**Diffusion in Multicomponent Solids**
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Lecture No. 48
Experiment Determination of Intrinsic Diffusion Coefficients

Welcome to the forty eighth lecture of the open course on diffusion in Multicomponent Solids. In this lecture I have explained the methodology for Experimental Determination of Intrinsic Diffusion Coefficients. In the end I have also derived the interrelation between interdiffusion coefficients and intrinsic diffusion coefficients as applicable to multi component systems.

So, in last class we talked about intrinsic diffusion and we derived Darken's equation which relates the binary interdiffusion coefficients to the intrinsic diffusion coefficients. Today we will go over how we can experimentally determine the intrinsic diffusion coefficients in binary system. In the end I will also explain how we analyze intrinsic diffusion in multicomponent systems.

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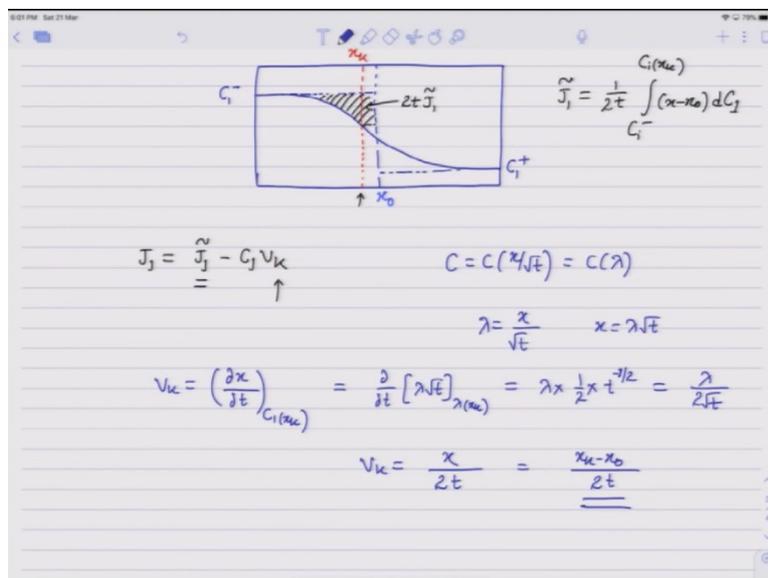
Let us consider a binary diffusion couple and I am showing one concentration profile here let us call that of component one. So, left terminal alloy concentration is C_1^{-} and right terminal alloy concentration is C_1^{+}. And suppose we placed some inert markers at the initial interface before the diffusion started and after the diffusion annealing for time T the markers have

shifted to position x_K. This is the Matano plane position x_o here which is the initial contact plane.

We know we can write the intrinsic diffusion flux as:

$$J_1 = \tilde{J}_1 - C_1 V_K$$

where V_K is the velocity of the marker plane. Now, out of this we know how to determine $\tilde{J}_1$ directly from the concentration profile. So, this all we are considering at the marker position x_K, because that is the only lattice plane that we are able to track, because the marker can be placed only at that plane, that is at the initial contact plane. So, if we want to find out $\tilde{J}_1$ that is the interdiffusion flux at x_K it will be simply:

$$\tilde{J}_1 = \frac{1}{2t} \int\limits_{C_1^{-L} \dot{c}} C_1(x_o)(x - x_o) d C_1$$

$2t$ times the area under this curve would be this shaded area. This is basically $2t \tilde{J}_1$ because we derived the above expression for $\tilde{J}_1$. Now, at the marker plane we know what is the concentration C_1 and we need to know V_K that is the velocity at which the marker plane is moving at the diffusion time t.

Now, this marker plane are usually travelling at a constant composition. In an infinite diffusion couple we know that each composition plane is moving parabolically with time. In other words we say:

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

λ is the Boltzmann parameter. So, we can also write:

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

V_K it is nothing but the change in distance coordinate with respect to time of the composition plane corresponding to λ:

$$V_K = \left(\frac{\partial x}{\partial t}\right)_{C_1(x_K)}$$

We can write:

$$V_K = \left(\frac{\partial x}{\partial t}\right)_{C_1(x_K)} = \frac{\partial}{\partial t}\left[\lambda \sqrt{t}\right]_{\lambda(x_K)}$$

λ is constant, so we can write this as:

$$V_K = \left(\frac{\partial x}{\partial t}\right)_{C_1(x_K)} = \frac{\partial}{\partial t}\left[\lambda \sqrt{t}\right]_{\lambda(x_K)} = \lambda \times \frac{1}{2} \times \frac{1}{\sqrt{t}} = \frac{\lambda}{2\sqrt{t}}$$

If you substitute for λ again, we get:

$$V_K = \frac{x}{2t}$$

And if x_o is my origin then this is nothing but:

$$V_K = \frac{x}{2t} = \frac{x_K - x_o}{2t}$$

So, by determining the position of marker plane with respect to the Matano plane we can find out the velocity of marker or the Kirkendall velocity V_K. And so once we know $\tilde{J}_1, C_1$ and V_K we can find out J_1.

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And J_1 can be written as:

$$J_1 = -D_1\left(\frac{\partial C_1}{\partial x}\right)_{x_K}$$

D_1 at the composition corresponding to x_K is nothing but:

$$D_1(x_K) = \frac{-J_1(x_K)}{\left(\frac{\partial C_1}{\partial x}\right)_{x_K}}$$

This way we can find out D_2 also which is simply:

$$D_2(x_K) = \frac{-J_2(x_K)}{\left(\frac{\partial C_2}{\partial x}\right)_{x_K}}$$

and thus we can get the intrinsic diffusion coefficients from a diffusion couple experiment. Remember we can determine the interdiffusion coefficient at every composition that has developed within the diffusion zone, but each composition is characterized by 2 intrinsic diffusivities and so we cannot do so for intrinsic diffusivities, we can determine the intrinsic diffusivities only when we can track the location of the lattice plane with the help of the markers. And so only at the marker plane we can find the intrinsic diffusivities.

There are also other methods which have also been proposed for determination of this intrinsic fluxes. One of the popular methods out of this is the graphical method proposed by hymen.

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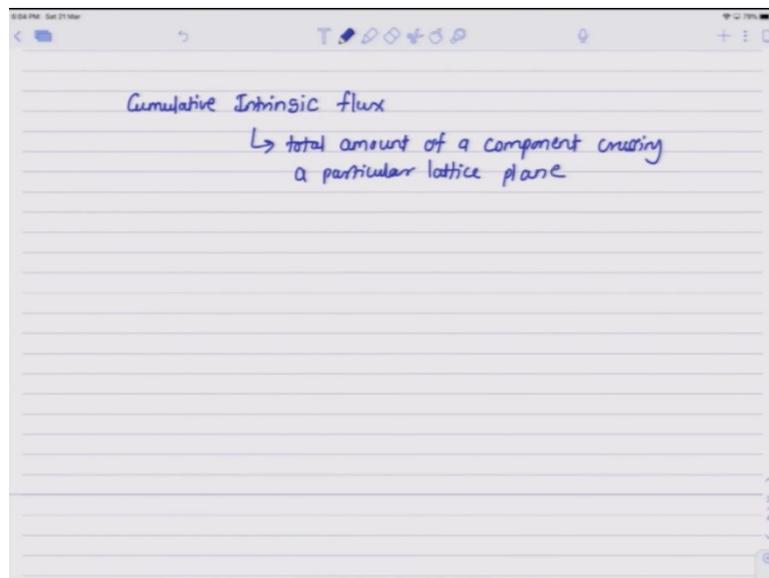
I will talk about the Heumann's method here for which we need to define something called as Cumulative Intrinsic flux, this is nothing but the total amount of a component crossing a particular lattice plane. So, the intrinsic cumulative flux is also denoted as A_i.

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We can write:

$$A_i = \int_0^t J_i \, dt$$

Now, if we solve this integral and if we substitute for J_i and let us say we are talking of components 1 so we have:

$$A_1 = -\int_0^t D_1 \left(\frac{\partial C_1}{\partial x} \right)_{x_K} dt$$

This is at the composition plane corresponding to the marker plane that is at x_K, and this corresponds to a fixed value of λ, because the markers are moving at constant composition. So, at that composition D_1 is constant and we can take it outside the integral. We can write:

$$\frac{\partial C_1}{\partial x} = \frac{d C_1}{d \lambda} \cdot \frac{\partial \lambda}{\partial x} = \frac{1}{\sqrt{t}} \frac{d C_1}{d \lambda}$$

since $\lambda = \dfrac{1}{\sqrt{t}}$. So, we have:

$$A_1 = -D_1 \int_0^t \frac{1}{\sqrt{t}} \frac{d C_1}{d \lambda} dt$$

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Now, we know that C is a function of:

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

So if we convert C versus distance coordinate x profile into C versus λ, it should be independent of time. Because the λ takes care of both x and $\sqrt{t}$ and for a given composition there is a fixed value of λ. So, C verses λ profile are independent of time and so $\dfrac{d C_1}{d \lambda}$ should be independent of time at a given composition. So, we can take this outside the integral and so we can write:

$$A_1 = -D_1 \frac{d C_1}{d \lambda} \int_0^t \frac{1}{\sqrt{t}} dt = -2 \sqrt{t} D_1 \frac{d C_1}{d \lambda}$$

Again $\dfrac{d C_1}{d \lambda}$ we resubstitute as:

$$\frac{d C_1}{d \lambda} = \frac{\dfrac{\partial C_1}{\partial x}}{\dfrac{\partial \lambda}{\partial x}} = \sqrt{t} \frac{\partial C_1}{\partial x}$$

So we get:

$$A_1 = -2 t D_1 \frac{\partial C_1}{\partial x}$$

This is nothing but J_1 and we get the expression for A_i:

$$A_i = 2t J_i$$

Now, for a binary diffusion similarly we can write A_2 as:
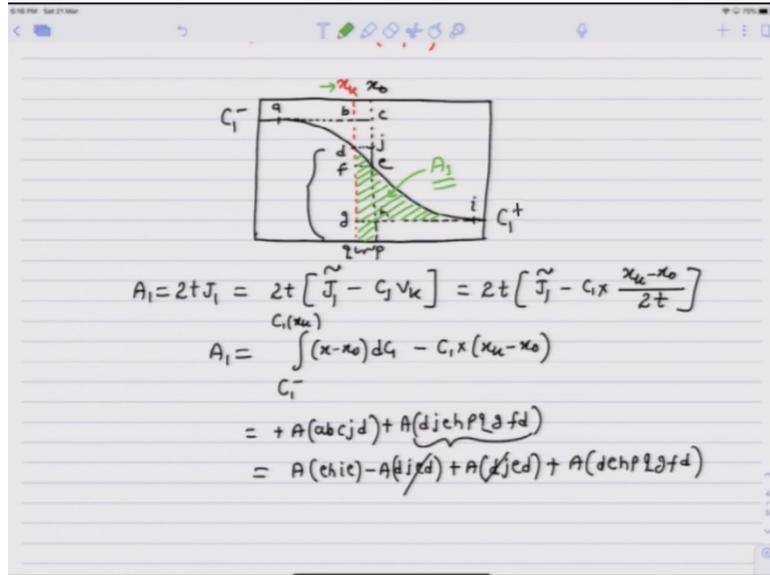
$$A_2 = -2t D_2 \frac{\partial C_2}{\partial x}$$

So if we take the ratio of A_1 and A_2 that should be equal to:

$$\frac{A_1}{A_2} = \frac{D_1}{D_2} \times \frac{\dfrac{-\partial C_2}{\partial x}}{\dfrac{\partial C_2}{\partial x}} = \frac{-D_1}{D_2}$$

So, by taking the ratio of cumulative intrinsic fluxes we can get the ratio of intrinsic diffusion coefficients.

So, how do we go about graphically measuring this, so let us consider the concentration profile again, so we have $C_1^{-\dot{\iota}\dot{\iota}}$ as the left terminal alloy concentration $C_1^{+\dot{\iota}\dot{\iota}}$ as the right terminal alloy concentration, x_K is the location of the marker plane, x_o is the location of the matano plane. To get the areas let me label this points $a, b, c, d, e, f, g, h, i$. We know:

$$A_1 = 2t\, J_1 = 2t\left[\tilde{J}_1 - C_1 V_K\right] = 2t\left[\tilde{J}_1 - C_1 \frac{x_K - x_o}{2t}\right]$$

So, after substituting for $2t\,\tilde{J}_1$ we have A_1 is equal to:

$$A_1 = \int\limits_{C_1^{-\dot{\iota}}\dot{\iota}} C_1\left(x_K\right)\left(x - x_o\right) d C_1 - C_1\left(x_K - x_o\right)$$

In terms of the area the first integral on the right hand side here is nothing but the area $a\,b\,c\,j\,d$ and for the sign of the area, $\left(x - x_o\right)$ is negative and $d C_1$ is also negative, so this area should be positive. In Second term, we have $\left(x_K - x_o\right)$ is this length and C_1 is this length and so we have this as area $d\,j\,e\,h$. Let us call this $p \wedge q$, $p\,q\,g\,f\,d$ and C_1 is positive but $\left(x_K - x_o\right)$ is negative and this area has a negative sign. So, this area there should be a negative here and with this negative sign this becomes positive.

Now, based on the equation with which we obtain Matano plane we know this area $a\,b\,c\,e\,a$ is equal to $e\,h\,i\,e$ and so we can replace this area with area $e\,h\,i\,e$ minus area $d\,j\,e\,d$ plus the second can be split as this area $d\,j\,e\,d$ plus $d\,e\,h\,p\,q\,g\,f\,d$ and so this two will get canceled and we get this area plus this area. So in effect if I mark this area this shaded total area is nothing but the cumulative intrinsic diffusion flux A_1 of component 1.

$$A_1 = \int\limits_{C_1^{-i}i} C_1(x_K)(x-x_o)\, d\, C_1 - C_1(x_K - x_o) = A(abcjd) + A(djehpqgfd) = A(ehie) - A(djed) + A(djed) + A(dehpqgf$$

This is basically the total amount of component 1 which has crossed this marker plane in time t, this is the Heumann's method to find cumulative intrinsic diffusion fluxes.

This was about binary intrinsic diffusion. Now, if I want to evaluate ternary intrinsic diffusion coefficient it is much more difficult, because we will need at least 2 diffusion couples yielding the marker location at the same composition, which is almost not possible to obtain. But we do need the relations between intrinsic and interdiffusion coefficients to relate this phenomenological coefficient to the fundamental mobilities and jump frequencies. So, let us quickly look into it.

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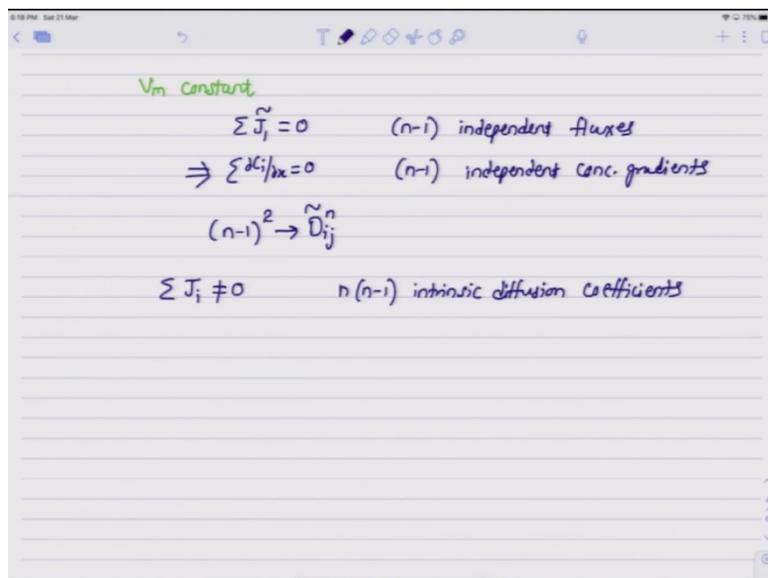
Again, let us work with constant molar volume in the laboratory fixed frame:

$$\sum \tilde{J}_i = 0$$

and so we have only $(n-1)$ independent fluxes. Also, the summation of concentration gradient is 0:

$$\sum_{i=1}^{n} \frac{\partial C_i}{\partial x} = 0$$

so we have only $(n-1)$ independent concentration gradients. And so, we need $(n-1)^2$ interdiffusion coefficients $\left(\widetilde{D}_{ij}^n\right)$ to define interdiffusion at a given composition. But as we have seen for intrinsic diffusion:

$$\sum J_i \neq 0$$

because we need to consider the net vacancy flow also or the term related to J_v, the vacancy flux. And so, we have N independent intrinsic fluxes while the constraints on gradient will still apply and so instead of $(n-1)^2$, we have $n(n-1)$ intrinsic diffusion coefficients.

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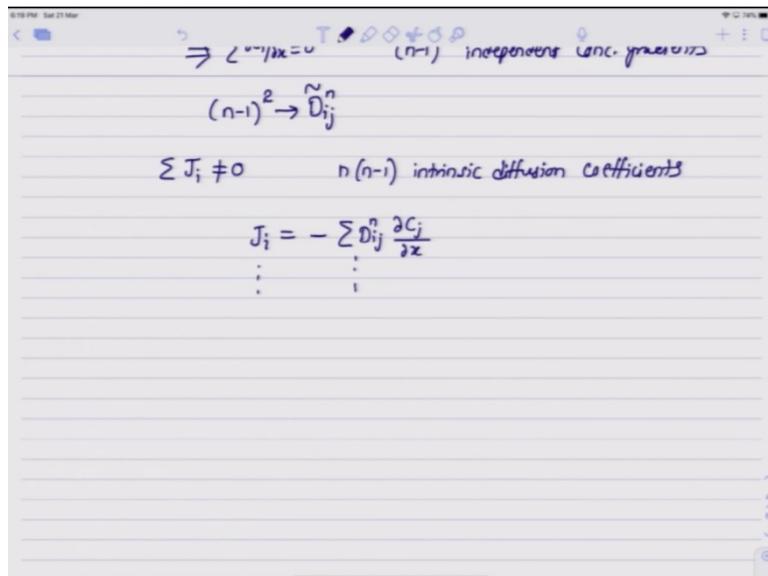
And we can write:

$$J_i = -\sum D_{ij}^n \frac{\partial C_1}{\partial x}$$

Again we need to treat one concentration gradient as dependent $\dfrac{\partial C_j}{\partial x}$, so $(n-1)$ terms for each flux and there will be n such fluxes so there will be $n(n-1)$ intrinsic diffusion coefficients. How do we convert one from the another?

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If we write interdiffusion flux in terms of intrinsic diffusion flux, let us say for component 1 we get:

$$\tilde{J}_1 = J_1 + C_1 V_K$$

If we take this summation over all components:

$$\sum_{i=1}^{n} \tilde{J}_i = \sum J_i + V_K \sum C_i$$

Summation of C_i we know is nothing but $\dfrac{1}{V_m}$ and $\displaystyle\sum_{i=1}^{n} \tilde{J}_i = 0$ so:

$$V_K = -V_m \sum J_i$$

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If we substitute back into this equation here, we get:

$$\tilde{J}_1 = J_1 - C_1 V_m \sum_{i=1}^{n} J_i$$

Now:

$$C_1 V_m = X_1$$

i.e. the mole fraction of component 1, so we can also write this as:

$$\tilde{J}_1 = J_1 - C_1 V_m \sum_{i=1}^{n} J_i = J_1 - X_1 J_1 - X_1 \sum_{s \neq i} J_s$$

Last summation is performed over all components except $s \neq i$. Because I took $X_1 J_1$ out here and this can be represented as:

$$\tilde{J}_1 = \left(1 - X_1\right) J_1 - X_1 \sum_{s \neq i} J_s$$

So if we substitute for all J_1 in terms of Fick's law and compare the corresponding term, we can obtain the interrelation between interdiffusion coefficients and intrinsic diffusion coefficients. I will skip the steps in between and directly write this relation which comes out to be:

$$\tilde{D}_{ij}^n = \left(1 - X_i\right) D_{ij}^n - X_i \sum_{s \neq i} D_{sj}^n$$

and the summation is over all s except i. And this is applicable for constant molar volume. So, we can say this is the extension of Darken's equation to multicomponent systems. This relation will be useful when we are converting or when we are trying to correlate our interdiffusion coefficients, which can be easily obtained, to intrinsic coefficients or to the fundamental atomic mobilities through thermodynamic factors. I would like to stop here for today. Thank you.