Diffusion in Multicomponent Solids
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Lecture No. 47
Intrinsic Diffusion and Kirkendall Effect

Welcome to the forty seventh lecture of the open course on diffusion in multicomponent solids. In this lecture, I will discuss intrinsic diffusion that is diffusion studied with respect to the lattice fixed frame of reference or in other words Kirkendall frame. I shall first explain the Kirkendall effect and later describe how the net vacancy flow gives rise to shift of marker plane. We will also go over the derivation of Darken's equation that relates the binary interdiffusion coefficient to the intrinsic diffusion coefficients of the two components. Today, we will talk about intrinsic diffusion.

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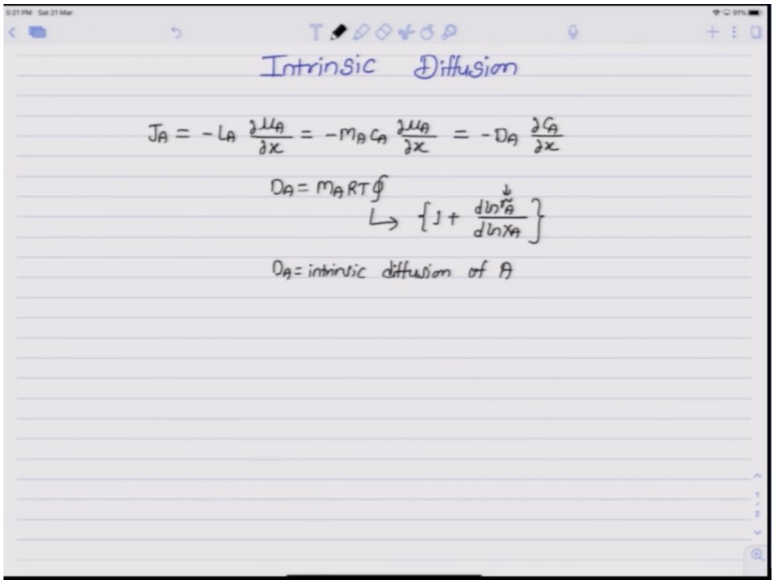

Intrinsic Diffusion

$$J_A = -L_A \frac{\partial \mu_A}{\partial x} = -M_A C_A \frac{\partial \mu_A}{\partial x} = -D_A \frac{\partial C_A}{\partial x}$$

$$D_A = M_A RT \phi$$

$$\hookrightarrow \left\{1 + \frac{d\ln \overset{\downarrow}{\gamma_A}}{d\ln X_A}\right\}$$

D_A = intrinsic diffusion of A

So, when we studied the diffusion under thermodynamic driving forces or under the chemical potential gradients, we wrote the equation:

$$J_A = -L_A \frac{\partial \mu_A}{\partial x}$$

Remember, this applies when there is a vacancy equilibrium achieved at every plane within the diffusion zone. In terms of mobility, we can write it as:

$$J_A = -L_A \frac{\partial \mu_A}{\partial x} = -M_A C_A \frac{\partial \mu_A}{\partial x}$$

where M_A is the mobility of A and C_A is the concentration of A. And in terms of intrinsic diffusion, we wrote:

$$J_A = -L_A \frac{\partial \mu_A}{\partial x} = -M_A C_A \frac{\partial \mu_A}{\partial x} = -D_A \frac{\partial C_A}{\partial x}$$

and we derived the relation:

$$D_A = M_A RT\phi$$

where ϕ is the thermodynamic factor which is nothing but:

$$\phi = 1 + \frac{d \ln \gamma_A}{d \ln X_A}$$

Here $\gamma_A$is the thermodynamic activity coefficient. Now, J_A is actually intrinsic flux and D_A here is basically the intrinsic diffusion coefficient of A. When I say intrinsic diffusion, it is the diffusion under purely thermodynamic driving forces that means, we are not considering any movement that might occur in the lattice planes.

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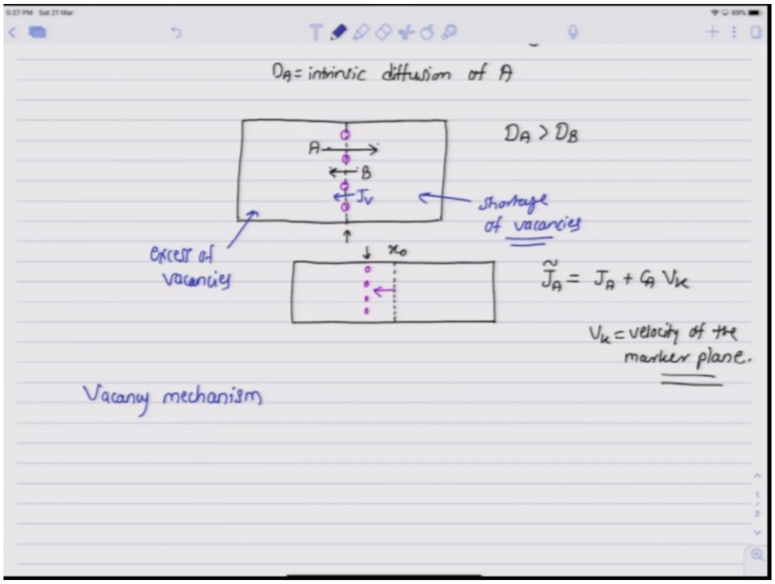

So, to illustrate this, consider the diffusion between two different alloys and suppose, A diffuses from left to right and B diffuses from right to left. And suppose, the intrinsic diffusivity of A is greater than that of B:

$$D_A > D_B$$

Obviously, in a given interval of time, there will be more number of A atoms moving from left to right compared to the number of B atoms moving from right to left. Because of this, there will be a net mass transfer across this initial contact plane. Hence, it will look like the left portion of the alloy has shrunk whereas, the right portion of the alloy has expanded.

Now, if we can track the lattice plane, which was originally at this initial contact plane here by some kind of markers. I am showing the markers with the circles here such that the markers stick to that lattice plane and move with the lattice plane if the lattice plane moves. Now after diffusion, the left side has shrunk and the right side has expanded. If we obtain the initial contact plane by the Matano analysis, it will look like this marker plane has shifted to left and this is called the marker movement or Kirkendall effect, because Smigelskas and Kirkendall were the first one who reported this kind of movement.

Now, if we measure the diffusion flux with respect to a frame of reference, which is fixed to the Matano plane, that is the plane which we found as initial contact plane, the flux would be different than if we measure the flux with respect to the frame of reference, which is stuck to this marker plane. The diffusion flux with respect to this frame of reference stuck to the lattice plane or the marker plane is referred to as the intrinsic flux because it will give only the Fickian term. Whereas, if we measure with respect to the matano plane, there will be a term also because of the drift that has caused because of this lattice movement. So, in other words, if we write the equation for interdiffusion flux $\tilde{J}_A$, it would be:

$$\tilde{J}_A = J_A + C_A V_K$$

the intrinsic flux J_A is with respect to the lattice fixed frame and V_K is the velocity of the marker plane. This new frame of reference that is the lattice fixed frame of reference is also referred to as Kirkendall frame and so we write the notation for velocity as V subscript K. Why this movement occurs? Let us try to understand physically what is happening. We are assuming here that the diffusion is occurring by vacancy mechanism. And since, more number of A atoms are moving from left to right than the number of B atoms from right to left, there is a net vacancy flow which is occurring from right to left which we can denote as J_V. Because of this as the time progresses, there tend to be excess of vacancies on the left side of the alloy whereas, vacancies will be in short on the right side of the alloys. This excess and shortage I am talking with respect to the equilibrium concentrations of vacancies. Now, in order to maintain the equilibrium concentration on the left side, the vacancies have to be annihilated whereas, on the right side of this couple, the vacancies have to be created. And so, the sources and sinks of vacancies will play an important role here.

What are the sources and sinks? As we have seen earlier, dislocations and grain boundaries would act as sources and sinks. Since the diffusion couples usually are prepared with coarse grain size, the availability of grain boundaries is not much, but dislocations play a crucial role here. So, the vacancies will annihilate at dislocations. Similarly, wherever required, the vacancies can also be created from the dislocations.

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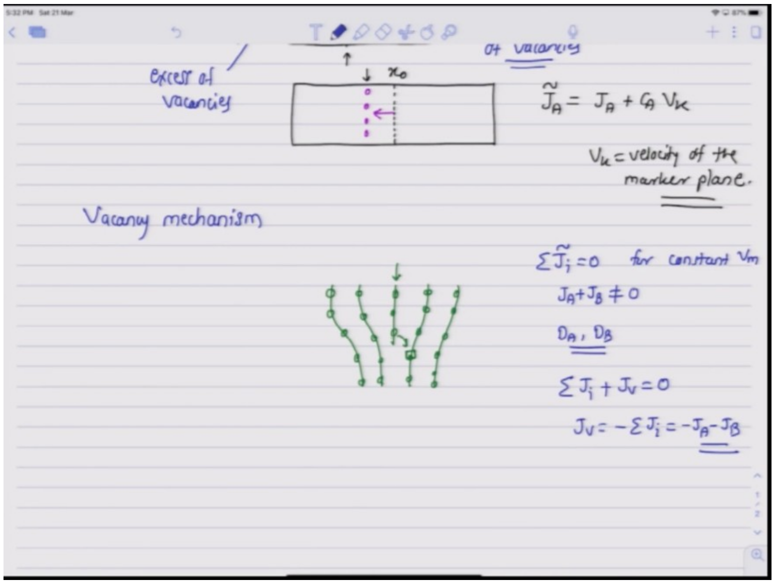

$\tilde{J}_A = J_A + C_A V_K$

V_K = velocity of the marker plane.

$\sum \tilde{J}_i = 0$ for constant V_m

$J_A + J_B \neq 0$

D_A, D_B

$\sum J_i + J_V = 0$

$J_V = -\sum J_i = -J_A - J_B$

And how does this take place? So, if we consider an edge dislocation and suppose there is a vacancy which comes closer to a dislocation line. Now the vacancies may be somewhere there in the bulk. In the presence of excess of the vacancies, the vacancies will be transported to the nearest dislocation to get annihilated and then when it comes to the near to the dislocation line the vacancy will jump into the dislocation line and atom will make a reverse jump.

This way a vacancy will be introduced into the dislocation and the atom will be introduced from this extra half plane into the bulk of the crystal. This way, if more and more vacancies get annihilated at this dislocation, this entire dislocation line or this entire extra half plane will vanish. So, wherever there is an excess of vacancies, in this case on the left side of the alloy, the extra half planes will vanish and so this side would look like it is shrinking. Whereas on the right hand side exactly opposite process will occur, because the vacancies will be created there. So, the vacancies will be introduced into the lattice and extra half planes will be introduced. And hence, this side will look like it has expanded and this is how physically the marker will look like as if they are moving in the direction opposite to the direction of diffusion of the faster moving components. In this case opposite to the diffusion direction of A.

Now we know whenever a vacancy is created, there will be one lattice site added to the lattice and whenever a vacancy is annihilated, there will be reduction of one lattice site. And so, when we are considering the intrinsic diffusion, there will be an imbalance of the fluxes of A and B and so, typically:

$$J_A + J_B \neq 0$$

In case of interdiffusion we know:

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

This is for constant molar volume when the volume fixed frame coincides with stationary frame. If the molar volume is not constant, then:

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

But this is not the case for intrinsic diffusion. And that is why D_A and D_B will be different. But, if we consider the conservation of lattice site, then we also have to take into account the vacancy flow or the vacancy flux. In this case we can write:

$$\sum J_i + J_V = 0$$

Or

$$J_V = -\sum J_i$$

And so for binary diffusion:

$$J_V = -\sum J_i = -J_A - J_B$$

So, in order to get to the intrinsic diffusion coefficient, we need to track the original lattice plane. And this can be done only with the help of markers. How do we select these markers? Let us consider an analogy for this.

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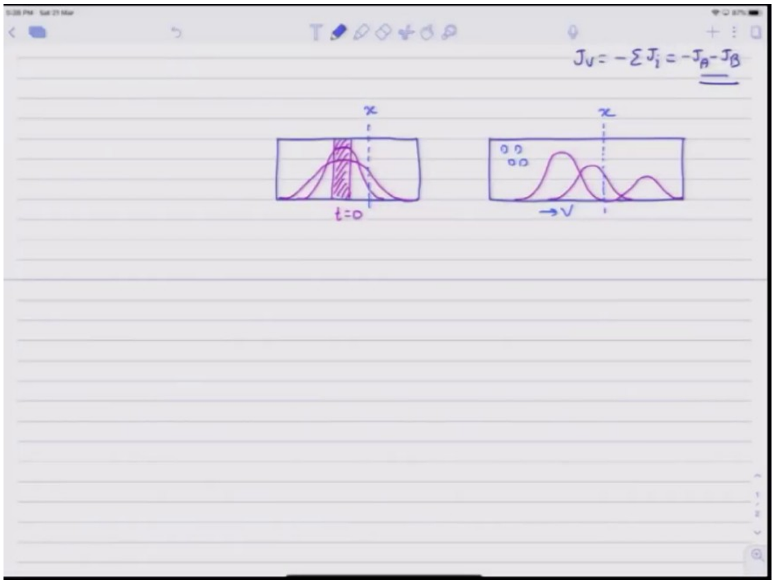

So, if we consider a small reservoir of water and let us say initially the water was still and if I introduce thin plane of ink at $t=0$, we know the ink will start diffusing as the time progresses and the diffusion profile would look something like this. They are the diffusion profiles at different times. So, at any plane x, if we want to find the diffusion flux of ink, we just need to consider the intrinsic diffusivity of ink in water. Because the diffusion is occurring only because of this concentration gradient and there is no drift present.

Now, in the second case, let us suppose that the water is flowing towards right, of course the flow is not as fast, so that the diffusive flow and the drift are comparable. Then in that case, as the time progresses, this Gaussian type distribution will also shift with time because the water is now flowing. Now, if I want to evaluate the flux at the same position x, I now need to consider intrinsic diffusion as well as the velocity of water.

What I can measure is the total flux that is the interdiffusion flux. But in order to separate the intrinsic term from there, I need to measure the velocity of water, let us call it v. How can we go about it? One easiest way is I put some wooden chips on the surface of water and I track the velocity of wooden chips. And I can approximately take the velocity of wooden chips as the velocity of water. Now what is the criteria for wooden chip to act as the marker here?

First it should flow with water, then it should not react with water that means it should not dissolve or it should not have any chemical reaction with water. Otherwise, we will lose the chips and we will not be able to track. In the same fashion, we need a marker which can stick to the lattice plane and which is stable at the diffusion temperature. In other words, the marker should not diffuse in the matrix and also it should not react with the matrix or with the other diffusing elements. And that can be done if we place these markers on the initial contact plane before we sandwich the two alloy blocks before the start of the diffusion experiments. Typically, the oxide particles like alumina or yttria are used for this purpose. Also, molybdenum is a very high melting element and the diffusivity of molybdenum at lower temperature is usually very, very low. So, molybdenum particles can also be used as markers.

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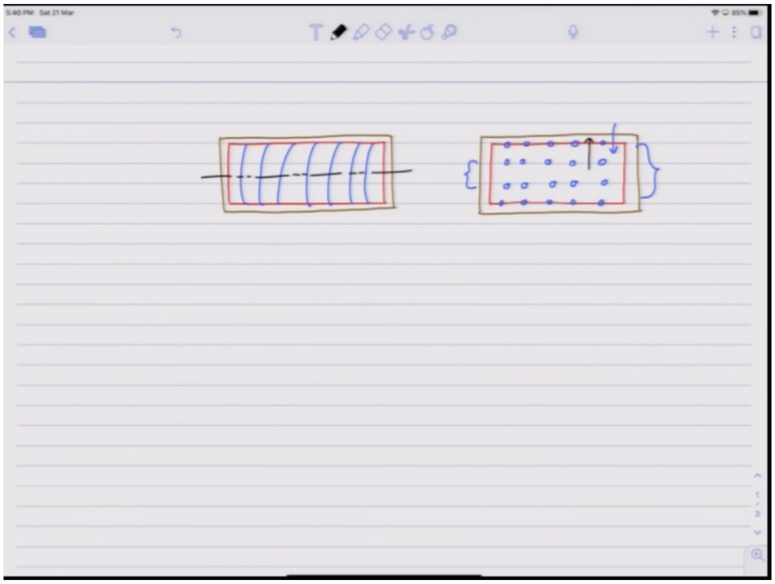

In fact, in the first experiment reported by Smigelskas and Kirkendall they used the molybdenum wire as the marker. I would like to describe that experiment briefly here. So, what they did, they took a rectangular bar of brass and they wrapped that bar with molybdenum wires. Then they deposited about 0.1-inch-thick layer of copper onto this block. So, if we take a cross section, it would look something like this. So we could see the molybdenum wire cross sections at the initial contact plane. Then they diffusion annealed this assembly at a higher temperature isothermally for different times and after various time intervals they observed the distance between these two markers. And what they found as the diffusion time progressed, the distance between the two markers kept reducing. That means, the markers moved from the initial interface into the brass side.

Since copper was diffusing from outside into the brass and the zinc was diffusing from brass into the copper, obviously, this would have occurred because of the faster diffusion of zinc from inside out compared to the diffusion of copper from outside in. And this was a classic experiment, because it helped in establishing diffusion mechanism based on vacancies which was not popular at that time. Earlier the popular mechanisms were the direct exchange mechanisms or ring mechanisms, but this helped giving a strong foundation for the vacancy mechanism of diffusion. In fact, because of this Kirkendall also found it very hard to publish this work, but finally, it got published and then the vacancy mechanism also became very popular later on. Then Darken later on analyzed the diffusion based upon this new frame of reference, which is now called as Kirkendall frame of reference. And he developed the interrelation between the interdiffusion fluxes and intrinsic fluxes.

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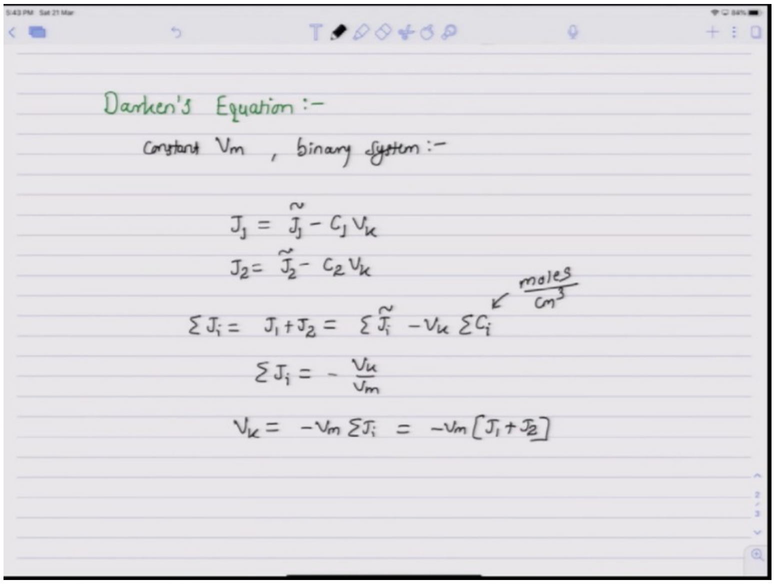

Darken's Equation :-

Constant Vm , binary system :-

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

$$J_2 = \tilde{J}_2 - C_2 V_K$$

$$\sum J_i = J_1 + J_2 = \sum \tilde{J}_i - V_K \underset{\swarrow \frac{\text{moles}}{\text{cm}^3}}{\sum C_i}$$

$$\sum J_i = -\frac{V_K}{V_m}$$

$$V_K = -V_m \sum J_i = -V_m [J_1 + J_2]$$

Now let us try to derive that equation which is known as Darken's equation. We will work with constant molar volume case and we will work with a binary system. We know, based upon the conversion of fluxes from one frame of reference to the other, the intrinsic flux J_1 with respect to the Kirkendall frame of reference can be expressed as:

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

where V_K is the velocity of the marker. We write the equation for 2 it will be:

$$J_2 = \tilde{J}_2 - C_2 V_K$$

And if we take the summation which is basically that should be equal to:

$$\sum J_i = J_1 + J_2 = \sum \tilde{J}_i - V_K \sum C_i$$

C_i is the concentration in moles per centimeter cube. So, the summation of C_i will be total number of moles per centimeter cube which is equal to the inverse of molar volume. So, we can write:

$$\sum J_i = \frac{-V_K}{V_m}$$

The velocity of the Kirkendall frame of reference can be written as:

$$V_K = -V_m \sum J_i$$

For binary this will be:

$$V_K = -V_m \sum J_i = -V_m (J_1 + J_2)$$

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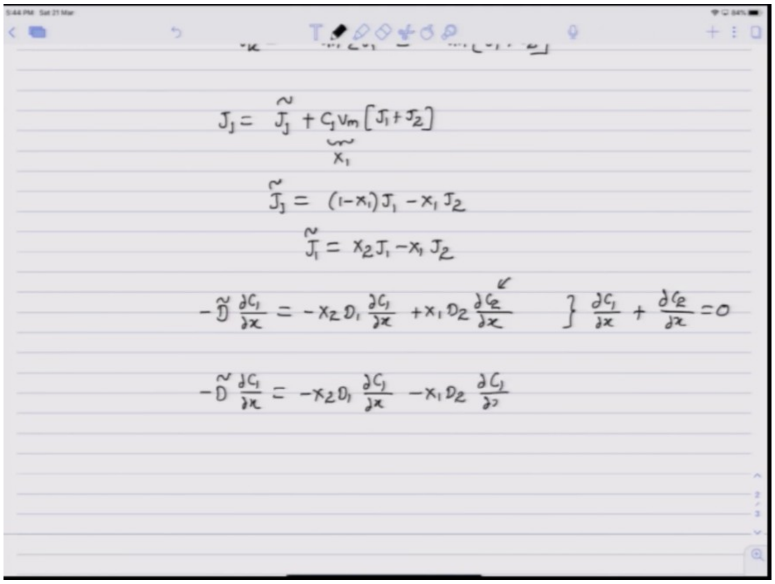

$$J_1 = \tilde{J}_1 + \underbrace{C_1 V_m}_{X_1} [J_1 + J_2]$$

$$\tilde{J}_1 = (1 - X_1) J_1 - X_1 J_2$$

$$\tilde{J}_1 = X_2 J_1 - X_1 J_2$$

$$-\tilde{D} \frac{\partial C_1}{\partial x} = -X_2 D_1 \frac{\partial C_1}{\partial x} + X_1 D_2 \frac{\partial C_2}{\partial x} \quad \Big\} \quad \frac{\partial C_1}{\partial x} + \frac{\partial C_2}{\partial x} = 0$$

$$-\tilde{D} \frac{\partial C_1}{\partial x} = -X_2 D_1 \frac{\partial C_1}{\partial x} - X_1 D_2 \frac{\partial C_1}{\partial x}$$

So, if we substitute back into the equation for J_1, we get:

$$J_1 = \tilde{J}_1 + C_1 V_m (J_1 + J_2) = \tilde{J}_1 + X_1 (J_1 + J_2)$$

where $C_1 V_m$ is nothing but the mole fraction of 1. And if we rearrange the terms we get;

$$\tilde{J}_1 = (1 - X_1) J_1 - X_1 J_2 = X_2 J_1 - X_1 J_2$$

So, the interdiffusion flux can be expressed in terms of intrinsic fluxes of the two components. Now, if we substitute for fluxes in terms of Fick's law, you get:

$$-\tilde{D} \frac{\partial C_1}{\partial x} = -X_2 D_1 \frac{\partial C_1}{\partial x} + X_1 D_2 \frac{\partial C_2}{\partial x}$$

and for constant molar volume we have:

$$\frac{\partial C_1}{\partial x}+\frac{\partial C_2}{\partial x}=0$$

So, $\frac{\partial C_2}{\partial x}$is simply negative $\frac{-\partial C_1}{\partial x}$. If we substitute here we get:

$$-\widetilde{D}\frac{\partial C_1}{\partial x}=-X_2 D_1\frac{\partial C_1}{\partial x}+X_1 D_2\frac{\partial C_2}{\partial x}=X_2 D_1\frac{\partial C_1}{\partial x}-X_1 D_2\frac{\partial C_1}{\partial x}$$

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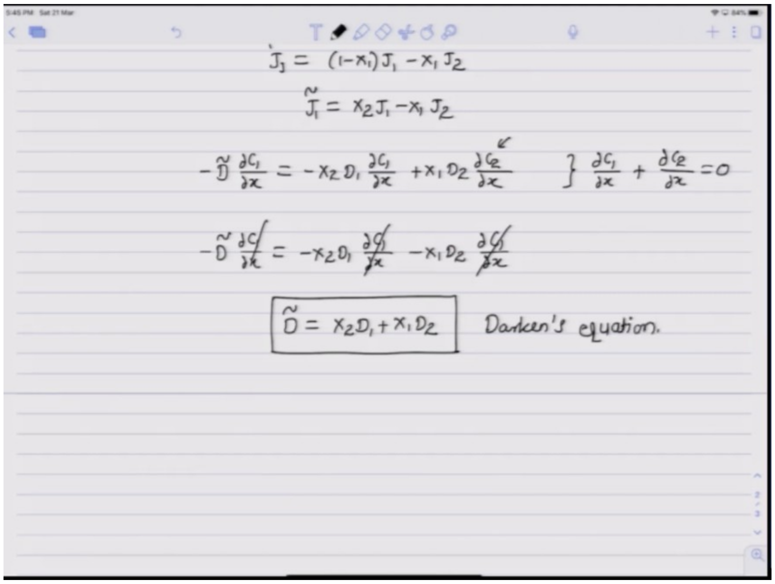

$$\tilde{J}_1 = (1-X_1)J_1 - X_1 J_2$$

$$\tilde{J}_1 = X_2 J_1 - X_1 J_2$$

$$-\tilde{D}\frac{\partial C_1}{\partial x} = -X_2 D_1 \frac{\partial C_1}{\partial x} + X_1 D_2 \frac{\partial C_2}{\partial x} \quad \Big\} \quad \frac{\partial C_1}{\partial x} + \frac{\partial C_2}{\partial x} = 0$$

$$-\tilde{D}\cancel{\frac{\partial C_1}{\partial x}} = -X_2 D_1 \cancel{\frac{\partial C_1}{\partial x}} - X_1 D_2 \cancel{\frac{\partial C_1}{\partial x}}$$

$$\boxed{\tilde{D} = X_2 D_1 + X_1 D_2}$$ Darken's equation.

Get rid of this gradient term and we get the interrelation between interdiffusion coefficient $\widetilde{D}$and the intrinsic coefficients D_1 and D_2 as:

$$\widetilde{D}=X_2 D_1+X_1 D_2$$

This is the famous Darken's equation. This helps in converting the interdiffusion coefficients into intrinsic or reverse. Now, how do we actually determine these intrinsic diffusion coefficients, we will see in the next class. Thank you.