Diffusion in Multicomponent Solids

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Lecture 17

Conversion of Set of Interdiffusion Coefficients from One Dependent Component to Another

Welcome to the 17th lecture, in the open course on Diffusion in Multicomponent Solids. In this lecture, we will see how to convert a set of multicomponent interdiffusion coefficient with respect to one dependent component to that with respect to another dependent component. I have illustrated this with a quaternary system to make the derivation more general. I have treated the case with varying partial molar volumes in this particular lecture.

In today's class we will work on kind of an exercise problem which would give you a flavour of multicomponent diffusion. We have seen in an n component system, we need n^2 interdiffusion coefficients according to Onsager's formalism of Fick's law. However, not all n concentration gradients are independent, only n-1 are independent and the nth one is dependent. Also if we choose the appropriate frame of reference, like volume fixed frame of reference only n-1 interdiffusion fluxes are independent.

Essentially, we have $(n-1)^2$ interdiffusion coefficient that define interdiffusion in an n component system. Of course, this $(n-1)^2$ interdiffusion coefficients are functions of composition. At any given composition which component can be selected as the dependent component is our choice.

Now, the set of interdiffusion coefficient that we determine with respect to one component as the dependent component can always be converted into the set with respect to another dependent component and that is the exercise that we are going to do today, we will look at the quaternary system.

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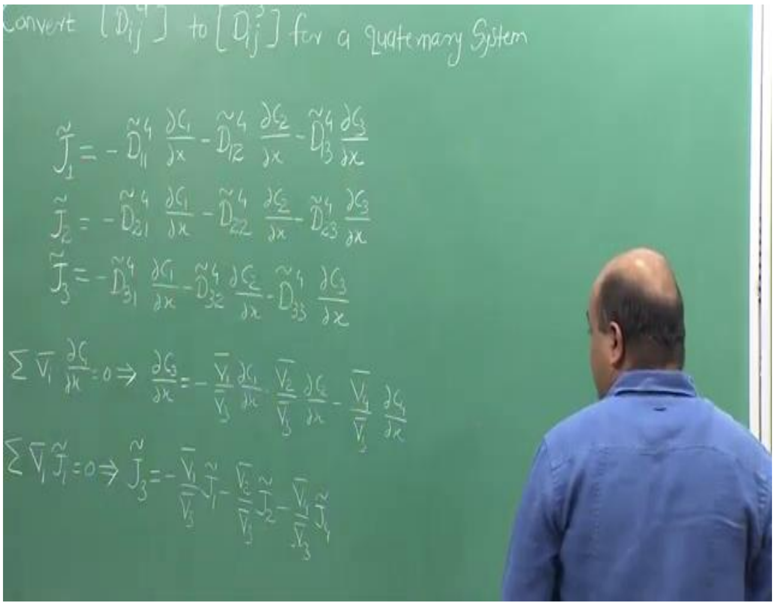

The problem is you have to convert $\widetilde{D}_{ij}^4$ to $\widetilde{D}_{ij}^3$ for quaternary system. A quaternary system means we have nine independent interdiffusion coefficients at any given composition. $\widetilde{D}_{ij}^4$ as you know denotes the set of interdiffusion coefficients with respect to component 4 as dependent. $\widetilde{D}_{ij}^3$ is the set of interdiffusion coefficients with respect to component 3 as the dependent component.

If we start with component 4 as the dependent component, we have 3 independent interdiffusion fluxes $\tilde{J}_1$, $\tilde{J}_2$ and $\tilde{J}_3$ and they can be expressed in terms of nine interdiffusion coefficients as:

$$\tilde{J}_1 = -\widetilde{D}_{11}^4 \frac{\partial C_1}{\partial x} - \widetilde{D}_{12}^4 \frac{\partial C_2}{\partial x} - \widetilde{D}_{13}^4 \frac{\partial C_3}{\partial x}$$

$$\tilde{J}_2 = -\widetilde{D}_{21}^4 \frac{\partial C_1}{\partial x} - \widetilde{D}_{22}^4 \frac{\partial C_2}{\partial x} - \widetilde{D}_{23}^4 \frac{\partial C_3}{\partial x}$$

$$\tilde{J}_3 = -\widetilde{D}_{31}^4 \frac{\partial C_1}{\partial x} - \widetilde{D}_{32}^4 \frac{\partial C_2}{\partial x} - \widetilde{D}_{33}^4 \frac{\partial C_3}{\partial x}$$

There are nine interdiffusion coefficients with respect to component 4 as dependent component. Suppose, we have determined the set of interdiffusion coefficients at a particular composition treating 4 as dependent and now, we need to use it somewhere else but, now we need to treat component 3 as dependent component. How do we obtain or how do we convert from one dependent to another.

Since we have to treat now 3 as dependent we have to get rid of the concentration gradient of 3 and obviously the flux of 3 and introduce the flux of 4. To get rid of concentration gradient of 3, we can use the constraint:

$$\sum \bar{V}_i \frac{\partial C_i}{\partial x} = 0$$

which will yield:

$$\frac{\partial C_3}{\partial x} = -\frac{\bar{V}_1}{\bar{V}_3}\frac{\partial C_1}{\partial x} - \frac{\bar{V}_2}{\bar{V}_3}\frac{\partial C_2}{\partial x} - \frac{\bar{V}_4}{\bar{V}_3}\frac{\partial C_4}{\partial x}$$

And also, if we use the volume fix frame of reference, the constraint on the fluxes is:

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

We can substitute:

$$\tilde{J}_3 = -\frac{\bar{V}_1}{\bar{V}_3}\tilde{J}_1 - \frac{\bar{V}_2}{\bar{V}_3}\tilde{J}_2 - \frac{\bar{V}_4}{\bar{V}_3}\tilde{J}_4$$

Now let us take the expression for $\tilde{J}_1$ and substitute for the gradient of 3.

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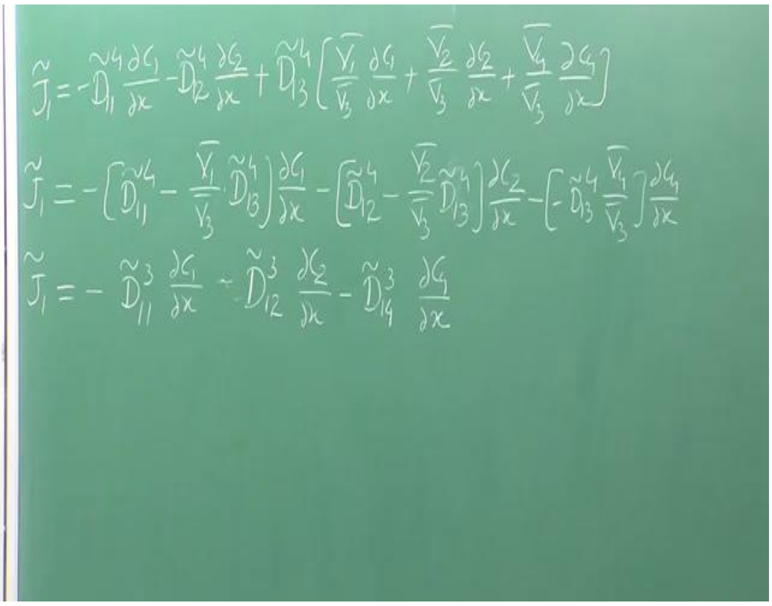

We get:

$$\tilde{J}_1 = -\tilde{D}_{11}^{4}\frac{\partial C_1}{\partial x} - \tilde{D}_{12}^{4}\frac{\partial C_2}{\partial x} + \tilde{D}_{13}^{4}\left(\frac{\bar{V}_1}{\bar{V}_3}\frac{\partial C_1}{\partial x} + \frac{\bar{V}_2}{\bar{V}_3}\frac{\partial C_2}{\partial x} + \frac{\bar{V}_4}{\bar{V}_3}\frac{\partial C_4}{\partial x}\right)$$

If you want to express $\tilde{J}_1$ using component 3 as dependent, then it will be:

$$\tilde{J}_1 = -\left(\tilde{D}_{11}^{4} - \frac{\bar{V}_1}{\bar{V}_3}\tilde{D}_{13}^{4}\right)\frac{\partial C_1}{\partial x} - \left(\tilde{D}_{12}^{4} - \frac{\bar{V}_2}{\bar{V}_3}\tilde{D}_{13}^{4}\right)\frac{\partial C_2}{\partial x} - \left(-\tilde{D}_{13}^{4}\frac{\bar{V}_4}{\bar{V}_3}\right)\frac{\partial C_4}{\partial x}$$

If you compare this with the following expression for $\tilde{J}_1$, we get the required conversion for coefficients of 1.

$$\tilde{J}_1 = -\tilde{D}_{11}^{3}\frac{\partial C_1}{\partial x} - \tilde{D}_{12}^{3}\frac{\partial C_2}{\partial x} - \tilde{D}_{14}^{3}\frac{\partial C_4}{\partial x}$$

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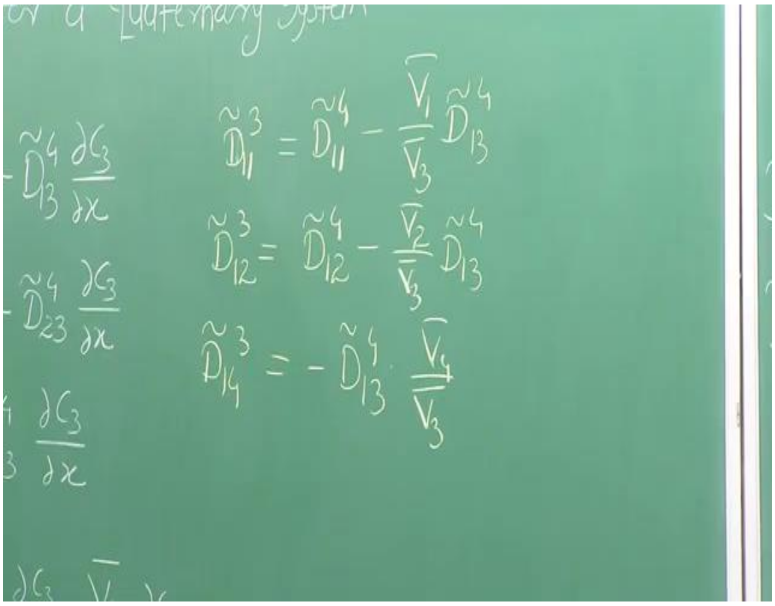

We can write:

$$\tilde{D}_{11}^{3} = \tilde{D}_{11}^{4} - \frac{\bar{V}_1}{\bar{V}_3}\tilde{D}_{13}^{4}$$

$$\tilde{D}_{12}^{3} = \tilde{D}_{12}^{4} - \frac{\bar{V}_2}{\bar{V}_3}\tilde{D}_{13}^{4}$$

$$\tilde{D}_{14}^{3} = -\tilde{D}_{13}^{4}\frac{\bar{V}_4}{\bar{V}_3}$$

Similarly you can find the coefficients for the flux of 2.

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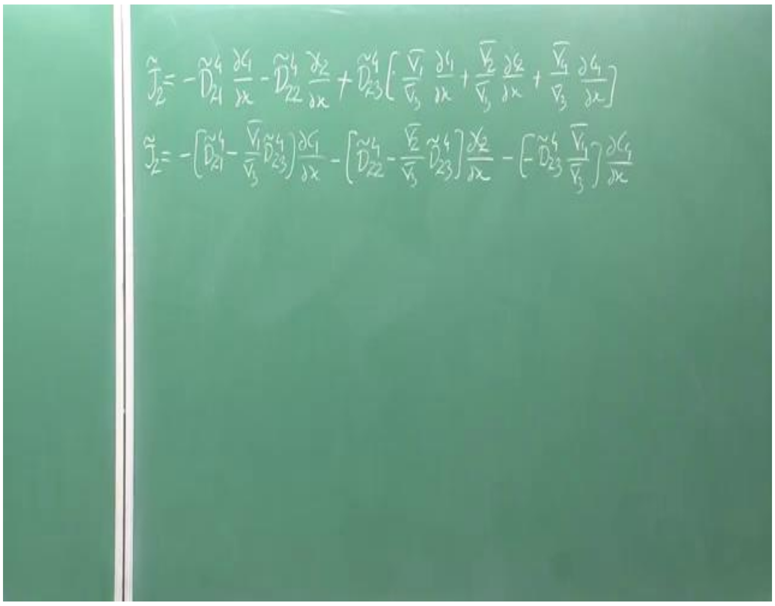

If you substitute for $\frac{\partial C_3}{\partial x}$ in the expression for $\tilde{J}_2$ we get:

$$\tilde{J}_2 = -\widetilde{D}_{21}^4 \frac{\partial C_1}{\partial x} - \widetilde{D}_{22}^4 \frac{\partial C_2}{\partial x} + \widetilde{D}_{23}^4 \left(\frac{\bar{V}_1}{\bar{V}_3} \frac{\partial C_1}{\partial x} + \frac{\bar{V}_2}{\bar{V}_3} \frac{\partial C_2}{\partial x} + \frac{\bar{V}_4}{\bar{V}_3} \frac{\partial C_4}{\partial x} \right)$$

$\tilde{J}_2$ comes out to be:

$$\tilde{J}_2 = -\left(\widetilde{D}_{21}^4 - \frac{\bar{V}_1}{\bar{V}_3} \widetilde{D}_{23}^4 \right) \frac{\partial C_1}{\partial x} - \left(\widetilde{D}_{22}^4 - \frac{\bar{V}_2}{\bar{V}_3} \widetilde{D}_{23}^4 \right) \frac{\partial C_2}{\partial x} - \left(-\widetilde{D}_{23}^4 \frac{\bar{V}_4}{\bar{V}_3} \frac{\partial C_4}{\partial x} \right)$$

Now, we can also write $\tilde{J}_2$ in terms of component 3 as dependent and if we compare the corresponding coefficients we get:

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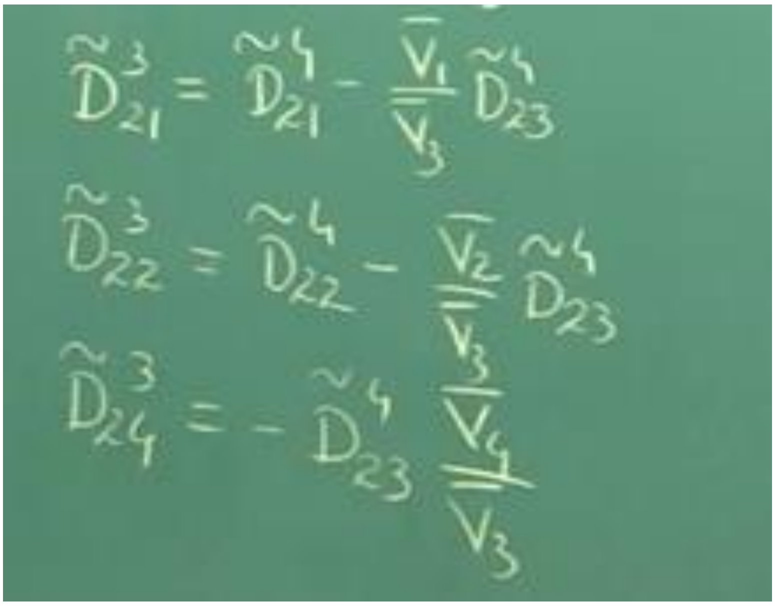

$$\widetilde{D}_{21}^{3} = \widetilde{D}_{21}^{4} - \frac{\bar{V}_1}{\bar{V}_3}\widetilde{D}_{23}^{4}$$

$$\widetilde{D}_{22}^{3} = \widetilde{D}_{22}^{4} - \frac{\bar{V}_2}{\bar{V}_3}\widetilde{D}_{23}^{4}$$

$$\widetilde{D}_{24}^{3} = -\widetilde{D}_{23}^{4}\frac{\bar{V}_4}{\bar{V}_3}$$

These are the coefficients for component 2. To obtain the coefficients for flux of 4 will be a little more complicated, but, essentially we do the similar thing we need $\tilde{J}_4$.

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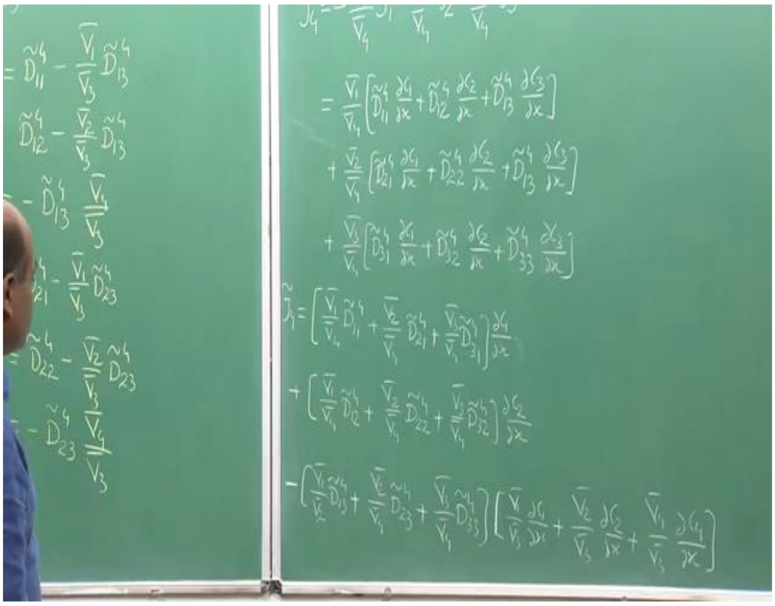

We substitute:

$$\tilde{J}_4 = -\frac{\bar{V}_1}{\bar{V}_4}\tilde{J}_1 - \frac{\bar{V}_2}{\bar{V}_4}\tilde{J}_2 - \frac{\bar{V}_3}{\bar{V}_4}\tilde{J}_3$$

and then we substitute for $\tilde{J}_1, \tilde{J}_2, \tilde{J}_3$ using the extended Fick's law, we get:

$$\tilde{J}_4 = \frac{\bar{V}_1}{\bar{V}_4}\left(\tilde{D}_{11}^4 \frac{\partial C_1}{\partial x} + \tilde{D}_{12}^4 \frac{\partial C_2}{\partial x} + \tilde{D}_{13}^4 \frac{\partial C_3}{\partial x}\right) + \frac{\bar{V}_2}{\bar{V}_4}\left(\tilde{D}_{21}^4 \frac{\partial C_1}{\partial x} + \tilde{D}_{22}^4 \frac{\partial C_2}{\partial x} + \tilde{D}_{23}^4 \frac{\partial C_3}{\partial x}\right) + \frac{\bar{V}_3}{\bar{V}_4}\left(\tilde{D}_{31}^4 \frac{\partial C_1}{\partial x} + \tilde{D}_{32}^4 \frac{\partial C_2}{\partial x} + \tilde{D}_{33}^4 \frac{\partial C_3}{\partial x}\right)$$

Now, let us take the respective derivatives out and we obtain:

$$\tilde{J}_4 = \frac{\partial C_1}{\partial x}\left(\frac{\bar{V}_1}{\bar{V}_4}\tilde{D}_{11}^4 + \frac{\bar{V}_2}{\bar{V}_4}\tilde{D}_{21}^4 + \frac{\bar{V}_3}{\bar{V}_4}\tilde{D}_{31}^4\right) + \frac{\partial C_2}{\partial x}\left(\frac{\bar{V}_1}{\bar{V}_4}\tilde{D}_{12}^4 + \frac{\bar{V}_2}{\bar{V}_4}\tilde{D}_{22}^4 + \frac{\bar{V}_3}{\bar{V}_4}\tilde{D}_{32}^4\right) - \left(\frac{\bar{V}_1}{\bar{V}_3}\frac{\partial C_1}{\partial x} + \frac{\bar{V}_2}{\bar{V}_3}\frac{\partial C_2}{\partial x} + \frac{\bar{V}_4}{\bar{V}_3}\frac{\partial C_4}{\partial x}\right)\left(\frac{\bar{V}_1}{\bar{V}_4}\tilde{D}_{13}^4 + \frac{\bar{V}_2}{\bar{V}_4}\tilde{D}_{23}^4 + \frac{\bar{V}_3}{\bar{V}_4}\tilde{D}_{33}^4\right)$$

after substituting for $\frac{\partial C_3}{\partial x}$. Again, we have derivatives of 1, 2 appearing here, and if we take this common and rearrange the corresponding terms we will get the equations for conversion of coefficients for component 4.

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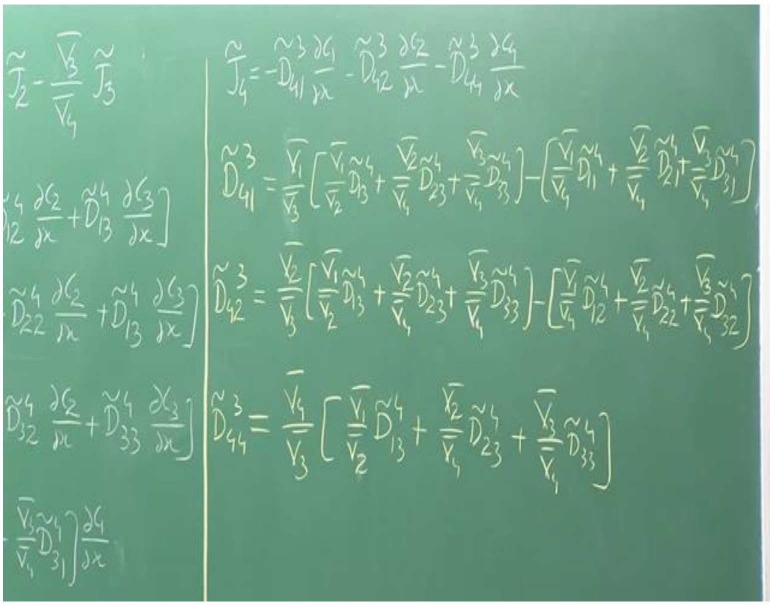

We have to compare with:

$$\tilde{J}_4 = -\tilde{D}_{41}^3 \frac{\partial C_1}{\partial x} - \tilde{D}_{42}^3 \frac{\partial C_2}{\partial x} - \tilde{D}_{44}^3 \frac{\partial C_4}{\partial x}$$

We obtain

$$\tilde{D}_{41}^3 = \frac{\bar{V}_1}{\bar{V}_3}\left(\frac{\bar{V}_1}{\bar{V}_4}\tilde{D}_{13}^4 + \frac{\bar{V}_2}{\bar{V}_4}\tilde{D}_{23}^4 + \frac{\bar{V}_3}{\bar{V}_4}\tilde{D}_{33}^4\right) - \left(\frac{\bar{V}_1}{\bar{V}_4}\tilde{D}_{11}^4 + \frac{\bar{V}_2}{\bar{V}_4}\tilde{D}_{21}^4 + \frac{\bar{V}_3}{\bar{V}_4}\tilde{D}_{31}^4\right)$$

$$\tilde{D}_{42}^3 = \frac{\bar{V}_2}{\bar{V}_3}\left(\frac{\bar{V}_1}{\bar{V}_4}\tilde{D}_{13}^4 + \frac{\bar{V}_2}{\bar{V}_4}\tilde{D}_{23}^4 + \frac{\bar{V}_3}{\bar{V}_4}\tilde{D}_{33}^4\right) - \left(\frac{\bar{V}_1}{\bar{V}_4}\tilde{D}_{12}^4 + \frac{\bar{V}_2}{\bar{V}_4}\tilde{D}_{22}^4 + \frac{\bar{V}_3}{\bar{V}_4}\tilde{D}_{32}^4\right)$$

$$\tilde{D}_{44}^3 = \frac{\bar{V}_4}{\bar{V}_3}\left(\frac{\bar{V}_1}{\bar{V}_4}\tilde{D}_{13}^4 + \frac{\bar{V}_2}{\bar{V}_4}\tilde{D}_{23}^4 + \frac{\bar{V}_3}{\bar{V}_4}\tilde{D}_{33}^4\right)$$

This way now, we have obtained nine interdiffusion coefficients with respect to 3 as dependent component that is $\tilde{D}_{ij}^3$ in terms of interdiffusion coefficients with respect to 4 as the dependent component. We have obtained $\tilde{D}_{ij}^3$ in terms of $\tilde{D}_{ij}^4$.

Similarly we can make other conversions if you want to use component 2 as dependent component, for example. Follow the similar, steps and we can convert one set of interdiffusion coefficients into another.

This we have done by not assuming constant molar volumes. That is, we are allowing the partial molar volumes to vary. Now, if the molar volume is constant, then all the partial molar volumes are constant and are equal. If we assume molar volume is constant, than trivially we will get rid of those $\frac{\bar{V}_i}{\bar{V}_j}$ terms and we will get a simpler expression for assumption of constant molar volumes. Any questions? We will stop here.