Diffusion in Multicomponent solids

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Lecture 15

Fick’s Low for Multicomponent Diffusion

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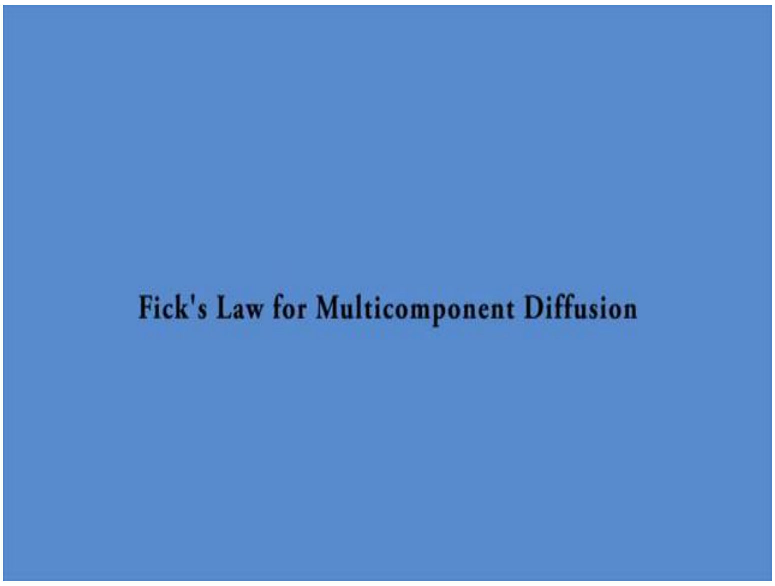

Fick's Law for Multicomponent Diffusion

Welcome to the fourth week of this open course on diffusion in multi-component solids. This is the fifteenth lecture in this series and in this lecture; I will discuss how diffusion in multi-component system can be described based on Onsager’s formalism of Fick’s law. We will also ee how Gibbs-Duhem equation along with use of an appropriate frame of reference helps to reduce the number of interdiffusion coefficients from $n^2$to $(n-1)^2$ in an n component system.

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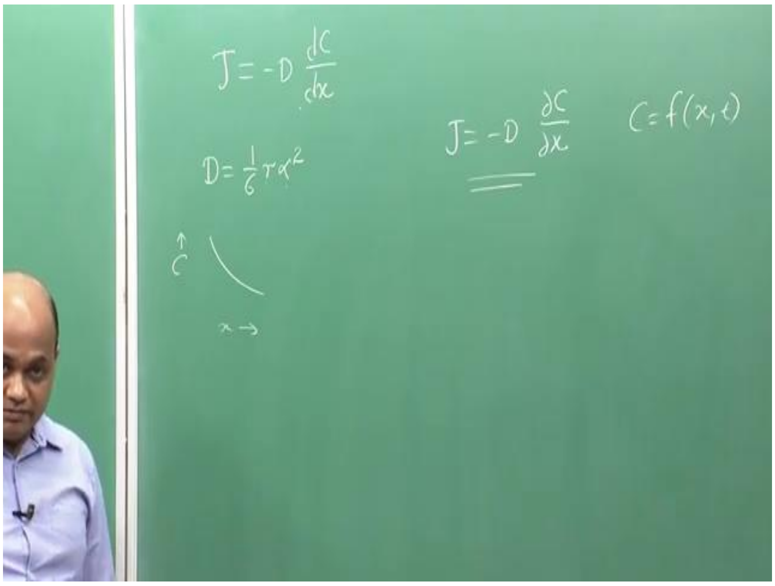

We have seen the expression for Fick’s law for diffusion of a component:

$$J = -D\frac{dC}{dx}$$

Now, in this expression D is constant which is called diffusivity, but it is valid when the concentration gradient is very small because only then D is constant. We have derived this expression for D:

$$D = \frac{1}{6}\alpha^2\gamma$$

where γ is the successful jump frequency and α is the jump distance. If the composition changes, both γ and α would change. So, D is a function of composition. Only when we have a dilute solution or small concentration gradient, you have D constant and you can use this expression, but if the concentration gradient is larger, then we know that D has to vary with composition because in the concentration gradient C varies as a function of x. Obviously, D will also vary with x, in fact under these concentration gradient or if the concentration gradient is larger and if the thermodynamic interactions between the atoms are stronger then the jump in forward direction is not same as in the backward direction.

So, we need to take that into account and thus expressions for diffusivities will become more complicated. D is a function of composition, but it does not depend upon the gradient of composition just like in Fourier’s law, thermal conductivity does not depend upon the temperature gradient and in Ohm's law electrical conductivity does not depend upon gradient of electric potential.

Similarly, diffusivity does not depend upon gradient of concentration but it does depend upon composition, keep that in mind. Infact whenever there is a diffusion occurring at any given plane or at any given x we should more appropriately write this as:

$$J = -D\frac{\partial C}{\partial x}$$

as the composition also varies with t. $\frac{\partial C}{\partial x}$ is partial of C with respect to x, and the sign for partial, I will call it as ∂, because $C = f(x,t)$. How we take into account parameter t, we will talk in the next class, but right now keep this in mind. In fact this is valid only for binary systems. If we have multi-component system then we need to modify the above expression.

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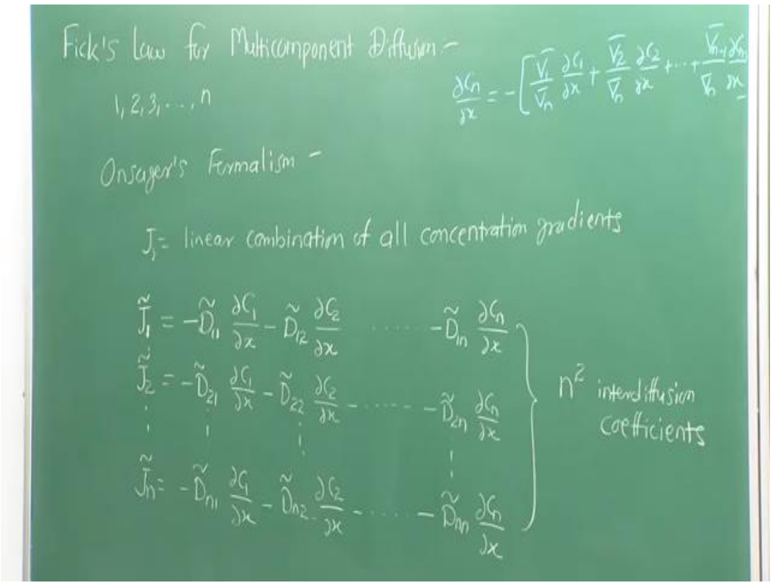

Fick's law for Multicomponent Diffusion –

1, 2, 3, . . . , n

$$\frac{\partial C_n}{\partial x} = -\left[\frac{\bar{V}_1}{\bar{V}_n}\frac{\partial C_1}{\partial x} + \frac{\bar{V}_2}{\bar{V}_n}\frac{\partial C_2}{\partial x} + \dots + \frac{\bar{V}_{n-1}}{\bar{V}_n}\frac{\partial C_{n-1}}{\partial x}\right.$$

Onsager's Formalism –

J_1 = linear combination of all concentration gradients

$$\left.\begin{aligned}
\tilde{J}_1 &= -\tilde{D}_{11}\frac{\partial C_1}{\partial x} - \tilde{D}_{12}\frac{\partial C_2}{\partial x} \cdots\cdots - \tilde{D}_{1n}\frac{\partial C_n}{\partial x}\\
\tilde{J}_2 &= -\tilde{D}_{21}\frac{\partial C_1}{\partial x} - \tilde{D}_{22}\frac{\partial C_2}{\partial x} \cdots\cdots - \tilde{D}_{2n}\frac{\partial C_n}{\partial x}\\
&\vdots\\
\tilde{J}_n &= -\tilde{D}_{n1}\frac{\partial C_1}{\partial x} - \tilde{D}_{n2}\frac{\partial C_2}{\partial x} \cdots\cdots - \tilde{D}_{nn}\frac{\partial C_n}{\partial x}
\end{aligned}\right\} n^2 \text{ interdiffusion coefficients}$$

Let us look at Fick's law as applied to multicomponent diffusion. The multicomponent system means it has typically three or more components. If we consider n component systems, let us say components 1, 2, 3…n then we use Onsager's formalism. So we extend the Fick's law using Onsager's formalism. Using Onsager's formalism we express the flux as a linear combination of all the concentration gradients. We can write the flux of component say one, let us denote this by $\tilde{J}_1$ as a linear combination of all concentration gradients. ~ denotes that we are considering interdiffusion or diffusion due to the presence of strong concentration gradients.

Since we have n components, there are n concentration variables and n concentration gradients. We need to express flux as linear combination of n concentration gradients which we write as:

$$\tilde{J}_1 = -\widetilde{D}_{11}\frac{\partial C_1}{\partial x} - \widetilde{D}_{12}\frac{\partial C_2}{\partial x} \dots - \widetilde{D}_{1n}\frac{\partial C_n}{\partial x}$$

$$\tilde{J}_n = -\widetilde{D}_{n1}\frac{\partial C_1}{\partial x} - \widetilde{D}_{n2}\frac{\partial C_2}{\partial x} \dots - \widetilde{D}_{nn}\frac{\partial C_n}{\partial x}$$

The effect of component 1 on to flux of 1 is denoted by $\widetilde{D}_{11}$ and obviously we give negative sign. Similarly for $\widetilde{D}_{12} \dots\dots n$. For contribution from component n, it is $\widetilde{D}_{1n}$. Similarly, the flux of 2 we express as:

$$\tilde{J}_2 = -\widetilde{D}_{21}\frac{\partial C_1}{\partial x} - \widetilde{D}_{22}\frac{\partial C_2}{\partial x} \dots - \widetilde{D}_{2n}\frac{\partial C_n}{\partial x}$$

and we have n such flux equations:

$$\tilde{J}_n = -\widetilde{D}_{n1}\frac{\partial C_1}{\partial x} - \widetilde{D}_{n2}\frac{\partial C_2}{\partial x} \dots - \widetilde{D}_{nn}\frac{\partial C_n}{\partial x}$$

So how many coefficients we have? For each flux we have n diffusion coefficient terms and there are n such fluxes. $n \times n$ or n^2 and these are called interdiffusion coefficients, but all of them are not independent, why? Because there are constraints on both the concentration gradients and the fluxes, which means not all concentration gradients are independent, similarly not all fluxes are independent provided we use the right frame of reference. I have introduced you to the different frames of reference before.

It is worth to mention here that most of the time the volume fixed reference frame is used for diffusion measurements, that is most popularly used frame of reference. In volume fixed frame, all n fluxes are not independent. We can reduce some of these coefficients. Let us see how do we reduce the number of coefficients using the constraints on gradients and fluxes.

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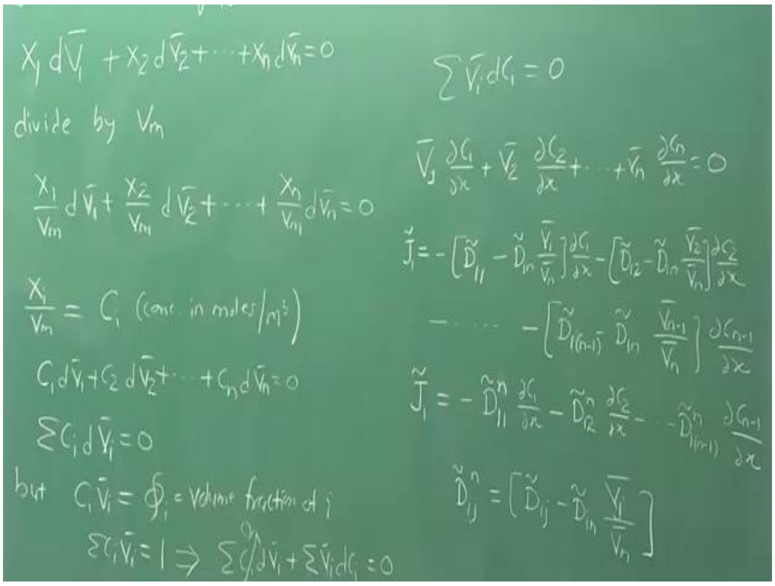

$$X_1 d\bar{V}_1 + X_2 d\bar{V}_2 + \cdots + X_n d\bar{V}_n = 0$$

divide by V_m

$$\frac{X_1}{V_m} d\bar{V}_1 + \frac{X_2}{V_m} d\bar{V}_2 + \cdots + \frac{X_n}{V_m} d\bar{V}_n = 0$$

$$\frac{X_1}{V_m} = C_1 \text{ (conc. in moles}/m^3)$$

$$C_1 d\bar{V}_1 + C_2 d\bar{V}_2 + \cdots + C_n d\bar{V}_n = 0$$

$$\Sigma C_i d\bar{V}_i = 0$$

but $C_i \bar{V}_i = \phi_i$ = volume fraction of i

$$\Sigma C_i \bar{V}_i = 1 \Rightarrow \Sigma \cancelto{0}{C_i d\bar{V}_i} + \Sigma \bar{V}_i dC_i = 0$$

$$\Sigma \bar{V}_i dC_i = 0$$

$$\bar{V}_1 \frac{\partial C_1}{\partial x} + \bar{V}_2 \frac{\partial C_2}{\partial x} + \cdots + \bar{V}_n \frac{\partial C_n}{\partial x} = 0$$

$$\tilde{J}_1 = -\left[\tilde{D}_{11} - \tilde{D}_{1n}\frac{\bar{V}_1}{\bar{V}_n}\right]\frac{\partial C_1}{\partial x} - \left[\tilde{D}_{12} - \tilde{D}_{1n}\frac{\bar{V}_2}{\bar{V}_n}\right]\frac{\partial C_2}{\partial x} - \cdots - \left[\tilde{D}_{1(n-1)} - \tilde{D}_{1n}\frac{\bar{V}_{n-1}}{\bar{V}_n}\right]\frac{\partial C_{n-1}}{\partial x}$$

$$\tilde{J}_1 = -\tilde{D}^n_{11}\frac{\partial C_1}{\partial x} - \tilde{D}^n_{12}\frac{\partial C_2}{\partial x} - \cdots - \tilde{D}^n_{1(n-1)}\frac{\partial C_{n-1}}{\partial x}$$

$$\tilde{D}^n_{ij} = \left[\tilde{D}_{ij} - \tilde{D}_{in}\frac{\bar{V}_i}{\bar{V}_n}\right]$$

First consider the constraint on concentration gradients and its origin lies in the Gibbs-Duhem equation which we have seen during the refreshers on thermodynamics. If we apply Gibbs-Duhem equation to partial molar volumes, what do I get?

$$X_1 d\bar{V}_1 + X_2 d\bar{V}_2 \ldots + X_n d\bar{V}_n = 0$$

If we divide both sides by V_m which is the molar volume, we get:

$$\frac{X_1}{V_m} d\bar{V}_1 + \frac{X_2}{V_m} d\bar{V}_2 \ldots + \frac{X_n}{V_m} d\bar{V}_n = 0$$

$\bar{V}_i$ here are the partial molar volumes of components i varying from 1 to n and X_i denote the mole fractions of components i from 1 to n. Now:

$$\frac{X_i}{V_m} = C_i$$

Where C_i is the concentration in number of moles per volume unit, m^3or cm^3. We can write:

$$C_1 d\bar{V}_1 + C_2 d\bar{V}_2 \ldots + C_n d\bar{V}_n = 0$$

which means:

$$\sum C_i d\bar{V}_i = 0$$

But you know what is $C_i d\bar{V}_i$. It is the volume fraction. Remember we have derived this, some time back.

$$C_i\bar{V}_i = \phi_i$$

ϕ_i is nothing but the volume fraction of i and:

$$\sum C_i\bar{V}_i = 1$$

The summation of all volume fractions should be equal to 1. If we take the differential of the above equation we get:

$$\sum C_i d\bar{V}_i + \sum \bar{V}_i dC_i = 0$$

And the first term as we know from earlier is already 0. So, we have;

$$\sum \bar{V}_i dC_i = 0$$

If you differentiate with respect to x coordinate, we can write more specifically for this as:

$$\bar{V}_1\frac{\partial C_1}{\partial x} + \bar{V}_2\frac{\partial C_2}{\partial x} \ldots + \bar{V}_n\frac{\partial C_n}{\partial x} = 0$$

This is the constraint that we have to use. We can write the constraint here as:

$$\frac{\partial C_n}{\partial x} = -\left(\frac{\bar{V}_1}{\bar{V}_n}\frac{\partial C_1}{\partial x} + \frac{\bar{V}_2}{\bar{V}_n}\frac{\partial C_2}{\partial x} + \cdots + \frac{\bar{V}_{n-1}}{\bar{V}_n}\frac{\partial C_{n-1}}{\partial x}\right)$$

If we substitute for $\frac{\partial C_n}{\partial x}$ in the equation for $\tilde{J}_1$we get:

$$\tilde{J}_1 = -\left(\widetilde{D}_{11} - \widetilde{D}_{1n}\frac{\bar{V}_1}{\bar{V}_n}\right)\frac{\partial C_1}{\partial x} - \left(\widetilde{D}_{12} - \widetilde{D}_{1n}\frac{\bar{V}_2}{\bar{V}_n}\right)\frac{\partial C_2}{\partial x} \ldots - \left(\widetilde{D}_{1n-1} - \widetilde{D}_{1n}\frac{\bar{V}_{n-1}}{\bar{V}_n}\right)\frac{\partial C_{n-1}}{\partial x}$$

Each of the bracketed term term can be substituted with one term. First one can be denoted as as $\widetilde{D}^n_{11}$ in this particular case. Similarly, second bracketed term will be $\widetilde{D}^n_{12}$ until $\widetilde{D}^n_{1n-1}$. In general we can write:

$$\tilde{J}_i = -\widetilde{D}^n_{i1}\frac{\partial C_1}{\partial x} - \widetilde{D}^n_{i2}\frac{\partial C_2}{\partial x} \ldots - \widetilde{D}^n_{in-1}\frac{\partial C_{n-1}}{\partial x}$$

Where:

$$\widetilde{D}_{ij}^{n} = \widetilde{D}_{ij} - \widetilde{D}_{in}\frac{\bar{V}_j}{\bar{V}_n}$$

Hence we have only n-1 independent coefficients for a given flux term. Now how many such fluxes are there?

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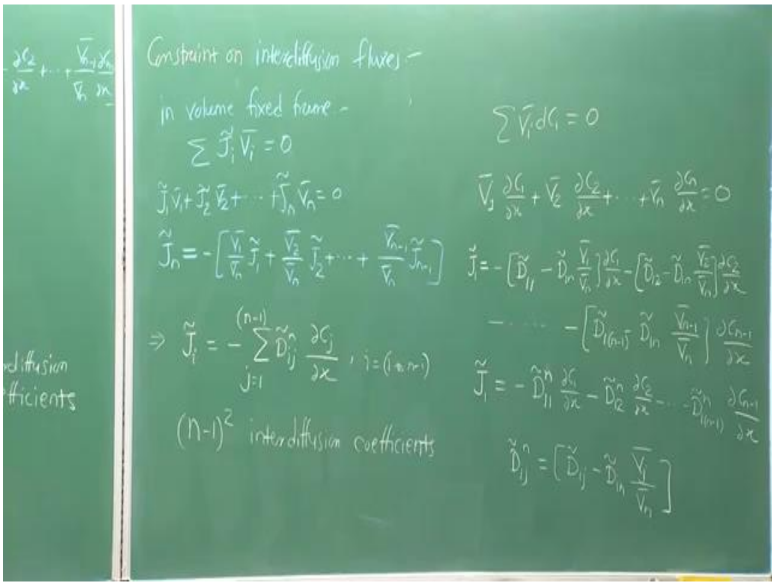

Constraint on interdiffusion fluxes –

in volume fixed frame –

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

$$\tilde{J}_1\bar{V}_1 + \tilde{J}_2\bar{V}_2 + \cdots + \tilde{J}_n\bar{V}_n = 0$$

$$\tilde{J}_n = -\left[\frac{\bar{V}_1}{\bar{V}_n}\tilde{J}_1 + \frac{\bar{V}_2}{\bar{V}_n}\tilde{J}_2 + \cdots + \frac{\bar{V}_{n-1}}{\bar{V}_n}\tilde{J}_{n-1}\right]$$

$$\Rightarrow \tilde{J}_i = -\sum_{j=1}^{(n-1)} \tilde{D}_{ij}^{n}\frac{\partial C_j}{\partial x}, \quad i = (1 \text{ to } n-1)$$

$(n-1)^2$ interdiffusion coefficients

$$\sum \bar{V}_i dC_i = 0$$

$$\bar{V}_1\frac{\partial C_1}{\partial x} + \bar{V}_2\frac{\partial C_2}{\partial x} + \cdots + \bar{V}_n\frac{\partial C_n}{\partial x} = 0$$

$$\tilde{J}_1 = -\left[\tilde{D}_{11} - \tilde{D}_{1n}\frac{\bar{V}_1}{\bar{V}_n}\right]\frac{\partial C_1}{\partial x} - \left[\tilde{D}_{12} - \tilde{D}_{1n}\frac{\bar{V}_2}{\bar{V}_n}\right]\frac{\partial C_2}{\partial x}$$

$$\cdots\cdots - \left[\tilde{D}_{1(n-1)} - \tilde{D}_{1n}\frac{\bar{V}_{n-1}}{\bar{V}_n}\right]\frac{\partial C_{n-1}}{\partial x}$$

$$\tilde{J}_1 = -\tilde{D}_{11}^{n}\frac{\partial C_1}{\partial x} - \tilde{D}_{12}^{n}\frac{\partial C_2}{\partial x} - \cdots - \tilde{D}_{1(n-1)}^{n}\frac{\partial C_{n-1}}{\partial x}$$

$$\tilde{D}_{ij}^{n} = \left[\tilde{D}_{ij} - \tilde{D}_{in}\frac{\bar{V}_j}{\bar{V}_n}\right]$$

There is also a constraint on fluxes and what is that constraint? Constraints on interdiffusion fluxes if we use volume fixed frame is:

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

Remember our fluxes here are expressed as expressed in the unit of moles per cm^2 or per m^2 per second.

We can write:

$$\bar{V}_1\tilde{J}_1 + \bar{V}_2\tilde{J}_2 + \cdots + \bar{V}_n\tilde{J}_n = 0$$

which means $\tilde{J}_n$ is given as:

$$\tilde{J}_n = -\left[\frac{\bar{V}_1}{\bar{V}_n}\tilde{J}_1 + \frac{\bar{V}_2}{\bar{V}_n}\tilde{J}_2 + \cdots + \frac{\bar{V}_{n-1}}{\bar{V}_n}\tilde{J}_{n-1}\right]$$

Again, not all n fluxes are independent, nth one is dependent, so only $n-1$ independent fluxes. Therefore, we have each flux expressed by $n-1$ independent terms and there are $n-1$ such independent fluxes, so in total $(n-1)^2$ interdiffusion coefficients.

In general, we can express the flux of any components $\tilde{J}_i$ as:

$$\tilde{J}_i = -\sum_{j=1}^{n-1} \widetilde{D}_{ij}^{n} \frac{\partial C_j}{\partial x} \qquad i = 1\ to\ n-1$$

j here varies from 1 to $n-1$ and also i is from 1 to $n-1$. And there are $(n-1)^2$ interdiffusion coefficients. This is how we can express interdiffusion in a n component system. We can describe interdiffusion in n component system by using Fick's law extended to the multi-component system by Onsager's formalism.

So, we need $(n-1)^2$ interdiffusion coefficients to completely describe interdiffusion in an n component system. Moreover, the set of these $(n-1)^2$ interdiffusion coefficients are functions of composition, which means with varying composition this set will vary or for a given composition we have a fixed set of $(n-1)^2$ interdiffusion coefficients.

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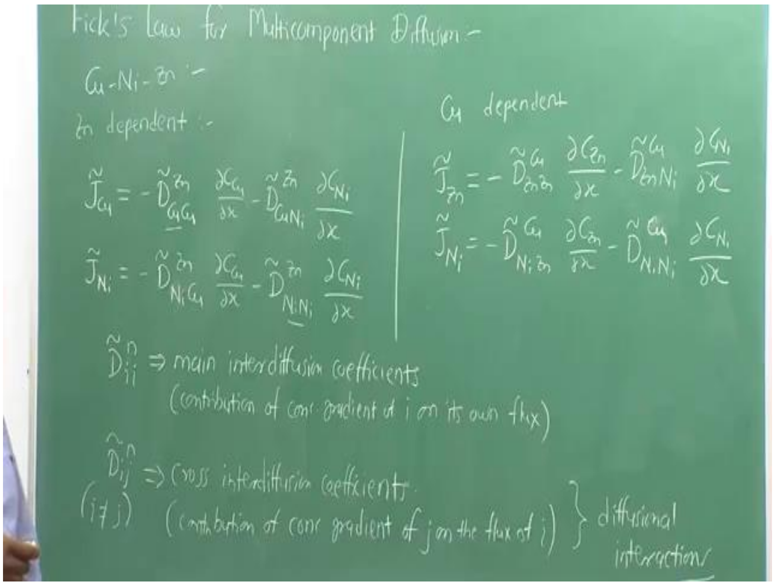

Fick's Law for Multicomponent Diffusion –

Cu-Ni-Zn :–

Zn dependent :–

$$\tilde{J}_{Cu} = -\tilde{D}^{Zn}_{CuCu} \frac{\partial C_{Cu}}{\partial x} - \tilde{D}^{Zn}_{CuNi} \frac{\partial C_{Ni}}{\partial x}$$

$$\tilde{J}_{Ni} = -\tilde{D}^{Zn}_{NiCu} \frac{\partial C_{Cu}}{\partial x} - \tilde{D}^{Zn}_{NiNi} \frac{\partial C_{Ni}}{\partial x}$$

Cu dependent

$$\tilde{J}_{Zn} = -\tilde{D}^{Cu}_{ZnZn} \frac{\partial C_{Zn}}{\partial x} - \tilde{D}^{Cu}_{ZnNi} \frac{\partial C_{Ni}}{\partial x}$$

$$\tilde{J}_{Ni} = -\tilde{D}^{Cu}_{NiZn} \frac{\partial C_{Zn}}{\partial x} - \tilde{D}^{Cu}_{NiNi} \frac{\partial C_{Ni}}{\partial x}$$

$\tilde{D}^{n}_{ii}$ ⇒ main interdiffusion coefficients
(contribution of conc gradient of i on its own flux)

$\tilde{D}^{n}_{ij}$ ⇒ cross interdiffusion coefficients
$(i \neq j)$ (contribution of conc gradient of j on the flux of i) } diffusional interactions

If I describe this for a ternary system, let us consider a ternary system of copper, nickel, zinc. Now which component to treat as dependent component is our choice, we can treat either copper or nickel or zinc. If I treat zinc as dependent, then I have two independent fluxes one for copper and one for nickel. I can write:

$$\tilde{J}_{Cu} = -\widetilde{D}_{CuCu}^{Zn} \frac{\partial C_{Cu}}{\partial x} - \widetilde{D}_{CuNi}^{Zn} \frac{\partial C_{Ni}}{\partial x}$$

The superscript refers to the dependent component which is Zinc here. And:

$$\tilde{J}_{Ni} = -\widetilde{D}^{Zn}_{NiCu}\frac{\partial C_{Cu}}{\partial x} - \widetilde{D}^{Zn}_{NiNi}\frac{\partial C_{Ni}}{\partial x}$$

I have four interdiffusion coefficients in a ternary system. $(n-1)^2$ is four for $n=3$ because there are two independent fluxes and two independent concentration gradients. In this case $\widetilde{D}^{Zn}_{CuCu}$, $\widetilde{D}^{Zn}_{NiNi}$ or $\widetilde{D}^{n}_{ij}$ where $i=j$ are called main interdiffusion coefficients.

So, $\widetilde{D}^{n}_{ii}$ are called main interdiffusion coefficients, and they quantify the effect of concentration gradient of i on its own interdiffusion flux. It is basically the contribution of concentration gradient of i on its own interdiffusion flux. $\widetilde{D}^{n}_{ij}$ where $i \neq j$ are referred to as cross or interactive interdiffusion coefficients. In this case $\widetilde{D}^{Zn}_{CuNi}$ and $\widetilde{D}^{Zn}_{NiCu}$ are the two cross interdiffusion coefficients. And they are basically the contribution of concentration gradient of j on the flux of i.

These are basically the quantification of what we refer to as diffusional interactions or the cross effects. These cross coefficients quantify the cross effects. If we consider $\widetilde{D}^{Zn}_{CuNi}$ term where zinc is dependent, it means how the gradient of nickel is affecting the flux of copper. Similarly, $\widetilde{D}^{Zn}_{NiCu}$ indicates how the gradient of copper is affecting the flux of nickel. $\widetilde{D}^{Zn}_{CuNi}$ quantify the interaction of nickel with copper and $\widetilde{D}^{Zn}_{NiCu}$ quantifies the interaction of copper with nickel during the diffusion.

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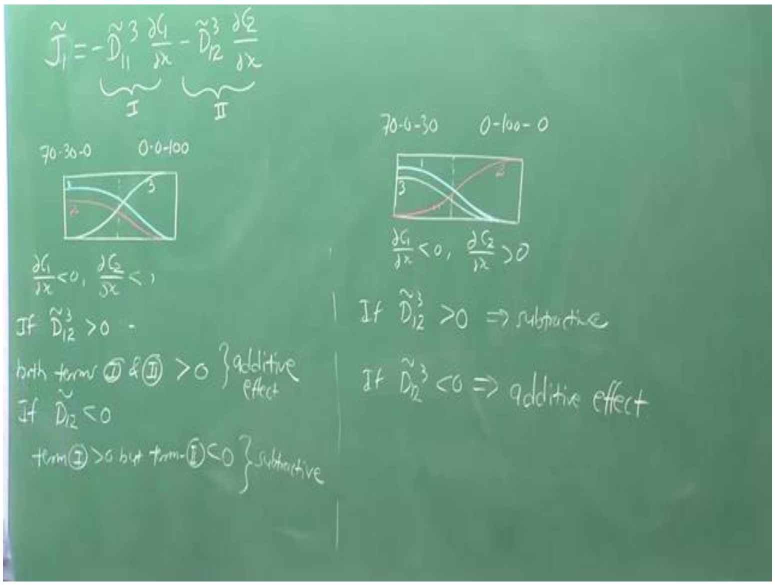

$$\tilde{J}_1 = \underbrace{-\tilde{D}^3_{11}\frac{\partial C_1}{\partial x}}_{I} \underbrace{-\tilde{D}^3_{12}\frac{\partial C_2}{\partial x}}_{II}$$

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$\frac{\partial C_1}{\partial x} < 0$, $\frac{\partial C_2}{\partial x} < 0$

If $\tilde{D}^3_{12} > 0$

both terms Ⓘ & Ⓘⅰ > 0 } additive effect

If $\tilde{D}_{12} < 0$

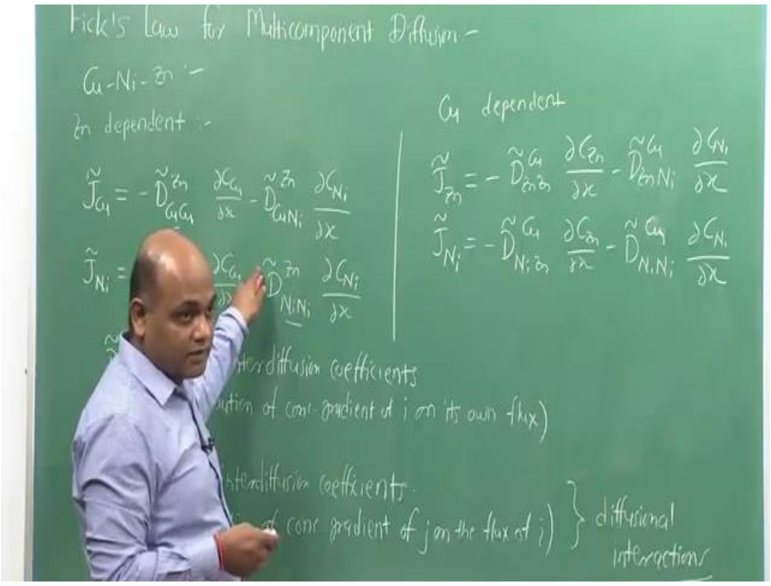
term Ⓘ > 0 but term-Ⓘⅰ < 0 } subtractive

70-0-30 0-100-0

$\frac{\partial C_1}{\partial x} < 0$, $\frac{\partial C_2}{\partial x} > 0$

If $\tilde{D}^3_{12} > 0 \Rightarrow$ subtractive

If $\tilde{D}^3_{12} < 0 \Rightarrow$ additive effect



Now, for example in a ternary system if I write:

$$\tilde{J}_1 = -\tilde{D}_{11}^3 \frac{\partial C_1}{\partial x} - \tilde{D}_{12}^3 \frac{\partial C_2}{\partial x}$$

the main term here, $\tilde{D}_{11}^3$, most of the time will be positive although it is not necessary. This is because for constant molar volume:

$$\tilde{D}_{11}^3 = \tilde{D}_{11} - \tilde{D}_{13}$$

the cross effect term $\tilde{D}_{13}$ would be much smaller compared to the main term $\tilde{D}_{11}$. So, most of the time $\tilde{D}_{11}^3$ will be positive. The cross term $\tilde{D}_{12}^3$ may be negative or positive, what does it mean basically? If $\tilde{D}_{12}^3$ is positive, it means the interdiffusion flux of 1 is enhanced down the gradient of 2 and reduced up the gradient of 2. Similarly, if $\tilde{D}_{12}^3$ is negative it means interdiffusion flux of 1 is enhanced up the gradient of 2 and reduced down the gradient of 2. Let us try to illustrate this, let us call $-\tilde{D}_{11}^3 \frac{\partial C_1}{\partial x}$ as term 1 which is the main term. Remember we need to take into account both gradient and the interdiffusion coefficient. Term 2 is $-\tilde{D}_{12}^3 \frac{\partial C_2}{\partial x}$ including this negative sign.

Let us suppose $\tilde{D}_{11}^3$ is always positive then the first term should be depending upon the sign of the gradient, so the entire 1 term may be positive or negative. What is the convention? Typically the flux if it moves from left to right it is given a positive sign. If the flux is from right to left it is given a negative sign. So, let us consider two cases. I am allowing the diffusion between two different compositions in system 1-2-3.

Let us say first one is 70-30-0 and second terminal alloy is 100 % of 3, i.e 0-0-100. We can draw concentration profile for component1, 2 and 3 in the diffusion zone. So, in this case component 1 and 2 are moving in the same direction. In other words, the both the gradients have same sign, but what is the sign? Negative.

It means:

$$\frac{\partial C_1}{\partial x} < 0, \quad \frac{\partial C_2}{\partial x} < 0$$

The second case I am considering when the two gradients are opposite. Let us assemble couple with terminal compositions 70-0-30 with 0-100-0. The second alloy contains 100 percent of component 2 to start with. For terminal alloy 1: we have 70% and 30% of component 1 and 3 respectively. In this case, now the two gradients are opposite:

$$\frac{\partial C_1}{\partial x} < 0, \quad \frac{\partial C_2}{\partial x} > 0$$

As I am increasing x, the concentration of 2 is increasing, that is why the gradient is positive.

For first case, first term is positive as $\frac{\partial C_1}{\partial x} < 0$. If $\widetilde{D}_{12}^3 > 0$ and $\frac{\partial C_2}{\partial x} < 0$ the second term will be positive. So both the terms are positive which means the flux of 1 is enhanced down the gradient of 2 because $\widetilde{D}_{12}^3$ is positive. If $\widetilde{D}_{12}^3$ was negative, what should happen? Term 1 is positive but $\widetilde{D}_{12}^3$ is negative, so second term becomes negative. So, the first term is positive while second term is negative, so the cross term is having a subtractive effect that is why we say the flux of 1 is reduced down the gradient of 2. When $\widetilde{D}_{12}^3$ is positive, this is an additive effect when $\widetilde{D}_{12}^3$ is negative subtractive effect.

Now in the second case we will have the reverse scenario. If $\widetilde{D}_{12}^3 > 0$, then here the gradient is also positive. Therefore, second term is negative and we will have subtractive effect. So, we say if $\widetilde{D}_{12}^3$ is positive the flux of component 1 is reduced up the gradient of 2. And if $\widetilde{D}_{12}^3 < 0$, we will similarly have additive effect.

Now, here we have expressed the fluxes of copper and nickel with zinc as dependent component. I can as well write, these equations with copper as dependent component. If we write for let us say copper as dependent component then I will get equations for two independent fluxes for zinc and nickel as:

$$\tilde{J}_{Zn} = -\tilde{D}^{Cu}_{ZnZn}\frac{\partial C_{Zn}}{\partial x} - \tilde{D}^{Cu}_{ZnNi}\frac{\partial C_{Ni}}{\partial x}$$

$$\tilde{J}_{Ni} = -\tilde{D}^{Cu}_{NiZn}\frac{\partial C_{Zn}}{\partial x} - \tilde{D}^{Cu}_{NiNi}\frac{\partial C_{Ni}}{\partial x}$$

So, I get a different set of interdiffusion coefficients.

Now, these two sets are different like, $\tilde{D}^{Zn}_{NiNi}$ is not the same as $\tilde{D}^{Cu}_{NiNi}$, but they are inter convertible. We can have equations with which we can convert from one dependent component to the set with another dependent component for an n component system. That you do as exercise.

Basically, there are only four independent coefficients for ternary; we do not say 4+4=8 interdiffusion coefficients from two different dependent components. Because once you have a set with one dependent component, you can obtain the set with other dependent component. You can use them depending upon whichever component you want to use as dependent component. Now let us try to apply Onsager's formalism of Fick's law to binary system, binary means two components. We have only one independent interdiffusion flux and one independent concentration gradient.

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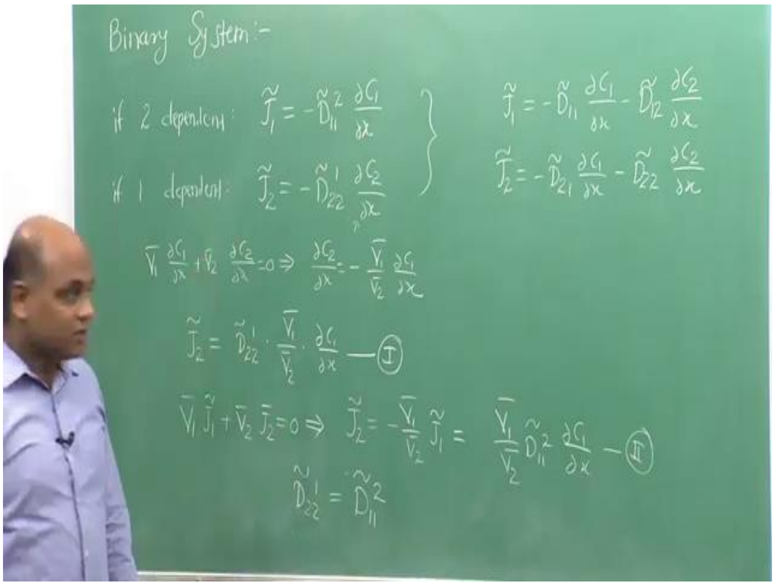

Binary System:-

if 2 dependent: $\tilde{J}_1 = -\tilde{D}^2_{11}\frac{\partial C_1}{\partial x}$

if 1 dependent: $\tilde{J}_2 = -\tilde{D}^1_{22}\frac{\partial C_2}{\partial x}$

$\tilde{J}_1 = -\tilde{D}_{11}\frac{\partial C_1}{\partial x} - \tilde{D}_{12}\frac{\partial C_2}{\partial x}$

$\tilde{J}_2 = -\tilde{D}_{21}\frac{\partial C_1}{\partial x} - \tilde{D}_{22}\frac{\partial C_2}{\partial x}$

$\bar{V}_1\frac{\partial C_1}{\partial x} + \bar{V}_2\frac{\partial C_2}{\partial x} = 0 \Rightarrow \frac{\partial C_2}{\partial x} = -\frac{\bar{V}_1}{\bar{V}_2}\frac{\partial C_1}{\partial x}$

$\tilde{J}_2 = \tilde{D}^1_{22}\cdot\frac{\bar{V}_1}{\bar{V}_2}\cdot\frac{\partial C_1}{\partial x}$ — (I)

$\bar{V}_1\tilde{J}_1 + \bar{V}_2\tilde{J}_2 = 0 \Rightarrow \tilde{J}_2 = -\frac{\bar{V}_1}{\bar{V}_2}\tilde{J}_1 = \frac{\bar{V}_1}{\bar{V}_2}\tilde{D}^2_{11}\frac{\partial C_1}{\partial x}$ — (II)

$\tilde{D}^1_{22} = \tilde{D}^2_{11}$

If we treat two as dependent we can write:

$$\tilde{J}_1 = -\tilde{D}^2_{11}\frac{\partial C_1}{\partial x}$$

and if we treat 1 as dependent you can write:

$$\tilde{J}_2 = -\widetilde{D}_{22}^{1}\frac{\partial C_2}{\partial x}$$

In the original Onsager's formalism we will write:

$$\tilde{J}_1 = -\widetilde{D}_{11}\frac{\partial C_1}{\partial x} - \widetilde{D}_{12}\frac{\partial C_2}{\partial x}$$

$$\tilde{J}_2 = -\widetilde{D}_{21}\frac{\partial C_1}{\partial x} - \widetilde{D}_{22}\frac{\partial C_2}{\partial x}$$

And if we substitute for $\frac{\partial C_2}{\partial x}$ here or for $\frac{\partial C_1}{\partial x}$ here, we will get term in both the equations. That is how we are reducing four coefficients to $(n-1)^2$ square which is 1 for binary. Again, the above two equations seem to be different but they are not. Let us see how. Because we can write:

$$\bar{V}_1\frac{\partial C_1}{\partial x} + \bar{V}_2\frac{\partial C_2}{\partial x} = 0$$

which means:

$$\frac{\partial C_2}{\partial x} = -\frac{\bar{V}_1}{\bar{V}_2}\frac{\partial C_1}{\partial x}$$

If we substitute this in the equation for $\tilde{J}_2$, we should get:

$$\tilde{J}_2 = \widetilde{D}_{22}^{1}\frac{\bar{V}_1}{\bar{V}_2}\frac{\partial C_1}{\partial x}$$

Let us call this equation 1. But we know, because we are using volume fixed frame:

$$\bar{V}_1\tilde{J}_1 + \bar{V}_2\tilde{J}_2 = 0$$

which tells me:

$$\tilde{J}_2 = -\frac{\bar{V}_1}{\bar{V}_2}\tilde{J}_1$$

and if we substitute for $\tilde{J}_1$ from here we get:

$$\tilde{J}_2 = \frac{\bar{V}_1}{\bar{V}_2}\widetilde{D}_{11}^{2}\frac{\partial C_1}{\partial x}$$

Let us call this equation 2. If you compare the right hand sides of 1 and 2, it tells me:

$$\widetilde{D}_{11}^{2} = \widetilde{D}_{22}^{1}$$

Both the coefficients should be same. So, in binary in effect we have only 1 coefficient.

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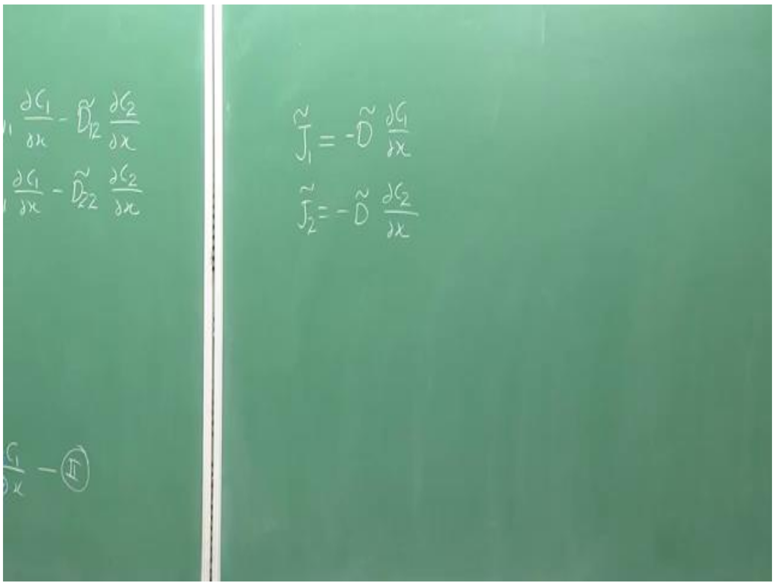

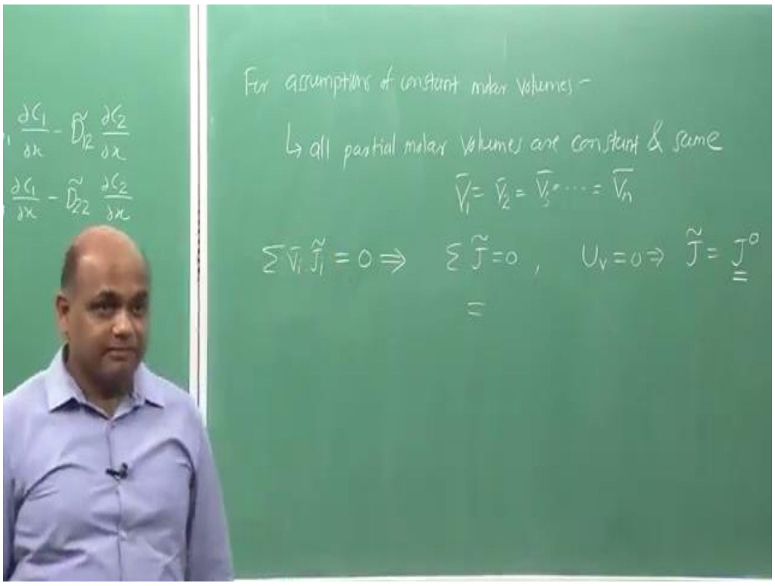

We can express both the fluxes using 1 coefficient. $\tilde{J}_1$ we call it as:

$$\tilde{J}_1 = -\widetilde{D}\frac{\partial C_1}{\partial x}$$

and

$$\tilde{J}_2 = -\widetilde{D}\frac{\partial C_2}{\partial x}$$

The binary interdiffusion simplifies to just knowing one interdiffusion coefficient.

Now, varying partial molar volumes is a complicated case. Typically, during the experimental measurements it is commonly assumed that the molar volumes remain constant. If the molar volume is constant, what does it imply? It implies that all the partial molar volumes are also constant and that means:

$$\bar{V}_1 = \bar{V}_2 = \bar{V}_3 = \cdots = \bar{V}_n$$

for an n component system. This makes the life simpler because it not only simplifies the constraint, for example:

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

and since all $\bar{V}_i$ are same this just implies that:

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

It also means that U_v, the velocity of volume fixed frame is 0 because there is no change in volume, there is no net flow of volume even in lab fixed frame. And because of that:

$$\tilde{J} = J^o$$

or the volume fixed frame coincides with the lab fixed frame.

J^o refers to the fluxes determined in lab fixed frame, and that is why for experimental analysis, most of the time molar volumes are assumed constant. In fact we will show it later even for the case when the partial molar volumes are constant, but changing. Which means:

$$\bar{V}_1 \neq \bar{V}_2 \neq \bar{V}_3 \neq \cdots \neq \bar{V}_n$$

but are constant with composition, even in that case U_v equal to 0. And the lab fixed frame coincides with volume fixed frame.