Diffusion in Multicomponent Solids
Lecture 45
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Last class, we talked about how we can analyse experimental concentration profiles for getting interdiffusion fluxes within the diffusion zone. Today, I would like to talk about various methodologies that we can use for determination of interdiffusion coefficients in multicomponent systems. We will first start with determination of fluxes, hence the analysis of interdiffusion fluxes becomes very important.

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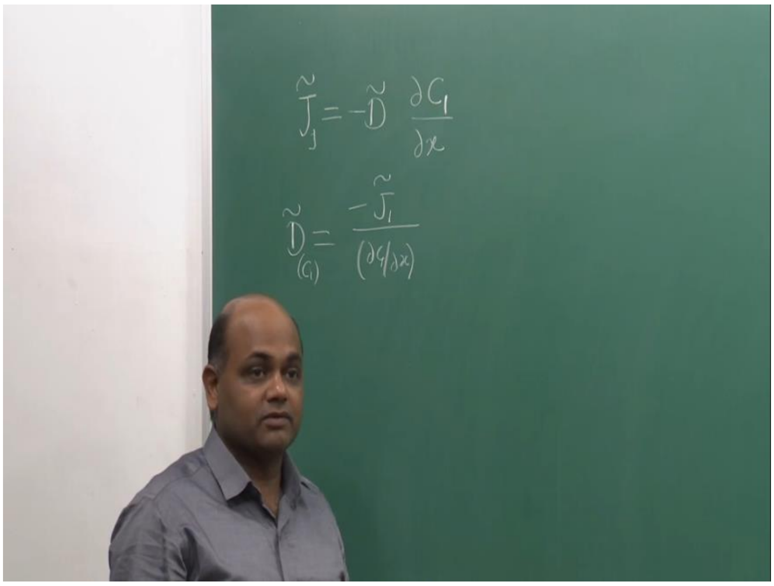

For binary it is very simple because there is only one interdiffusion coefficient that describes the interdiffusion flux of both components:

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

You can get:

$$\tilde{D}_{(C_1)} = -\frac{\tilde{J}_1}{\frac{\partial C_1}{\partial x}}$$

At every composition plane within the binary diffusion zone, we can determine the value of interdiffusion flux of any component, for example 1 here. We can divide flux by the gradient of that component at the same plane get the interdiffusion coefficient at that particular composition. We can do this throughout the diffusion zone, so we can get the binary interdiffusion coefficients as functions of composition. As we increase the number of components, the complicacies increase. If we consider ternary diffusion couple to start with; in ternary we know that there are two independent fluxes.

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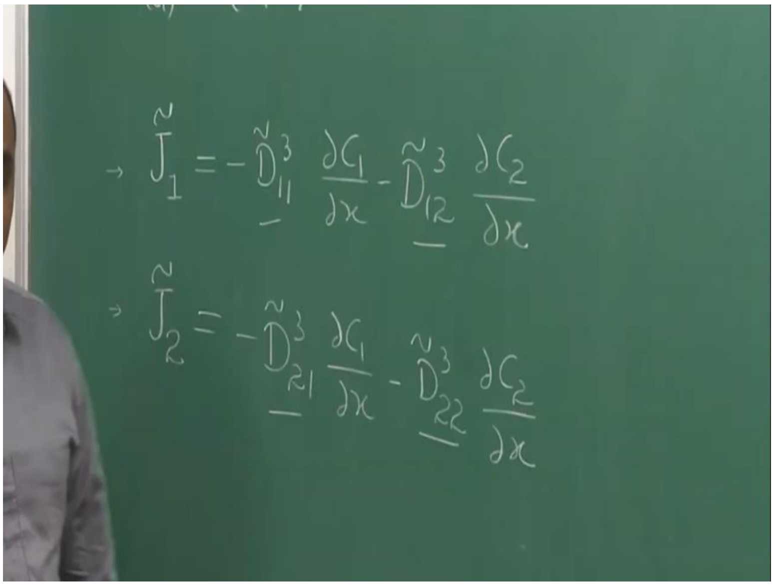

Let us consider the system, let us say 1-2-3. If you treat 3 as a dependent component, we can write:

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

The second independent flux, $\tilde{J}_2$ is:

$$\tilde{J}_2 = -\tilde{D}^3_{21}\frac{\partial C_1}{\partial x} - \tilde{D}^3_{22}\frac{\partial C_2}{\partial x}$$

We have four interdiffusion coefficients, at any composition plane of a single diffusion couple. And we can get only two equations one for $\tilde{J}_1$, the other for $\tilde{J}_2$. So, we cannot evaluate the entire set of four interdiffusion coefficients with a single diffusion couple. Obviously, I need more than one diffusion couple. Since the interdiffusion coefficients are functions of composition, we want to make sure that there will be a common composition in the diffusion zones of the independent diffusion couples that we assemble. Kirkaldy had proposed originally this approach. As per Kirkaldy's approach for a ternary system, we need two independent diffusion couples with intersecting diffusion paths. What is a diffusion path, this is an important concept that I would like to explain now before I go further in Kirkaldy's method. A diffusion path simply speaking, is the sequence of compositions that develop within the diffusion zone of a couple plotted on to the isotherm.

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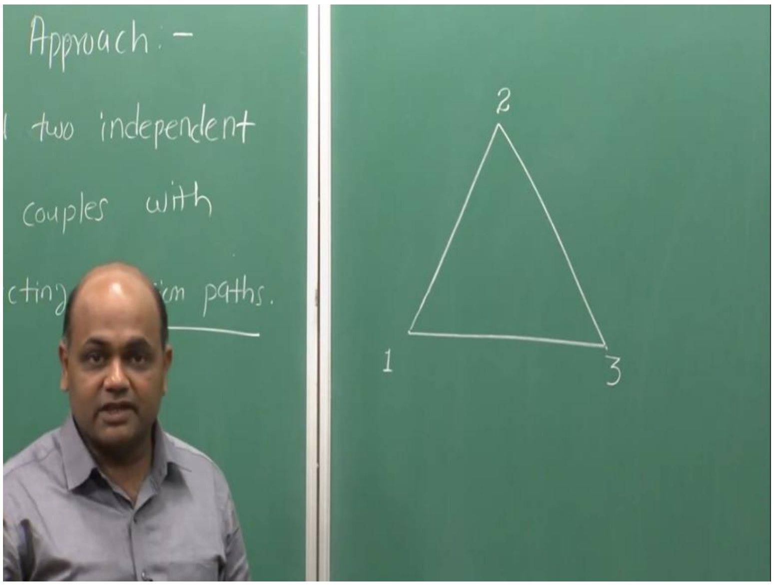

If we consider a ternary isotherm, it can be represented by an equilateral triangle which is referred to as Gibbs triangle. The three corners of the triangle represent hundred % of the three elements, 1-2-3. Each side of the triangle represents the binary system. So, we have 1-2 binary, 1-3 binary and 2-3 binary. Any composition that lies inside the triangle is a ternary composition. I would explain in little more detail the ternary isotherms as we would need it for multiphase diffusion. I will explain it in a separate class but, right now it is just sufficient to know this.

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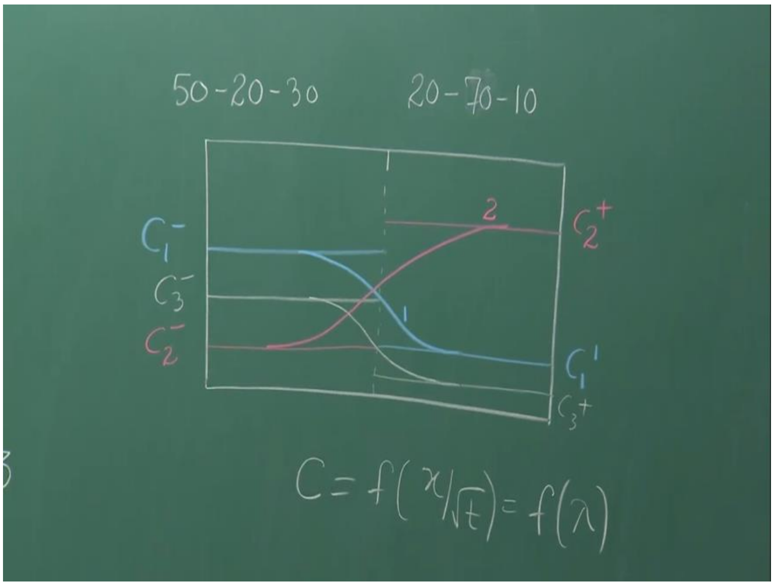

Now, if we consider any ternary diffusion couple. Let us say left terminal alloy is 50 % of one, 20 % of two and 30 % of three. Right alloy is 20 % of one, 70 % of two, 10 % of three.

The initial concentration profiles of a component in left and right terminal alloy can be represented by C_1^- and C_1^+ respectively. After diffusion annealing for a certain time, concentration profiles will develop. As the diffusion time increases, we know that the diffusion profiles will broaden. The composition profiles will change with time, that means each composition plane will move with time. We know each composition plane moves parabolically, that is:

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

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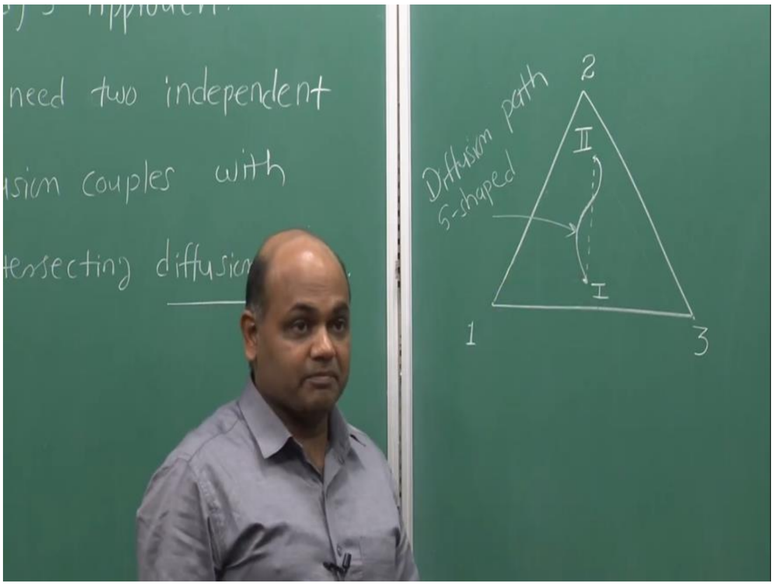

λ is the Boltzmann parameter. I can mark the compositions of alloy 1 and 2 on the ternary isotherm and I join these two compositions by a straight dotted line. Now, if I plot the compositions sequence that is developed in the diffusion profile on to this ternary isotherm what would it be like? One may tend to think that it will follow this straight line joining the two-terminal alloys? But it is not the case, we will find typically this sequence of composition takes shape of S on the ternary isotherm. So, the diffusion path is typically an S-shaped curve.

And, what is the significance of diffusion path? The significance of the diffusion path is that it is independent of time or it is invariant with time. We have seen if we plot concentration versus distance, x-axis here is distance coordinate, it is a function of time. With time each composition plane is moving. The diffusion profile is broadening, but not the diffusion path.

This is because; in an infinite diffusion couple the each composition plane moves parabolically with time. It is a function of Boltzmann parameter λ, there is no new composition plane added or any composition plane getting removed. Obviously, the sequence of composition will not change although the profiles will broaden with time such that the diffusion path is independent of time. This is an important concept.

When we conduct the diffusion couple experiments, in order to assess the reliability of our experiment we should usually prepare at least one diffusion couple three-four different times. The same couple which is the couple between the same two ternary alloys should be annealed for three-four different times, I have to make sure that at different times the diffusion paths are same. That helps to establish the reliability of the experiments.

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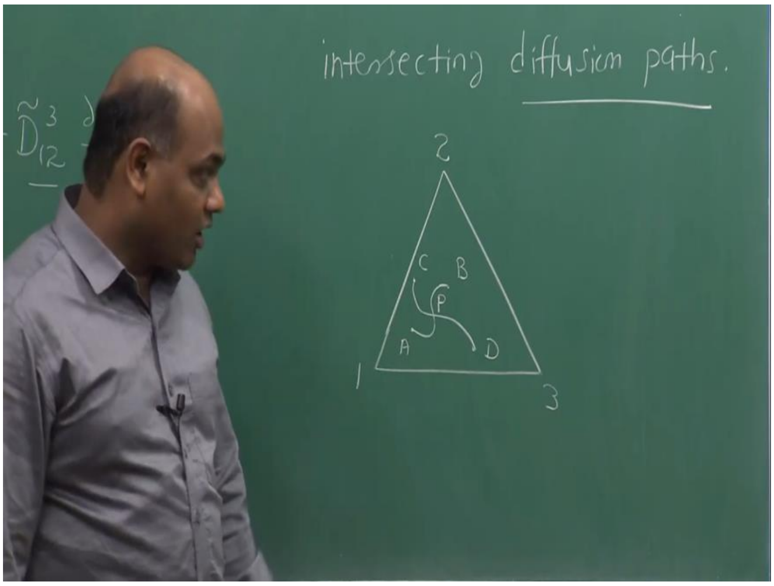

Now, coming back to Kirkaldy's method here for determining ternary interdiffusion coefficients. We want two independent couples. Let us say I prepared two independent couples, one between alloy A / alloy B and the other between alloy C / alloy D. These two couples should be such that there diffusion paths should intersect on the ternary isotherm. So, if I prepare the two diffusion couples such that the straight line joining the two-terminal alloys intersect, there is a high possibility that the diffusion paths of the two will intersect.

Both of the couples will develop S shape diffusion paths and they will intersect at some composition, let us denote this by P. It means the composition P is common to both the two diffusion couples A-B and C-D. Why it is important? Because, at point P or at the composition corresponding to point P in each of the couple, we can write the two independent flux equations.

One set of two equations for couple A-B, the second set of independent equations for couple C-D. This way we have four independent equations, now we can solve those for the four interdiffusion coefficients. Those four interdiffusion coefficients will correspond to the composition at point P. These are the exact values of the ternary interdiffusion coefficients.

In order to get interdiffusion coefficients at different compositions, we need to prepare such intersecting path diffusion couples and get the values. It is not possible to predict the diffusion path exactly. We cannot really design the diffusion couples whose diffusion paths will intersect at the exact desired point. But, we can kind of design the couples in a way so that the straight line joining the two-terminal alloys intersect. We know somewhere the diffusion paths will intersect. This way the method has been applied to many ternary systems and the interdiffusion coefficients have been determined.

In principle, Kirkaldy's method can be extended to any n component system. For example, in quaternary we have three independent fluxes, $\tilde{J}_1$, $\tilde{J}_2$ and $\tilde{J}_3$which are expressed as functions of three independent gradients. So, there are nine interdiffusion coefficients at any given quaternary composition. If we extend this analysis to quaternary, we will need three independent diffusion couples whose diffusion paths will intersect at one point. Now, it is highly difficult to design such couples. For quaternary system, an isotherm is a 3D figure. In ternary it is a 2D figure because there are two independent concentrations. In quaternary, there are three independent concentrations, so it will be a 3D figure. Now, imagine three diffusion paths in three dimensions intersecting at one common point. It is almost not practical to design such couples. In principle, this method can be extended to n component system, but practically it had not been possible far.

However, recently there has been one approach proposed that I will discuss next. Recently John Morral has proposed an approach called body diagonal diffusion couples which we can use in limited cases in order to get quaternary, quinary or even higher component interdiffusion coefficient matrices. I will explain that approach now. Body diagonal diffusion couple approach is essentially an extension of Kirkaldy's approach to n component system, but it gives a systematic way to design the multicomponent diffusion couples such that they would intersect possibly at one point. I will explain this with the help of a quaternary system, then I will explain how we can extend it to the higher-order systems. When I consider a quaternary system, I need three independent concentration variables to define one quaternary composition. So, if I plot a particular composition, I need a 3D composition space. The fourth component is of course dependent. If I design a couple between, let us say between alloy I and alloy II, concentration of the terminal alloy I can be defined by C_1^I, C_2^I and C_3^I. For alloy II composition is defined by C_1^{II}, C_2^{II} and C_3^{II}. The difference between the corresponding concentrations of the two terminal alloys is denoted as ΔC_i. The composition vector ΔC^o is written as:

$$\Delta C^o = (\Delta C_1 , \Delta C_2, \Delta C_3)$$

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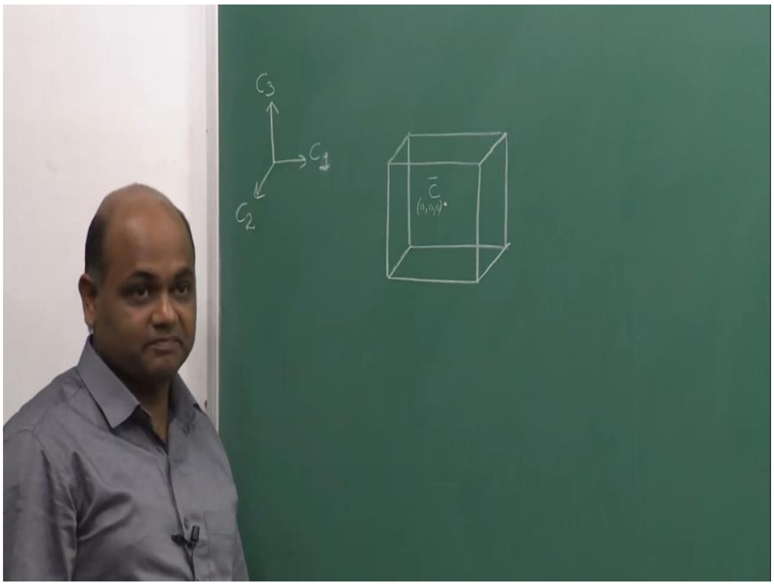

In body diagonal diffusion couple approach, the terminal alloys needs to be selected. Now, consider a composition $\bar{C}$ and imagine a cube around this composition $\bar{C}$ such that $\bar{C}$ is at the body centre of this cube. So, this cube is drawn in a 3D composition space of C_1, C_2 and C_3. C_2 axis and C_1 and C_3 is are as shown in the figure.

In body diagonal diffusion couple approach the two terminal alloys of a diffusion couple are selected from two ends of a body diagonal of this cube. That is why the name body diagonal diffusion couple. Now, why it is significant that you will realize soon. For quaternary for example, there is a cube here. For a cube, there are four body diagonals and we can form four such sets of diffusion couples. Now what is the special feature about the body diagonal couples? They are characterized by same difference in concentrations for three independent components.

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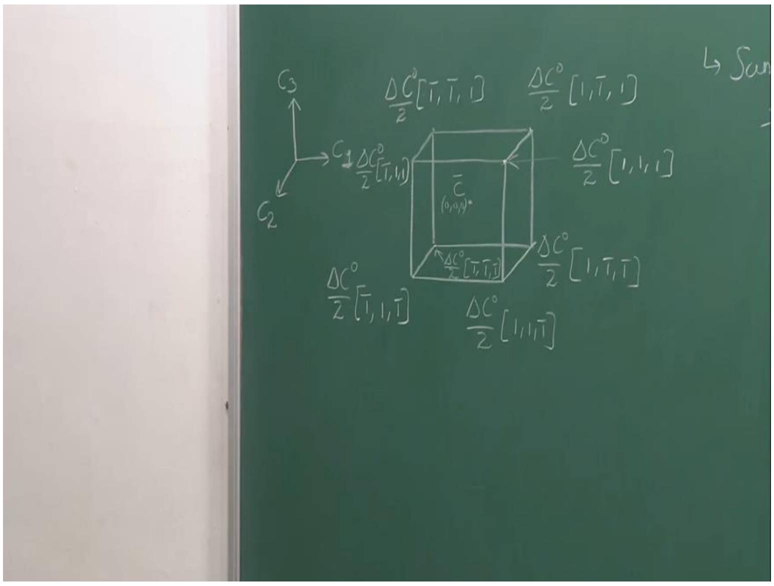

If we determined the difference between the concentrations of any two alloys selected from the two ends of the body diagonal, the three components will have the same difference of the concentrations. The fourth one of course, maybe different because it will make up for the total to be a 100 %. Now, if I imagine the origin (0,0,0) to be at $\bar{C}$ that is at the body centre, then I can mark the eight corners of the cube in terms of ΔC^o or more specifically, in terms of $\frac{\Delta C^o}{2}$ because ΔC^o is the composition vector. I have to select the terminal alloys from the ends of the body diagonals. That is the terminal alloys are from the eight corners of the cube. The eight corners have the coordinates as shown in the figure above.

Since there are four body diagonals, we can have four sets of diffusion couples. If we select a specific $\bar{C}$ and specific ΔC^o, we can write down the compositions of all the alloys on the eight corners of the cubes. If we write those compositions, now the question is why it is important to select the terminal alloy concentration from the two ends of a body diagonal. Because, if ΔC^o is very small then we expect the interdiffusivity matrix to be more or less constant throughout the diffusion zone. And if the interdiffusion coefficients are constant then the diffusion path is symmetric, which means for any of this body diagonal couple, the diffusion path will intersect the body diagonal exactly at the body centre position that is exactly at $\bar{C}$. We can have in quaternary four diffusion couples whose diffusion paths are expected to intersect at one single composition $\bar{C}$ here. This way the body diagonal diffusion couples help us to design the diffusion couples which will intersect at one desired composition.

The steps are easy, we select $\bar{C}$ which is the desired composition at which interdiffusion coefficients are to be evaluated. Then select particular ΔC^o, the small composition difference in which we expect the interdiffusivities to be constant. Then, we form a cube around $\bar{C}$ with the composition vector ΔC^o and based on these coordinatesprepare the body diagonal diffusion couples. For quaternary we need three couples although there are four body diagonals. We can form actually four diffusion couples, but that will be more than sufficient number of couples.

To get the variation with the composition we can shift $\bar{C}$ to form new sets of couples. Let us see an example here, let us say I want the quaternary interdiffusion coefficients at $\bar{C}$ equal to 25 % of 1, 25 % of 2, 25 % of 3. Obviously, the component four will also be 25 %. $\Delta C^o = 10$. With this, the centre is (25, 25, 25) and I need to find out the eight corner compositions.

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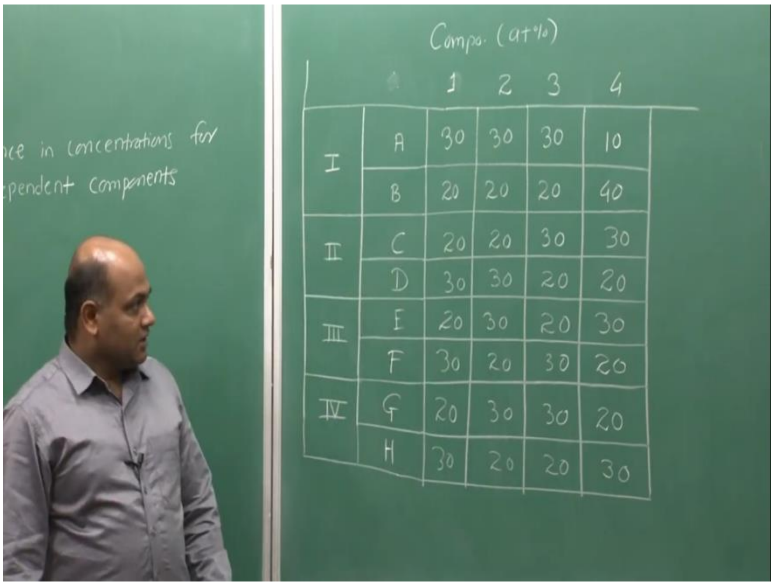

ce in concentrations for
pendent components

Compo. (at%)

		1	2	3	4
I	A	30	30	30	10
	B	20	20	20	40
II	C	20	20	30	30
	D	30	30	20	20
III	E	20	30	20	30
	F	30	20	30	20
IV	G	20	30	30	20
	H	30	20	20	30

These coordinates of the cube as already mentioned will help me to do that. For example, alloy A is diagonally opposite to B, together they will form couple I. if alloy B has coordinates $\frac{\Delta C^o}{2}(\bar{1},\bar{1},\bar{1})$ then A has coordinate $\frac{\Delta C^o}{2}(1,1,1)$. Composition for B is obtained by:

$$C_B = \bar{C} + \frac{\Delta C^o}{2}(\bar{1},\bar{1},\bar{1})$$

$$\bar{C} = (25,25,25)$$

Which gives:

$$C_B = (20, 20, 20)$$

Fourth component of alloy B is $(100 - 60) = 40$ %. The composition of A is:

$$C_A = \bar{C} + \frac{\Delta C^o}{2}(1, 1, 1) = (30, 30, 30)$$

Fourth component of alloy A is 10 %. We can see the difference is (10, 10, 10) for all three independent components between alloy A and B. The fourth one is different because it has to make up for the total weight % or the total atom % to be 100 %.Similarly we can write the composition of other alloys as given in Table below:

		1	**2**	**3**	**4**
I	A	30	30	30	10
	B	20	20	20	40
II	C	20	20	30	30
	D	30	30	20	20
III	E	20	30	20	30
	F	30	20	30	20
IV	G	20	30	30	20
	H	30	20	20	30

This way we can design four sets of diffusion couples, with eight terminal alloys from eight corners of the cube which is formed around $\bar{C}$ with the composition vector ΔC^o. We can see for each of the couples, the components 1,2 and 3 have the same difference 10, 10, 10. The fourth one makes up for hundred %. Now, since the four diffusion couples are expected to intersect at one composition $\bar{C}$, we can four diffusion couples whose diffusion paths are expected to intersect at the body centre position $\bar{C}$. We can select any three of them for our experiment so that at the common composition $\bar{C}$ we can get nine independent equations because there will be three independent fluxes in each couple at the common composition. We can write nine independent equations and we can solve for nine quaternary interdiffusion coefficients.

This method, we can extend even to the quinary or higher-order system in principle. In higher-order systems we need to imagine the hypercube formed in n-1 dimensional space. Like in, quaternary there was a 3 dimensional composition space and we can get four body diagonal diffusion couples. In an n component system, we have n-1 dimensional composition space and there would be 2^{n-2} body diagonals possible.

For example in quinary if we imagine a four-dimensional hypercube, there will be $2^3 = 8$ body diagonals. In quaternary, we have already seen in three-dimensional composition space there will be $2^2 = 4$ body diagonals which I have already got. Ternary, it's simple, there will be two body diagonals. This way we can extend this method for the higher-order system, so we have applied this to quaternary as well as quinary system. I will illustrate the application part of it, for each of the system, binary, ternary, quaternary, quinary of the methods.

We have seen how we can get the interdiffusion coefficients in binary, ternary, quaternary higher-order systems. I will also give some examples from the literature of actual determination of interdiffusion coefficient sets in practical systems that will be in the next class. Now, these are the methods which give exact values of entire sets of interdiffusion coefficients. There are also some additional techniques because it may not be always possible to design such couples.

For example, in the body diagonal couple approach, one limitation is, we need a large enough single-phase region. Because, if there is no large enough single-phase region, we won't get enough space for this cube in quaternary or hypercubes in quinary, etc to form. Also there is a possibility that one of the diffusion paths may cross the single-phase region so it will be a multiphase diffusion couple, again which is not desired.

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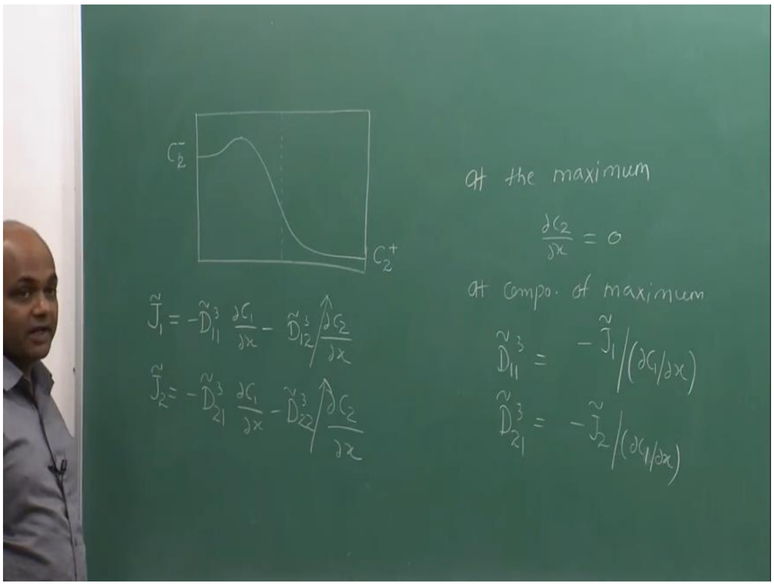

So, it is not always possible to form such couples, in that case, we should have access to at least some of the diffusion coefficients. There are a few techniques that we can use for that. I will talk about those techniques now. In multicomponent systems, it is frequently observed that some components develop a maximum or minimum on their concentration profile. One such profile I have shown here in an infinite diffusion couple of a component 2 with terminal composition C_2^- and C_2^+ on the left and right side respectively.

And this peak is of interest, why? Because we can get at least a couple of interdiffusion coefficients in the ternary system out of four. If I treat three as a dependent component, I can write two independent fluxes as:

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

$$\tilde{J}_2 = -\widetilde{D}_{21}^3 \frac{\partial C_1}{\partial x} - \widetilde{D}_{22}^3 \frac{\partial C_2}{\partial x}$$

At the maximum, the gradient of component 2 is zero which means:

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

I can get rid of the second term in both the flux equations. Essentially, I can get two coefficients $\widetilde{D}_{11}^3$ and $\widetilde{D}_{21}^3$ with respect to three as a dependent. These coefficients are obtained at the composition corresponding to maximum using:

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

$$\widetilde{D}_{21}^3 = -\frac{\tilde{J}_2}{\frac{\partial C_1}{\partial x}}$$

This is how we can get interdiffusion coefficient at a maximum or minimum. Of course, not the entire set but at least some of them. This gives us an idea about the main interdiffusion coefficient of 1 and also the kind of interaction that 1 has with 2 or how the gradient of 1 can affect the diffusion flux of 2.

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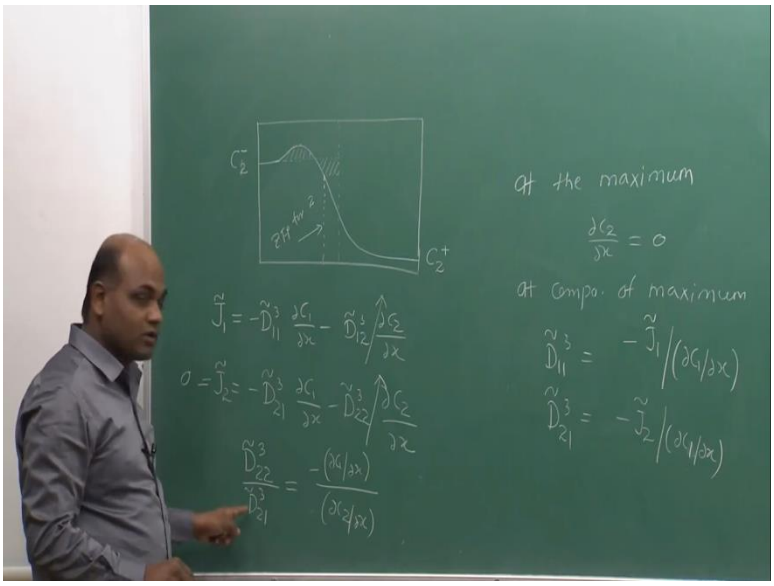

Also we have talked about ZFP's or zero flux plane yesterday. These are also important to the point of view of understanding the interdiffusion coefficients here. If there is a minimum or maximum formed, we expect that there may be a zero-flux plane. It is not necessary that there will be, but there may be. We find an area under this peak here and find we find an area on the right-hand side of this peak such that its area is equal to the first area. The zero-flux plane will be given at the position of the second area. This is the ZFP for 2.

Now, why this is important because, at ZFP, $\tilde{J}_2 = 0$ which means:

$$\tilde{J}_2 = -\tilde{D}_{21}^3 \frac{\partial C_1}{\partial x} - \tilde{D}_{22}^3 \frac{\partial C_2}{\partial x} = 0$$

we can get the ratio of :

$$\frac{\tilde{D}_{22}^3}{\tilde{D}_{21}^3} = -\frac{\left(\frac{\partial C_1}{\partial x}\right)}{\left(\frac{\partial C_2}{\partial x}\right)}$$

These gradients are evaluated at the location of ZFP. Remember the gradient is zero at the peak, not at the ZFP. At ZFP both component 2 and 1 would have developed some gradient. So, we can get the ratio of the main coefficient to cross coefficient.

This gives a good idea about how significant interactions are, because if the interactive coefficient is about similar order of magnitude to the main coefficient, then the ratio would be close to unity. If the interactions are more dominant, the ratio would be less than unity. If the interactions are less dominant, the ratio would be more than unity. The sign ofcourse gives us an idea about what kind of interactions these are. Because assuming $\tilde{D}_{22}^3$ is positive, right and sign will tell us whether $\widetilde{D}_{21}^{3}$ is negative or positive. Okay, this is how this zero-flux plane, maximum / minimum will give us an idea about at least some of the diffusion coefficients or the diffusional interactions.

Then, there is another approach proposed which is called pseudo-binary approach which is proposed by Aloke Paul. This is applicable to get the main coefficient of at least one component in a multicomponent system. In this what is done is, for example if you are dealing with a quaternary system, only two of the components will develop concentration profiles in the diffusion zone, the remaining two will not. The diffusion couples are designed such that let us say component 2 and 3 have the same concentration in both the terminal alloys.

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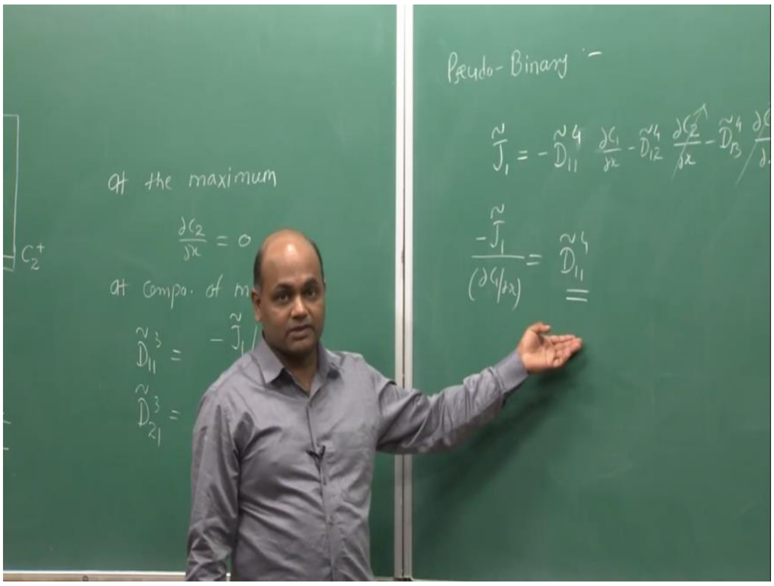

But, component 1 and 4 will have different concentrations, how it helps? Let us say if I write the equation for independent fluxes. In quaternary, let us treat component 4 as a dependent and we have three independent fluxes. We can write:

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

And suppose we have selected the diffusion couples such that only component 1 and 4 have different concentrations in the two-terminal alloys. But, component 2 and 3 have the same concentrations such that they will not develop any concentration profiles during diffusion. So in the above equation, last two terms will be zero. We can straightaway get:

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

This way we can find the value of $\widetilde{D}_{11}^{4}$ through the pseudo-binary diffusion couples. Of course, it won't give the entire set but it gives an idea about at least how, how fast or slow a particular component is diffusing based upon its main interdiffusion coefficients. We can design such couples to get different main coefficients. Then we can find out the main coefficients at different compositions based upon the pseudo-binary technique.

The advantage is that this can be applied to any component system as long as only two components develop the composition profiles. But the limitation is we are assuming that the interactions are not significant because if the interactions are significant, even if we start with the same concentrations of a component in both the terminal alloys, it will end up developing some concentration profile. There will be an uphill diffusion region developed, which is not desired for the pseudo-binary couple. In that case then we cannot solve for $\widetilde{D}_{11}^{4}$ directly.

Similarly, a pseudo-ternary approach has also been proposed in which instead of two, we will have three varying concentrations and remaining constant. We can design two such couples with the same set of components having invariant composition in the two terminal alloys. The two couples have at least one common composition in the diffusion zones similar to the Kirkaldy's approach for ternary that I explained. We can solve the four equations at the common composition and get four independent interdiffusion coefficients.

Again, it won't be an entire set because in quaternary, for example, we need nine interdiffusion coefficients. Through pseudo-ternary couples, we will get four out of the nine coefficients. Again, one assumption there will be all the components which are supposed to be invariant will not develop any uphill diffusion region, which means they will not exhibit significant diffusional interactions from the other components. Okay, these are some of the experimental techniques which we can use for determination of interdiffusion coefficients in multicomponent systems.

In the next class, I will show you some specific examples from the literature in which such estimation of interdiffusion coefficients has been reported. We will stop here, for now, thank you.