\sqrt{t}}$ outside, it will get cancelled. If you multiply both sides by $d\lambda$, we end up getting:

$$-\frac{x}{2\sqrt{t}}dC = d\left[\widetilde{D}\frac{dC}{d\lambda}\right]$$

Now, we substitute back for $\frac{dC}{d\lambda}$, we get from here:

$$-\frac{x}{2\sqrt{t}}dC = d\left[\widetilde{D}\frac{dC}{d\lambda}\right] = d\left[\sqrt{t}\widetilde{D}\left(\frac{\partial C}{\partial x}\right)_t\right]$$

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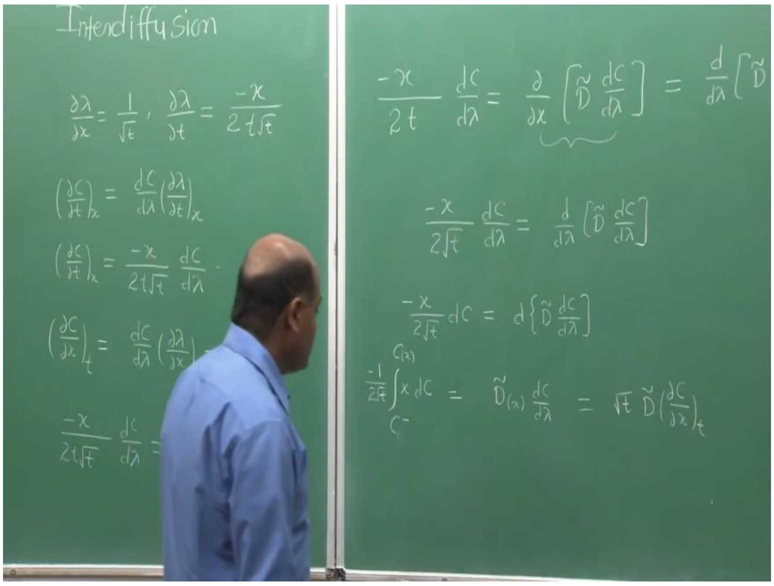

For the fixed diffusion annealing time, if we integrate both sides from the left terminal to the desired x, we can write:

$$-\frac{1}{2\sqrt{t}}\int_{C^-}^{C_{(x)}} x\,dC = \sqrt{t}\widetilde{D}\left(\frac{\partial C}{\partial x}\right)_t$$

If we see on the left terminal alloy, the value of $\widetilde{D}\left(\frac{\partial C}{\partial x}\right)_t = 0$. And at C at x, it should be equal to $\widetilde{D}\left(\frac{\partial C}{\partial x}\right)_t$ at that particular composition. $\frac{\partial C}{\partial x}$ is the derivative of concentration profile.

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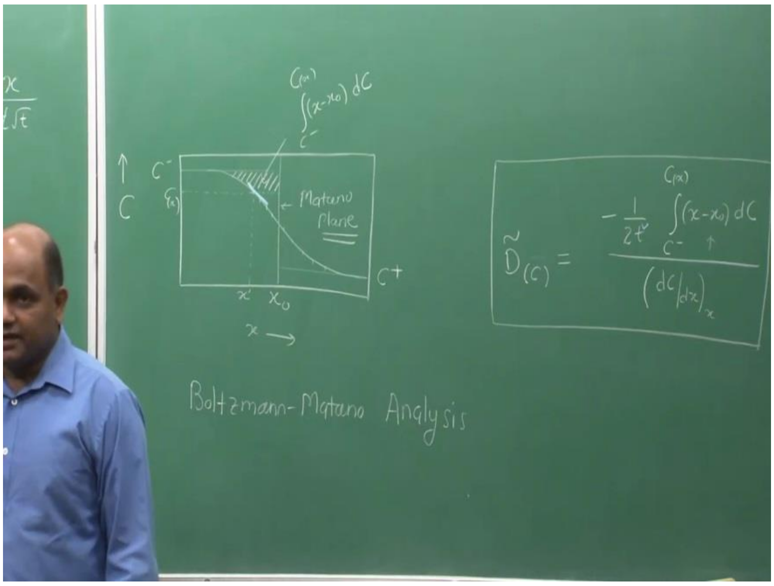

And if we rearrange, we get the equation for $\widetilde{D}_{(x)}$ and since $\widetilde{D}$ is actually function of C and C is varying with x and that is why $\widetilde{D}$ is varying with x. We should write appropriately as:

$$\widetilde{D}_{(C)} = \frac{-1}{2t\left(\frac{\partial C}{\partial x}\right)_t} \int_{C^-}^{C_{(x)}} (x - x_o) dC$$

Here we denote the reference plane as x_o. This gives the equation for binary interdiffusion coefficient. Now, what is this integral again? It is nothing but the area under the curve.

If we consider this concentration profile again, remember we were talking about the concentration of A and then we dropped the suffix, because we are considering the binary system here and for binary system to define any composition, we just need one concentration variable, C. Implicitly we are assuming here, it is C_A. To find out this integral is nothing but the area under the curve.

If we want to find $\widetilde{D}$ at some position x'. Then we evaluate this integral. That integral is nothing but the area under this curve drawn on to the Matano plane which is x_o . This is nothing but the integral $\int_{C^-}^{C_{(x)}}(x - x_o)dC$. Then we determine derivative of the concentration profile at this position which is the $\frac{\partial C}{\partial x}$ and we know diffusion annealing time t. And we can find $\widetilde{D}$ at this particular location and it corresponds to the composition which is there at this location, that is C_x.

Now, it can be easily seen this we can apply at any plane in the diffusion zone. And we can find out interdiffusion coefficient at every composition that develops in a binary diffusion couple using this technique. This technique is commonly known as Boltzmann-Matano analysis. This is how we can get binary interdiffusion coefficient from a single diffusion couple experiment. We can determine interdiffusion coefficient at every single composition that is developed within the diffusion zone of that couple. Now, how do we extend this to ternary and higher order diffusion couples, that we will see in the next class. Thank you.