Diffusion in Multicomponent Solids
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Lecture 39
Deriving Relation Between Diffusion Flux and Chemical Potential Gradients

Welcome to the 39th lecture in this open course on Diffusion in Multicomponent Solids. In this lecture, I shall discuss the derivation of expression for the diffusion flux of a component in terms of chemical potential gradients. We will see that for the substitutional diffusion by vacancy mechanism, the flux of a component depends not only on its own chemical potential gradient but also on the chemical potential gradients of other diffusing components.

It is said that gradient in chemical potential is the fundamental driving force for diffusion. Today, we will see why it is so. We will try to derive the expression for diffusion flux under the chemical potential gradients. We will use the simple kinetic theory for this derivation. This type of equation has been derived long back by Seeds, Fisher, Hollomon and Turnbull and by Bardeen.

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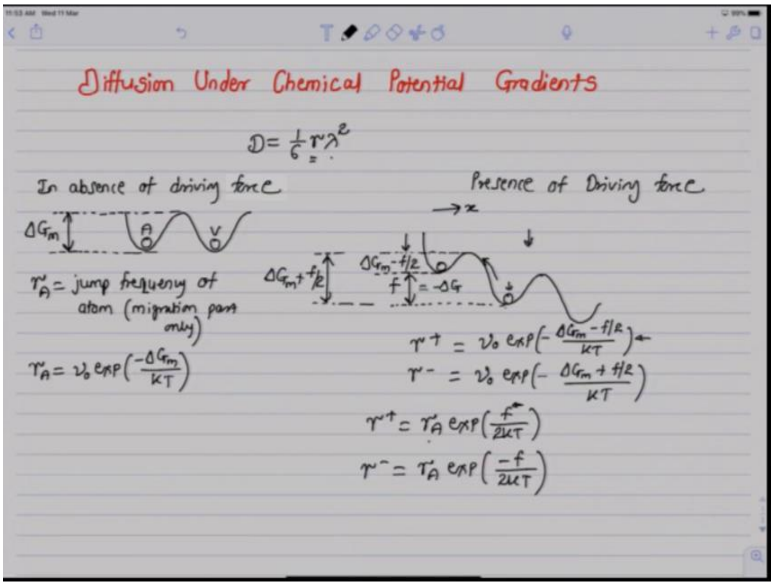


Diffusion Under Chemical Potential Gradients

$D = \frac{1}{6}\underset{=}{\Gamma}\lambda^2$

In absence of driving force

Γ_A = jump frequency of atom (migration part only)

$\Gamma_A = \nu_0 \exp\left(\frac{-\Delta G_m}{kT}\right)$

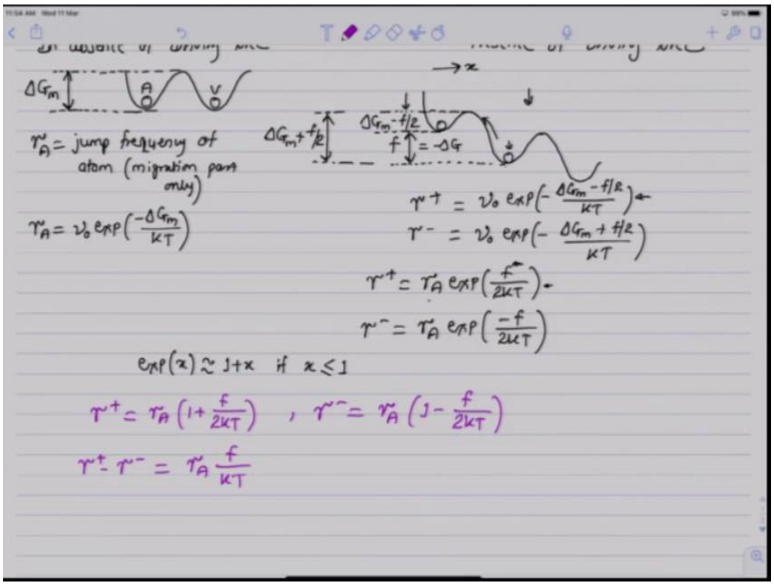
Presence of Driving force

$\Gamma^+ = \nu_0 \exp\left(-\frac{\Delta G_m - f/2}{kT}\right) \leftarrow$

$\Gamma^- = \nu_0 \exp\left(-\frac{\Delta G_m + f/2}{kT}\right)$

$\Gamma^+ = \Gamma_A \exp\left(\frac{f}{2kT}\right)$

$\Gamma^- = \Gamma_A \exp\left(\frac{-f}{2kT}\right)$



Γ_A = jump frequency of atom (migration part only)

$\Gamma_A = \nu_0 \exp\left(\frac{-\Delta G_m}{kT}\right)$

$\Gamma^+ = \nu_0 \exp\left(-\frac{\Delta G_m - f/2}{kT}\right)$

$\Gamma^- = \nu_0 \exp\left(-\frac{\Delta G_m + f/2}{kT}\right)$

$\Gamma^+ = \Gamma_A \exp\left(\frac{f}{2kT}\right)$

$\Gamma^- = \Gamma_A \exp\left(\frac{-f}{2kT}\right)$

$\exp(x) \simeq 1 + x$ if $x \leq 1$

$\Gamma^+ = \Gamma_A\left(1 + \frac{f}{2kT}\right)$, $\Gamma^- = \Gamma_A\left(1 - \frac{f}{2kT}\right)$

$\Gamma^+ - \Gamma^- = \Gamma_A \frac{f}{kT}$

I will try to explain this theory in today’s conventional terms. We have seen the expression for diffusivity:

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

in which γ is the successful jump frequency of an average atom and λ is the jump distance. Jump frequency term γ involves two types of contributions: one is the number of times an atom has energy equal to or greater than the activation energy for migration and second, the probability that an adjacent site is vacant. So, second term belongs to the activation barrier for vacancy formation.

In the absence of any driving force, at the regular atomic positions, the atoms are lying in a potential energy well. In the first figure, if this is an atom A and it jumps on to the next site let us call this V, there is no net change in the Gibbs free energy because of this jump. But in order for this jump to occur, the atom has to cross this energy barrier which is known as activation energy for migration ΔG_m. When there is a driving force present, the situation is little bit different, the jumps are biased in a particular direction because if the atom jumps in that particular direction, it causes decrease in Gibbs free energy. In presence of driving force, this potential energy well configuration is a little bit different. This potential energy well would look something like this. Let us say there is a driving force in the x direction. When the atom jumps from this position into the next site here, we will see that it is associated with decrease in Gibbs free energy and the decrease in Gibbs free energy is referred to as the driving force.

Let us call the jumps from left to right as forward jump and the jumps from right to left as reverse jump of the atom. For the forward jump we can see the atom has to cross a lesser energy barrier than reverse jump. For example, if the atom in this position wants to jump back, it has to cross a bigger activation barrier than for the forward jump and because of the symmetric condition, we can show that the activation barrier for the forward jump can be written as $\Delta G_m - \frac{f}{2}$ and the activation barrier for reverse jump would be $\Delta G_m + \frac{f}{2}$.

Now, the number of times an average atom has an energy equal to or greater than the activation energy for migration per second can be denoted as γ_A. It is the jump frequency of atom, this is in absence of driving force and this is only the migration part. You see the actual jump frequency γ will have the migration part as well as the vacancy formation part. In my notation here:

$$\gamma_A = jump\ frequency\ of\ atom\ (migration\ part\ only)$$

γ_A is in the absence of any driving force. Obviously, when there is a driving force present like here, the forward jump frequency γ^+ will be different than the reverse jump frequency, γ^-. In the absence of driving force, γ_A will be given as:

$$\gamma_A = \nu_o\, exp\left(\frac{-\Delta G_m}{kT}\right)$$

where ν_o is the debye frequency, the number of time atom vibrates per second. γ^+ would be given by:

$$\gamma^+ = \nu_o\, exp\left(-\frac{\Delta G_m - \frac{f}{2}}{kT}\right)$$

and γ^- would be:

$$\gamma^- = \nu_o\, exp\left(-\frac{\Delta G_m + \frac{f}{2}}{kT}\right)$$

We can expand them further as:

$$\gamma^+ = \nu_o\, exp\left(-\frac{\Delta G_m}{kT}\right) exp\left(\frac{f}{2kT}\right)$$

So γ^+ becomes:

$$\gamma^+ = \gamma_A \, exp\left(\frac{f}{2kT}\right)$$

and similarly γ^- would be:

$$\gamma^- = \gamma_A \, exp\left(-\frac{f}{2kT}\right)$$

γ_A represents the jump frequency of atom A in absence of any driving force. The jump frequency in the forward and reverse direction will be modified by this driving force f and the driving force is usually a positive quantity and f will be given as $-\Delta G$. ΔG is the difference between the Gibbs free energy of this site and this site and it will include only the non-ideal part, we will come back to it later. With this, we can use an approximation:

$$\exp \mathrm{x} \approx 1 + \mathrm{x} \qquad \text{if } \mathrm{x} \ll 1$$

Now, in the expressions for γ^+ and γ^-, f is usually much less than kT and we can use this approximation. We can write:

$$\gamma^+ = \gamma_A \left(1 + \frac{f}{2kT}\right)$$

$$\gamma^- = \gamma_A \left(1 - \frac{f}{2kT}\right)$$

and the difference between the forward and reverse jump frequencies would be:

$$\gamma^+ - \gamma^- = \gamma_A \frac{f}{kT}$$

It will be clear why we got the expression for the difference between $\gamma^+ - \gamma^-$ as we proceed, We have now expressed the forward and reverse jump frequencies in terms of the driving force and the jump frequency in absence of the driving force.

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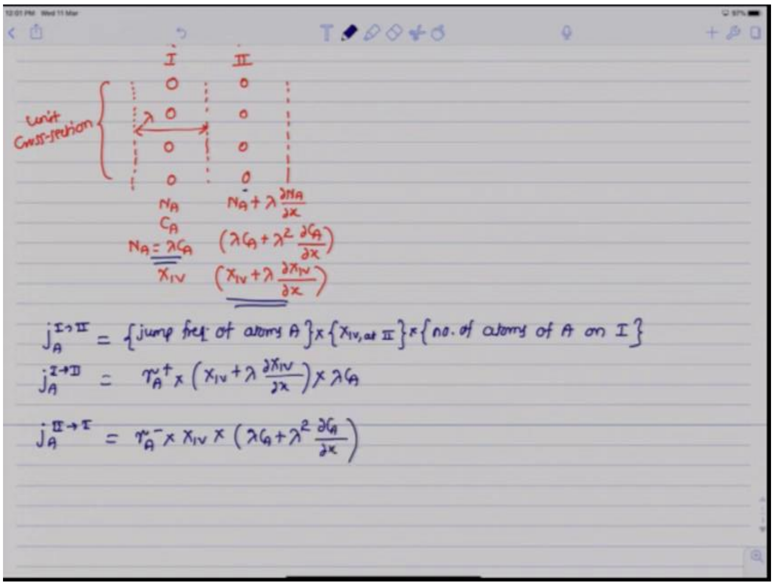


N_A $\quad N_A + \lambda \frac{\partial N_A}{\partial x}$

C_A

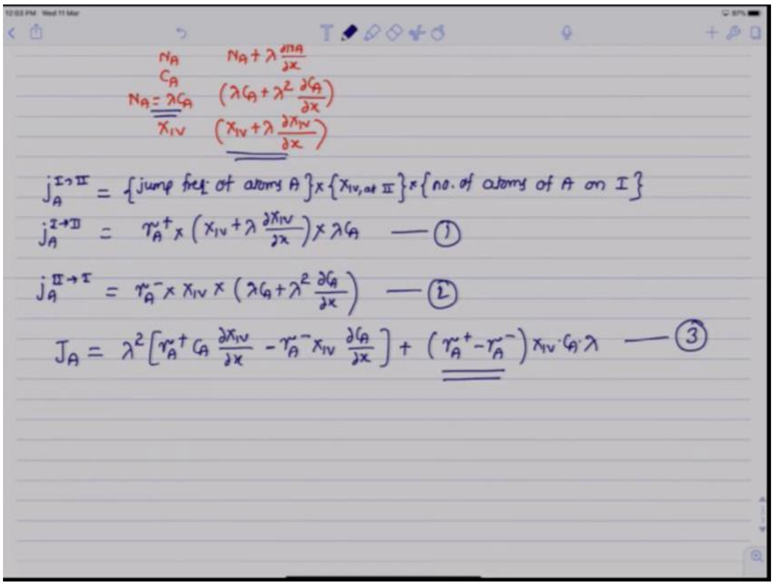
$N_A = \lambda C_A$ $\quad (\lambda C_A + \lambda^2 \frac{\partial C_A}{\partial x})$

X_{IV} $\quad (X_{IV} + \lambda \frac{\partial X_{IV}}{\partial x})$

$j_A^{I \to II} = \{\text{jump freq. of atoms } A\} \times \{X_{IV,\text{at } II}\} \times \{\text{no. of atoms of } A \text{ on } I\}$

$j_A^{I \to II} = \Gamma_A^{+} \times (X_{IV} + \lambda \frac{\partial X_{IV}}{\partial x}) \times \lambda C_A$

$j_A^{II \to I} = \Gamma_A^{-} \times X_{IV} \times (\lambda C_A + \lambda^2 \frac{\partial C_A}{\partial x})$



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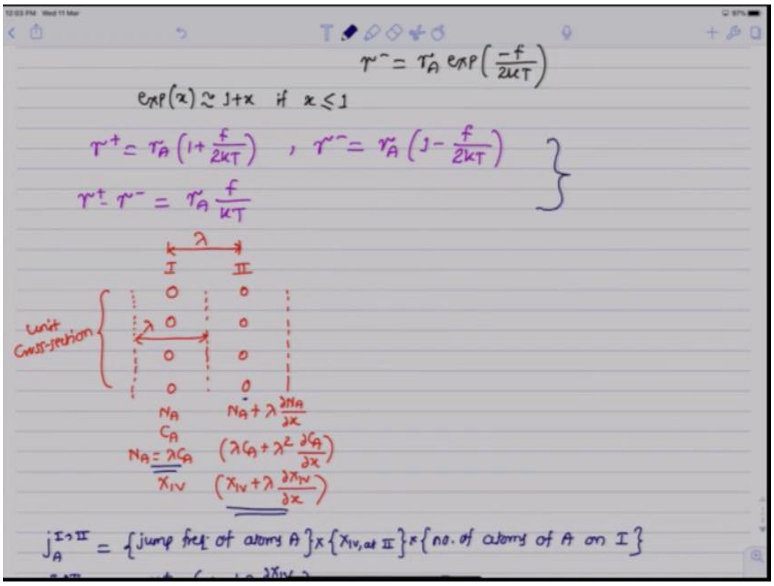
$j_A^{I \to II} = \Gamma_A^{+} \times (X_{IV} + \lambda \frac{\partial X_{IV}}{\partial x}) \times \lambda C_A$ — ①

$j_A^{II \to I} = \Gamma_A^{-} \times X_{IV} \times (\lambda C_A + \lambda^2 \frac{\partial C_A}{\partial x})$ — ②

$J_A = \lambda^2 \left[\Gamma_A^{+} C_A \frac{\partial X_{IV}}{\partial x} - \Gamma_A^{-} X_{IV} \frac{\partial C_A}{\partial x}\right] + \underline{(\Gamma_A^{+} - \Gamma_A^{-})} X_{IV} \cdot C_A \cdot \lambda$ — ③



$\Gamma^{-} = \Gamma_A \exp\left(\frac{-f}{2kT}\right)$

$\exp(x) \simeq 1 + x$ if $x \leq 1$

$\Gamma^{+} = \Gamma_A \left(1 + \frac{f}{2kT}\right)$, $\Gamma^{-} = \Gamma_A \left(1 - \frac{f}{2kT}\right)$

$\Gamma^{+} - \Gamma^{-} = \Gamma_A \frac{f}{kT}$

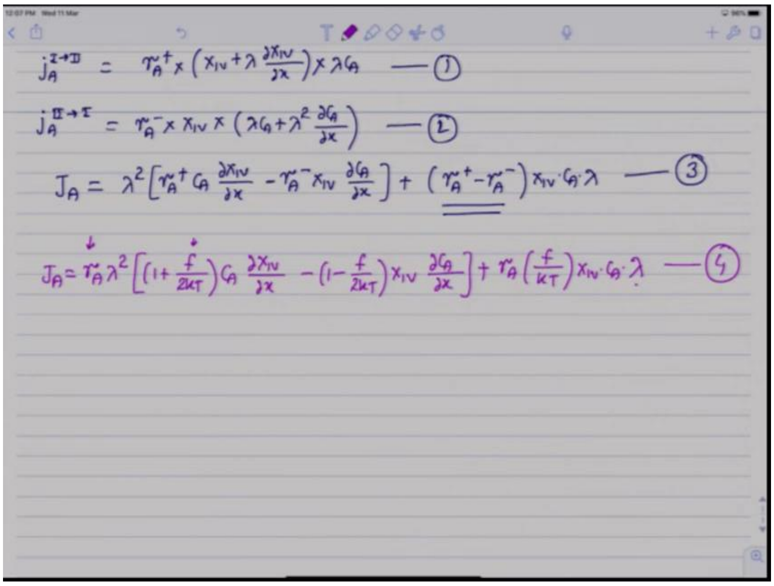
N_A $\quad N_A + \lambda \frac{\partial N_A}{\partial x}$

C_A

$N_A = \lambda C_A$ $\quad (\lambda C_A + \lambda^2 \frac{\partial C_A}{\partial x})$

X_{IV} $\quad (X_{IV} + \lambda \frac{\partial X_{IV}}{\partial x})$

$j_A^{I \to II} = \{\text{jump freq. of atoms } A\} \times \{X_{IV,\text{at } II}\} \times \{\text{no. of atoms of } A \text{ on } I\}$



$$j_A^{I \to II} = \Gamma_A^+ \times \left(X_{1V} + \lambda \frac{\partial X_{1V}}{\partial x} \right) \times \lambda C_A \quad — ①$$

$$j_A^{II \to I} = \Gamma_A^- \times X_{1V} \times \left(\lambda C_A + \lambda^2 \frac{\partial C_A}{\partial x} \right) \quad — ②$$

$$J_A = \lambda^2 \left[\Gamma_A^+ C_A \frac{\partial X_{1V}}{\partial x} - \Gamma_A^- X_{1V} \frac{\partial C_A}{\partial x} \right] + \underline{\underline{\left(\Gamma_A^+ - \Gamma_A^- \right)}} X_{1V} \cdot C_A \cdot \lambda \quad — ③$$

$$J_A = \overset{\downarrow}{\Gamma_A} \lambda^2 \left[\left(1 + \frac{\overset{\downarrow}{f}}{2kT} \right) C_A \frac{\partial X_{1V}}{\partial x} - \left(1 - \frac{f}{2kT} \right) X_{1V} \frac{\partial C_A}{\partial x} \right] + \Gamma_A \left(\frac{f}{kT} \right) X_{1V} \cdot C_A \cdot \lambda \quad — ④$$

Now, let us try to evaluate the diffusion fluxes in terms of these jump frequencies. Let us consider two atomic planes, plane 1 and plane 2 and the distance between the two planes is λ. Each plane can be thought of surrounded by an element of volume λ if we consider unit cross sectional area. Let us say the number of atoms of A on plane 1 are N_A and the concentration of the volume element around plane 1 is C_A. We know:

$$N_A = \lambda C_A$$

And if we consider that there is a concentration gradient from plane 1 to plane 2, then the number of atoms on plane 2 would be:

$$(N_A)_{plane\ 2} = N_A + \lambda \frac{\partial N_A}{\partial x}$$

$\frac{\partial N_A}{\partial x}$ is the gradient of number of atoms with respect to x. In terms of C_A it can be written as:

$$(N_A)_{plane\ 2} = \lambda C_A + \lambda^2 \frac{\partial C_A}{\partial x}$$

Now, we will be treating here the diffusion that occurs by vacancy mechanism. It is important to know the vacancy concentrations on the two planes. If we express the vacancy concentration of plane 1 as X_{1V} and there is also a gradient in vacancy concentration, the vacancy concentration on plane 2 would be:

$$(X_{1V})_{plane\ 2} = X_{1V} + \lambda \frac{\partial X_{1V}}{\partial x}$$

With this, if you want to evaluate the interdiffusion flux across a plane that lies in the middle of plane 1 and plane 2 we need to consider how many atoms are jumping from plane 1 to plane 2 per unit times and how many atoms are jumping from plane 2 to plane 1 per unit time and take the difference of the two. The difference will give me how many atoms of A are crossing this plane at the middle per unit time per unit cross sectional area, that is the diffusion flux across this plane in the middle of plane 1 and plane 2.

If I denote the number of atoms jumping from plane 1 to plane 2 per unit time as $j_A^{I\to II}$, that depends on three tems: the jump frequency of atoms A and this I am considering again including only the migration part times, once the atom has the required energy to jump, the next site also has to be vacant. This will also depend upon the probability that the vacancy exist on the adjacent site, or the vacancy concentration on plane 2 times the number of atoms of A on plane 1. This would be equal to:

$$j_A^{I\to II} = \{jump\ frequency\ of\ atom\ A\} \times \{X_{1V}\ at\ II\} \times \{no. of\ atoms\ of\ A\ on\ I\}$$

$$j_A^{I\to II} = \gamma_A^{+}\left(X_{1V} + \lambda\frac{\partial X_{1V}}{\partial x}\right)\lambda C_A$$

Similarly, $j_A^{II\to I}$ would be given by the jump frequency of atoms A and this will be the reverse jump frequency which is γ_A^{-} times the vacancy concentration on plane 1 times the number of atoms on plane 2. So:

$$j_A^{II\to I} = \gamma_A^{-}X_{1V}\left(\lambda C_A + \lambda^2\frac{\partial C_A}{\partial x}\right)$$

The interdiffusion flux J_A is given by the difference between 1 and 2:

$$J_A = j_A^{I\to II} - j_A^{II\to I} = \lambda^2\left[\gamma_A^{+}C_A\frac{\partial X_{1V}}{\partial x} - \gamma_A^{-}X_{1V}\frac{\partial C_A}{\partial x}\right] + (\gamma_A^{+} - \gamma_A^{-})X_{1V}C_A\lambda \qquad (3)$$

Now, it will be clear why we evaluated the difference between γ_A^{+} and γ_A^{-}, let denote this as equation 3. On substituting for γ_A^{+}, γ_A^{-} and their difference we will get:

$$J_A = \gamma_A\lambda^2\left[\left(1 + \frac{f}{2kT}\right)C_A\frac{\partial X_{1V}}{\partial x} - \left(1 - \frac{f}{2kT}\right)X_{1V}\frac{\partial C_A}{\partial x}\right] + \gamma_A\left(\frac{f}{kT}\right)X_{1V}C_A\lambda \qquad (4)$$

Let us call this equation 4. We have got the equation for diffusion flux of A in terms of the driving force f and the jump frequency γ_A in the absence of driving force and the gradient of vacancy concentration as well as the concentration of A and λ the jump length. This will be true for any type of driving force and the specific expression we will try to derive for driving force which is the chemical potential gradient.

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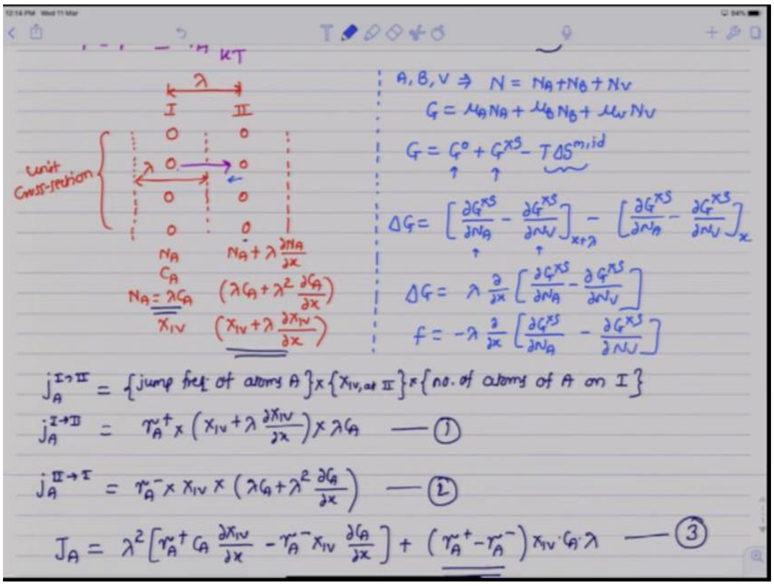

A, B, V ⇒ $N = N_A + N_B + N_V$

$G = \mu_A N_A + \mu_B N_B + \mu_V N_V$

$G = G^0 + G^{xs} - T\Delta S^{m,id}$

$\Delta G = \left[\frac{\partial G^{xs}}{\partial N_A} - \frac{\partial G^{xs}}{\partial N_V}\right]_{x+\lambda} - \left[\frac{\partial G^{xs}}{\partial N_A} - \frac{\partial G^{xs}}{\partial N_V}\right]_{x}$

$\Delta G = \lambda \frac{\partial}{\partial x}\left[\frac{\partial G^{xs}}{\partial N_A} - \frac{\partial G^{xs}}{\partial N_V}\right]$

$f = -\lambda \frac{\partial}{\partial x}\left[\frac{\partial G^{xs}}{\partial N_A} - \frac{\partial G^{xs}}{\partial N_V}\right]$

$j_A^{I \to II} = \{\text{jump freq. of atoms } A\} \times \{X_{1V,\text{at } II}\} \times \{\text{no. of atoms of } A \text{ on } I\}$

$j_A^{I \to II} = \Gamma_A^{+} \times \left(X_{1V} + \lambda \frac{\partial X_{1V}}{\partial x}\right) \times \lambda C_A$ — ①

$j_A^{II \to I} = \Gamma_A^{-} \times X_{1V} \times \left(\lambda C_A + \lambda^2 \frac{\partial C_A}{\partial x}\right)$ — ②

$J_A = \lambda^2\left[\Gamma_A^{+} C_A \frac{\partial X_{1V}}{\partial x} - \Gamma_A^{-} X_{1V} \frac{\partial C_A}{\partial x}\right] + \underline{(\Gamma_A^{+} - \Gamma_A^{-})} X_{1V} \cdot C_A \cdot \lambda$ — ③

Let us try to see what form the driving force *f* takes when there is a chemical potential gradient. For this, let us go back to this diagram of plane 1 and plane 2. When an atom A jumps from plane 1 to plane 2, the number of atoms of A on plane 2 have increased by 1 whereas the number of vacancies on plane 2 have decreased by 1 and the reverse has occurred in plane 1 that is the number of atoms of A on plane 1 has decreased 1 and the number of vacancies on plane 1 has increased by 1. We know the increase in Gibbs free energy when an atom is added to a homogenous alloy is the chemical potential of the atom.

We can similarly define the chemical potential of a vacancy. It is the change in Gibbs free energy when an atom is removed from the interior and placed on to the surface in which process one extra lattice site has been created. If there is a chemical potential gradient, suppose let us say chemical potential of A is decreasing from plane 1 to plane 2, obviously there will be a net decrease in Gibbs free energy and this will act as a driving force for diffusion from plane 1 to plane 2.

If we consider a binary alloy of A and B and since we are considering the diffusion by vacancy mechanism, let us also consider vacancy as one more species which is diffusing. This is because by creation or destruction of vacancies, there is a change in number of lattice sites. So we need to consider vacancy as one more species. We can write the total number of species on any plane of lattice sites as:

$$N = N_A + N_B + N_V$$

and the Gibbs free energy of this plane can be expressed as:

$$G = \mu_A N_A + \mu_B N_B + \mu_V N_V$$

Now, G can also be expressed as for any homogenous alloy as:

$$G = G^o + G^{XS} - T\Delta S^{m,id}$$

In this expression, G^o is the Gibbs free energy before mixing. Last part represents the change in Gibbs free energy if the mixing was ideal or this part is related to the change in configurational entropy because of mixing. G^{XS} is the excess Gibbs free energy which is basically the change in Gibbs free energy because of all the reasons other than the ideal configurational entropy change. Now, when atom is jumping from 1 to 2, the driving force associated with this jump will be related to the change in Gibbs free energy through the non-ideal part only. As the atom of A jumps from 1 to 2, we can write change in Gibbs free energy as:

$$\Delta G = \left[\frac{\partial G^{XS}}{\partial N_A} - \frac{\partial G^{XS}}{\partial N_V}\right]_{x+\lambda} - \left[\frac{\partial G^{XS}}{\partial N_A} - \frac{\partial G^{XS}}{\partial N_V}\right]_x$$

Now, the term $\frac{\partial G^{XS}}{\partial N_A}$ denotes the change in excess Gibbs free energy because of addition of one atom of A, whereas the term $\frac{\partial G^{XS}}{\partial N_V}$ denotes the change in Gibbs free energy because of addition of one vacancy. Since the vacancy is jumping away from the plane at $x + \lambda$ that is from plane 2 here, there is a negative sign attached to it. This total expression we can simplify as:

$$\Delta G = \lambda \frac{\partial}{\partial x}\left[\frac{\partial G^{XS}}{\partial N_A} - \frac{\partial G^{XS}}{\partial N_V}\right]$$

Since f is simply $-\Delta G$, we get the expression for f as:

$$f = -\lambda \frac{\partial}{\partial x}\left[\frac{\partial G^{XS}}{\partial N_A} - \frac{\partial G^{XS}}{\partial N_V}\right] \quad (5)$$

It will be a long expression but we can approximately neglect any term in λ which is greater than λ^2. Now let us substitute for f from this equation denoted as equation 5, into equation 4 given below:

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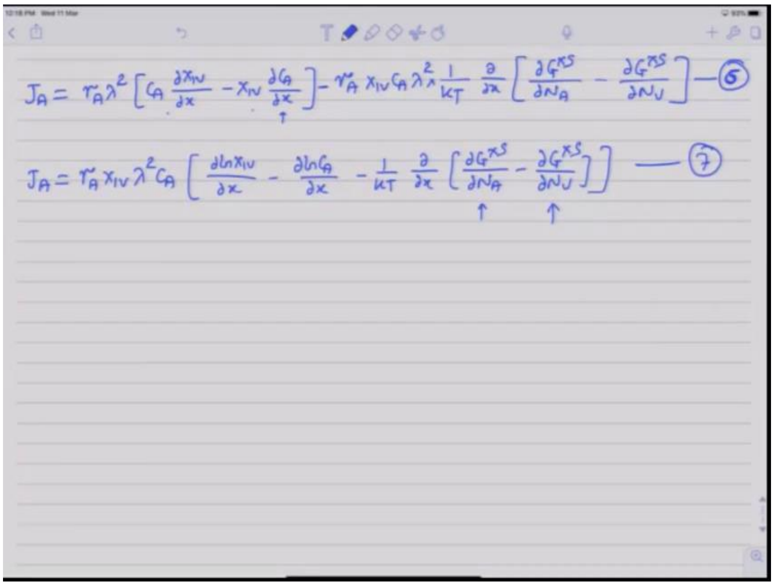

$$J_A = \gamma_A \lambda^2 \left[C_A \frac{\partial X_{1V}}{\partial x} - X_{1V} \underset{\uparrow}{\frac{\partial C_A}{\partial x}} \right] - \gamma_A X_{1V} C_A \lambda^2 \frac{1}{kT} \frac{\partial}{\partial x} \left[\frac{\partial G^{xs}}{\partial N_A} - \frac{\partial G^{xs}}{\partial N_V} \right] \text{ — ⑥}$$

$$J_A = \gamma_A X_{1V} \lambda^2 C_A \left[\frac{\partial \ln X_{1V}}{\partial x} - \frac{\partial \ln C_A}{\partial x} - \frac{1}{kT} \frac{\partial}{\partial x} \left[\underset{\uparrow}{\frac{\partial G^{xs}}{\partial N_A}} - \underset{\uparrow}{\frac{\partial G^{xs}}{\partial N_V}} \right] \right] \text{ — ⑦}$$

$$J_A = \gamma_A \lambda^2 \left[\left(1 + \frac{f}{2kT}\right) C_A \frac{\partial X_{1V}}{\partial x} - \left(1 - \frac{f}{2kT}\right) X_{1V} \frac{\partial C_A}{\partial x} \right] + \gamma_A \left(\frac{f}{kT}\right) X_{1V} C_A \lambda \quad (4)$$

Since the term f involves the term lambda and there is already a term λ^2 outside the bracket, $\lambda^2.f$ will involve a term in λ^3 which we will neglect and this expression can be rewritten as:

$$J_A = \gamma_A \lambda^2 \left[C_A \frac{\partial X_{1V}}{\partial x} - X_{1V} \frac{\partial C_A}{\partial x} \right] - \gamma_A X_{1V} C_A \lambda^2 \frac{1}{kT} \frac{\partial}{\partial x} \left[\frac{\partial G^{XS}}{\partial N_A} - \frac{\partial G^{XS}}{\partial N_V} \right] \quad (6)$$

Let us call this equation 6. Now, we can write this $\frac{\partial X_{1V}}{\partial x}$ term as $X_{1V} \frac{\partial \ln X_{1V}}{\partial x}$ and similarly this term second term also we can modify. So we can write the flux equation as:

$$J_A = \gamma_A X_{1V} C_A \lambda^2 \left[\frac{\partial \ln X_{1V}}{\partial x} - \frac{\partial \ln C_A}{\partial x} - \frac{1}{kT} \frac{\partial}{\partial x} \left[\frac{\partial G^{XS}}{\partial N_A} - \frac{\partial G^{XS}}{\partial N_V} \right] \right] \quad (7)$$

Let us denote this as equation 7. Now let us try to find out the nature of $\frac{\partial G^{XS}}{\partial N_A}$ and $\frac{\partial G^{XS}}{\partial N_V}$.

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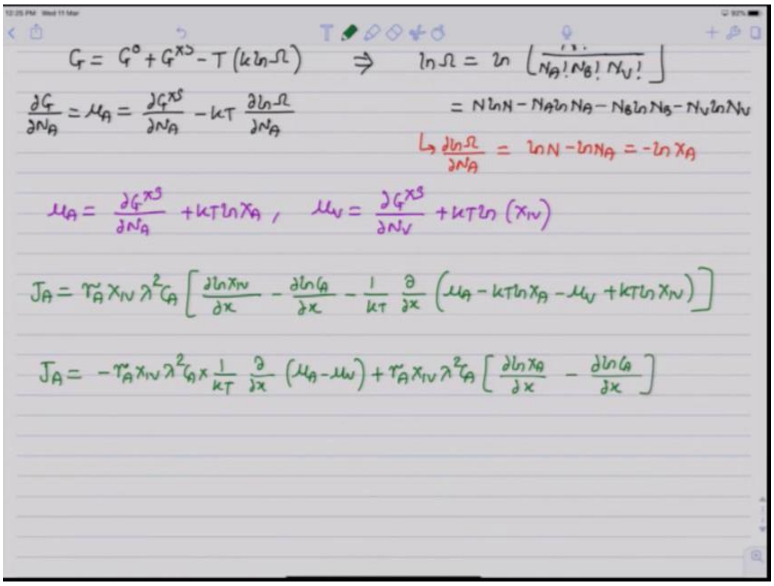


$$G = G^o + G^{xs} - T(k\ln\Omega) \Rightarrow \ln\Omega = \ln\left[\frac{N!}{N_A!\,N_B!\,N_V!}\right]$$

$$= N\ln N - N_A\ln N_A - N_B\ln N_B - N_V\ln N_V$$

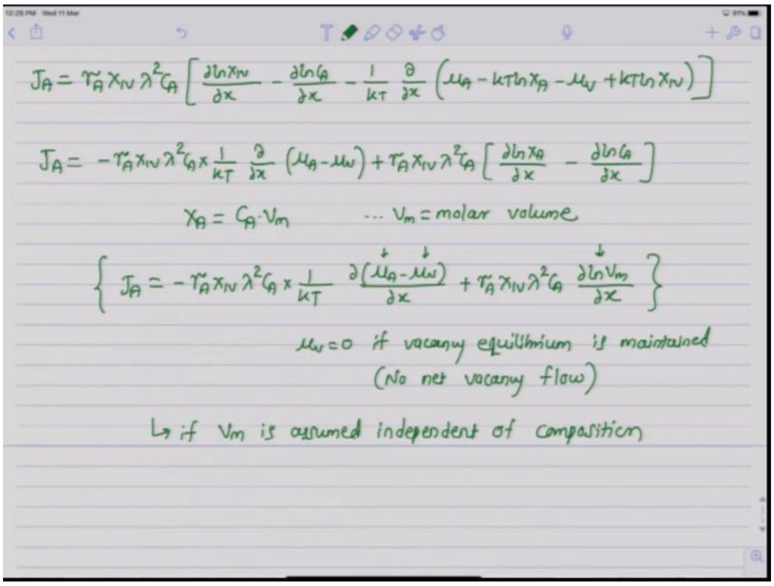
$$\frac{\partial G}{\partial N_A} = \mu_A = \frac{\partial G^{xs}}{\partial N_A} - kT\frac{\partial \ln\Omega}{\partial N_A}$$

$$\hookrightarrow \frac{\partial \ln\Omega}{\partial N_A} = \ln N - \ln N_A = -\ln X_A$$

$$\mu_A = \frac{\partial G^{xs}}{\partial N_A} + kT\ln X_A, \quad \mu_V = \frac{\partial G^{xs}}{\partial N_V} + kT\ln(X_V)$$

$$J_A = \tilde{\Gamma}_A X_V \lambda^2 C_A\left[\frac{\partial \ln X_V}{\partial x} - \frac{\partial \ln C_A}{\partial x} - \frac{1}{kT}\frac{\partial}{\partial x}\left(\mu_A - kT\ln X_A - \mu_V + kT\ln X_V\right)\right]$$

$$J_A = -\tilde{\Gamma}_A X_V \lambda^2 C_A \times \frac{1}{kT}\frac{\partial}{\partial x}(\mu_A - \mu_V) + \tilde{\Gamma}_A X_V \lambda^2 C_A\left[\frac{\partial \ln X_A}{\partial x} - \frac{\partial \ln C_A}{\partial x}\right]$$



$$J_A = \tilde{\Gamma}_A X_V \lambda^2 C_A\left[\frac{\partial \ln X_V}{\partial x} - \frac{\partial \ln C_A}{\partial x} - \frac{1}{kT}\frac{\partial}{\partial x}\left(\mu_A - kT\ln X_A - \mu_V + kT\ln X_V\right)\right]$$

$$J_A = -\tilde{\Gamma}_A X_V \lambda^2 C_A \times \frac{1}{kT}\frac{\partial}{\partial x}(\mu_A - \mu_V) + \tilde{\Gamma}_A X_V \lambda^2 C_A\left[\frac{\partial \ln X_A}{\partial x} - \frac{\partial \ln C_A}{\partial x}\right]$$

$$X_A = C_A \cdot V_m \quad \ldots V_m = \text{molar volume}$$

$$\left\{ J_A = -\tilde{\Gamma}_A X_V \lambda^2 C_A \times \frac{1}{kT}\,\frac{\partial(\overset{\downarrow}{\mu_A} - \overset{\downarrow}{\mu_V})}{\partial x} + \tilde{\Gamma}_A X_V \lambda^2 C_A\,\frac{\partial \ln \overset{\downarrow}{V_m}}{\partial x} \right\}$$

$\mu_V = 0$ if vacancy equilibrium is maintained

(No net vacancy flow)

↳ if V_m is assumed independent of composition

From this equation, we can write:

$$G = G^o + G^{XS} - T(k\ln\Omega)$$

We know for the mixing of A, B and vacancies, we can write:

$$\ln\Omega = \ln\frac{N!}{N_A!\,N_B!\,N_V!}$$

Where N is the total number of atoms. This we have derived when we went over the statistical model of mixing during our thermodynamic refresher.

It can be written simply as:

$$\ln \Omega = \ln \frac{N!}{N_A!\,N_B!\,N_V!} = N \ln N - N_A \ln N_A - N_B \ln N_B - N_V \ln N_V$$

Now, if we take the derivative of G with respect to N_A, which we know by definition is the chemical potential of A, we get:

$$\mu_A = \frac{\partial G}{\partial N_A} = \frac{\partial G^{XS}}{\partial N_A} - kT \frac{\partial \ln \Omega}{\partial N_A}$$

We have to calculate the derivative of $\ln \Omega$ with respect to N_A.

$$\frac{\partial \ln \Omega}{\partial N_A} = \frac{\partial}{\partial N_A}(N \ln N - N_A \ln N_A - N_B \ln N_B - N_V \ln N_V)$$

$N_B\ and\ N_V$ are independent of N_A, hence the derivative of the $N_B\ and\ N_V$ with respect to N_A will be zero. So, we can write this as:

$$\frac{\partial \ln \Omega}{\partial N_A} = \ln N - \ln N_A = -\ln X_A$$

Since we know $\frac{N_A}{N}$ is the mole fraction of A or the atom fraction of A which is denoted by X_A we get the expression for μ_A as:

$$\mu_A = \frac{\partial G^{XS}}{\partial N_A} + kT \ln X_A$$

With the similar logic we can write:

$$\mu_V = \frac{\partial G^{XS}}{\partial N_V} + kT \ln X_{1V}$$

X_{1V} is the site faction of vacancies. And from here if you substitute for $\frac{\partial G^{XS}}{\partial N_A}$ and $\frac{\partial G^{XS}}{\partial N_V}$ into equation 7 , we will get:

$$J_A = \gamma_A X_{1V} C_A \lambda^2 \left[\frac{\partial \ln X_{1V}}{\partial x} - \frac{\partial \ln C_A}{\partial x} - \frac{1}{kT}\frac{\partial}{\partial x}[\mu_A - kT \ln X_A - \mu_V + kT \ln X_{1V}]\right]$$

On simplifying we get the expression for J_A as:

$$J_A = -\gamma_A X_{1V} C_A \lambda^2 \frac{1}{kT}\frac{\partial}{\partial x}(\mu_A - \mu_V) + \gamma_A X_{1V} C_A \lambda^2 \left[\frac{\partial \ln X_A}{\partial x} - \frac{\partial \ln C_A}{\partial x}\right]$$

Now, we know the mole fraction X_A is given as:

$$X_A = C_A V_m \quad \text{where,}$$

$$V_m = molar\ volume$$

So:

$$\frac{\partial \ln X_A}{\partial x} - \frac{\partial \ln C_A}{\partial x} = \frac{\partial \ln V_m}{\partial x}$$

Substituting this relation in the flux equation we get the final expression:

$$J_A = -\gamma_A X_{1V} C_A \lambda^2 \frac{1}{kT} \frac{\partial}{\partial x} (\mu_A - \mu_V) + \gamma_A X_{1V} C_A \lambda^2 \frac{\partial \ln V_m}{\partial x}$$

This is the general expression for interdiffusion flux under chemical potential gradient. You can see there are 3 contributions here, one is form the chemical potential gradient of A, the chemical potential gradient of vacancy and also from the change in molar volume with x. The molar volume will change with x if the molar volume is a function of composition because the composition is changing with x.

The first two terms here are basically the Fickian flux, the flux because of the chemical potential gradient and the 3rd term here is the drift term associated with the change in molar volume. Obviously, if the molar volume will change with composition there will be a volume flow associated with the diffusion process and it will give rise to a drift and there will be a contribution from drift to the diffusion flux of A.

Now, if we assume that the vacancy equilibrium is quickly attained at every plane, in other words if there is no excess vacancy flow, then the chemical potential of vacancy is zero. Then the only contribution will be from the chemical potential gradient of A and the molar volume change. In addition, if V_m is assumed to be independent of composition, then the only contribution will be from chemical potential gradient of A.

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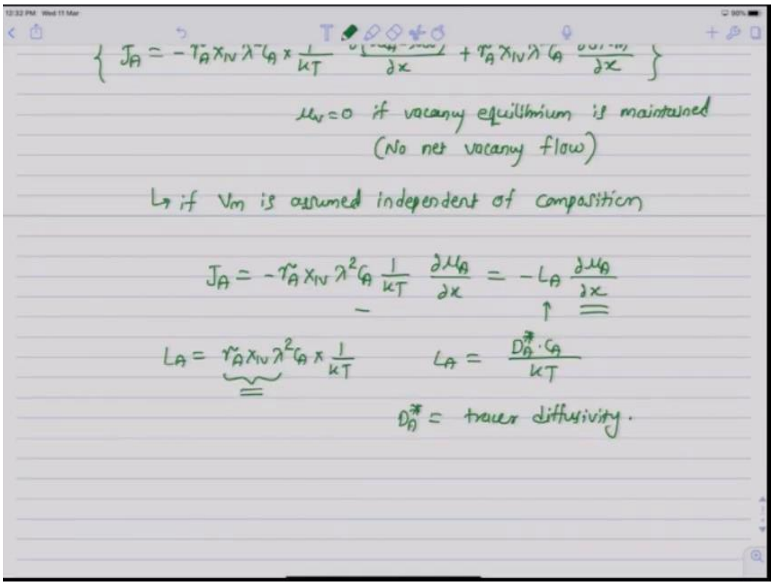

$\{ J_A = -\gamma_A X_{1V} \lambda C_A \times \frac{1}{kT} \frac{}{\partial x} + \gamma_A X_{1V} \lambda C_A \frac{}{\partial x} \}$

$\mu_V = 0$ if vacancy equilibrium is maintained
(No net vacancy flow)

↳ if V_m is assumed independent of composition

$$J_A = -\gamma_A X_{1V} \lambda^2 C_A \frac{1}{kT} \frac{\partial \mu_A}{\partial x} = -\underset{\uparrow}{L_A} \underline{\underline{\frac{\partial \mu_A}{\partial x}}}$$

$$L_A = \underbrace{\gamma_A X_{1V}}_{=} \lambda^2 C_A \times \frac{1}{kT} \qquad L_A = \frac{D_A^* \cdot C_A}{kT}$$

D_A^* = tracer diffusivity.

We can write J_A equal to:

$$J_A = -\gamma_A X_{1V} C_A \lambda^2 \frac{1}{kT} \frac{\partial \mu_A}{\partial x}$$

we can write this as:

$$J_A = -\gamma_A X_{1V} C_A \lambda^2 \frac{1}{kT} \frac{\partial \mu_A}{\partial x} = -L_A \frac{\partial \mu_A}{\partial x}$$

So, we have derived the equation for diffusion flux of A in terms of the chemical potential gradient of A and it is related to the chemical potential gradient of A through this term L_A. This is similar phenomenological type of equation that we used for flux as a function of concentration gradient which were related through the interdiffusivity term. More fundamentally, the diffusion is driven by chemical potential gradient. Now, this term L_A which is called kinetic coefficient can be obtained as if we equate these two sides:

$$L_A = \gamma_A X_{1V} C_A \lambda^2 \frac{1}{kT}$$

And if we look at this $\gamma_A X_{1V}$, this is nothing but the γ if we add the geometric factor, corresponding to the specific type of lattice. For cubic this geometric factor is usually $\frac{1}{6}$. So:

$$\gamma_A X_{1V} \lambda^2 = \frac{1}{6} \gamma \lambda^2$$

We know this is the Einstein's diffusivity or which we call as tracer diffusivity.

$$D_A^* = \gamma_A X_{1V} \lambda^2 = \frac{1}{6} \gamma \lambda^2$$

We can write this as:

$$L_A = \frac{D_A^* C_A}{kT}$$

The tracer diffusivity we know is essentially under negligible concentration gradient. When there is no concentration gradient or negligible concentration gradient, we are talking about the self or impurity diffusivity which is denoted by D_A^* and is also referred to as tracer diffusivity. So, we can express the kinetic coefficient in terms of the tracer diffusivity of particular atom. Now let us look into more general case when there is a net vacancy flow. It is bound to happen if:

$$D_A^* \neq D_B^*$$

D_B^* is the tracer diffusivity of B. In that case, we have to consider $\frac{\partial \mu_V}{\partial x}$ term also.

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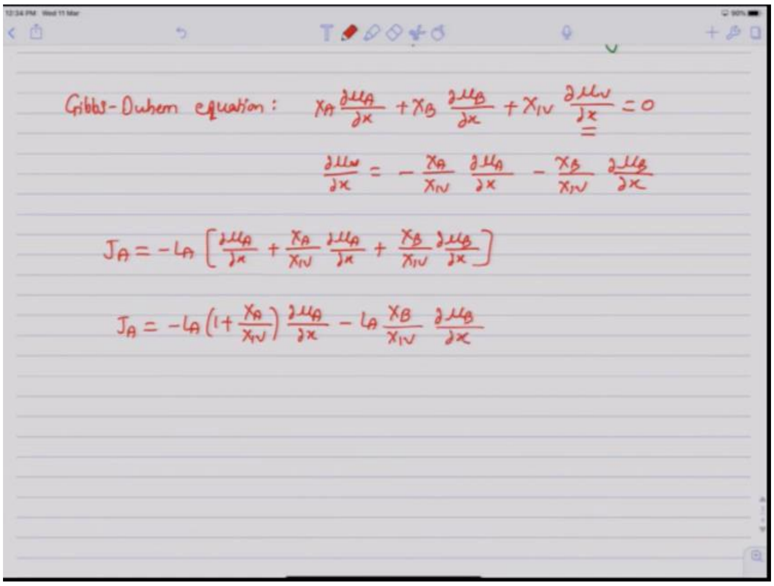
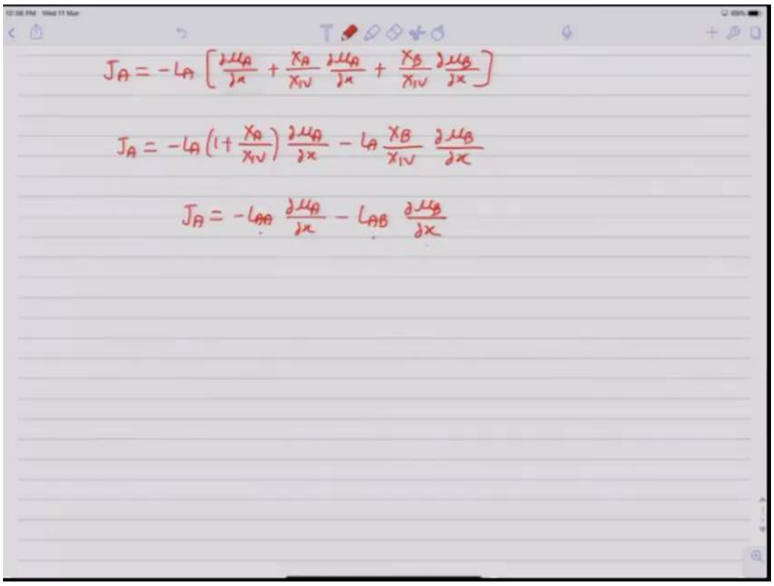


Gibbs-Duhem equation: $X_A \frac{\partial \mu_A}{\partial x} + X_B \frac{\partial \mu_B}{\partial x} + X_{1V} \underline{\underline{\frac{\partial \mu_V}{\partial x}}} = 0$

$$\frac{\partial \mu_V}{\partial x} = -\frac{X_A}{X_{1V}} \frac{\partial \mu_A}{\partial x} - \frac{X_B}{X_{1V}} \frac{\partial \mu_B}{\partial x}$$

$$J_A = -L_A \left[\frac{\partial \mu_A}{\partial x} + \frac{X_A}{X_{1V}} \frac{\partial \mu_A}{\partial x} + \frac{X_B}{X_{1V}} \frac{\partial \mu_B}{\partial x} \right]$$

$$J_A = -L_A \left(1 + \frac{X_A}{X_{1V}}\right) \frac{\partial \mu_A}{\partial x} - L_A \frac{X_B}{X_{1V}} \frac{\partial \mu_B}{\partial x}$$



$$J_A = -L_A \left[\frac{\partial \mu_A}{\partial x} + \frac{X_A}{X_{1V}} \frac{\partial \mu_A}{\partial x} + \frac{X_B}{X_{1V}} \frac{\partial \mu_B}{\partial x} \right]$$

$$J_A = -L_A \left(1 + \frac{X_A}{X_{1V}}\right) \frac{\partial \mu_A}{\partial x} - L_A \frac{X_B}{X_{1V}} \frac{\partial \mu_B}{\partial x}$$

$$J_A = -L_{AA} \frac{\partial \mu_A}{\partial x} - L_{AB} \frac{\partial \mu_B}{\partial x}$$

Now, we know by Gibbs Duhem equation:

$$X_A \frac{\partial \mu_A}{\partial x} + X_B \frac{\partial \mu_B}{\partial x} + X_{1V} \frac{\partial \mu_V}{\partial x} = 0$$

We can express the chemical potential gradient of vacancy in terms of the chemical potential gradients of A and B. That would be:

$$\frac{\partial \mu_V}{\partial x} = -\frac{X_A}{X_{1V}} \frac{\partial \mu_A}{\partial x} - \frac{X_B}{X_{1V}} \frac{\partial \mu_B}{\partial x}$$

If we substitute for $\frac{\partial \mu_V}{\partial x}$ from here into this expression for J_A and neglecting the dependence of molar volume on composition, we will get the equation of the sort:

$$J_A = -L_A \left[\frac{\partial \mu_A}{\partial x} + \frac{X_A}{X_{1V}} \frac{\partial \mu_A}{\partial x} + \frac{X_B}{X_{1V}} \frac{\partial \mu_B}{\partial x} \right]$$

J_A can be expressed as a function of chemical potential gradients of both the components A and B. We can in general express this as:

$$J_A = -L_A \left(1 + \frac{X_A}{X_{1V}}\right) \frac{\partial \mu_A}{\partial x} - L_A \frac{X_B}{X_{1V}} \frac{\partial \mu_B}{\partial x}$$

$$J_A = -L_{AA} \frac{\partial \mu_A}{\partial x} - L_{AB} \frac{\partial \mu_B}{\partial x}$$

The diffusion flux of A will be guided by chemical potential gradient of both A as well as B. The relation with chemical potential gradient of A will be expressed through this main kinetic coefficient L_{AA}. And the contribution from the chemical potential gradient of B will be expressed through this cross kinetic coefficient L_{AB} and this will be true whenever the vacancy diffusion is involved or whenever we are considering substitutional diffusion by vacancy mechanism because to more or less extent, there will always be a net vacancy flow as long as $D_A^* \neq D_B^*$. Only the relative contributions will keep changing depending upon the difference between D_A^* and D_B^*.

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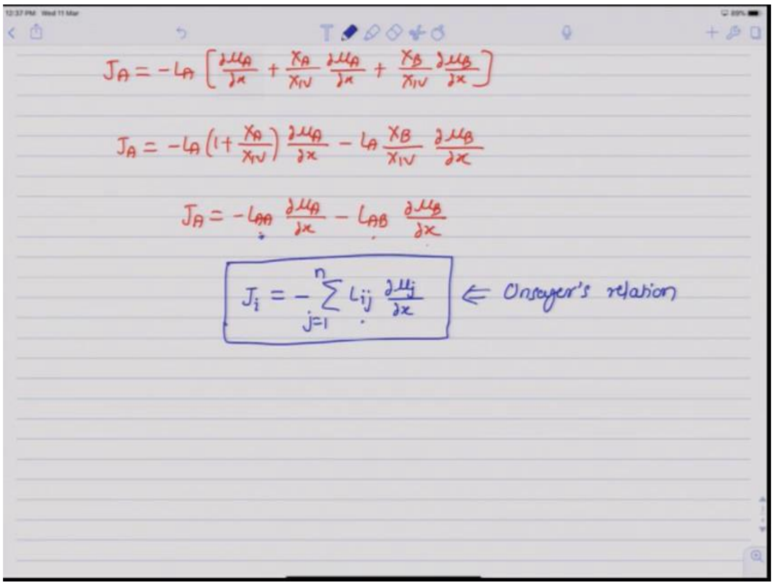

$$J_A = -L_A\left[\frac{\partial \mu_A}{\partial x} + \frac{X_A}{X_V}\frac{\partial \mu_A}{\partial x} + \frac{X_B}{X_V}\frac{\partial \mu_B}{\partial x}\right]$$

$$J_A = -L_A\left(1+\frac{X_A}{X_V}\right)\frac{\partial \mu_A}{\partial x} - L_A\frac{X_B}{X_V}\frac{\partial \mu_B}{\partial x}$$

$$J_A = -L_{AA}\frac{\partial \mu_A}{\partial x} - L_{AB}\frac{\partial \mu_B}{\partial x}$$

$$\boxed{J_i = -\sum_{j=1}^{n} L_{ij}\frac{\partial \mu_j}{\partial x}} \Leftarrow \text{Onsager's relation}$$

Now, we did this for binary but this is in general true for an N component system in general. We can express the diffusion flux of the component i as:

$$J_i = -\sum_{j=1}^{n} L_{ij}\frac{\partial \mu_j}{\partial x}$$

So, we have obtained Onsager's relation for diffusion under chemical potential gradient. It is important to note here that as long as the vacancy mechanism is involved in order to define diffusion flux, we need both the main kinetic coefficient, L_{ii} similar to L_{AA} here as well as the cross kinetic coefficient L_{ij} when i is not equal to j, similar to L_{AB} here.

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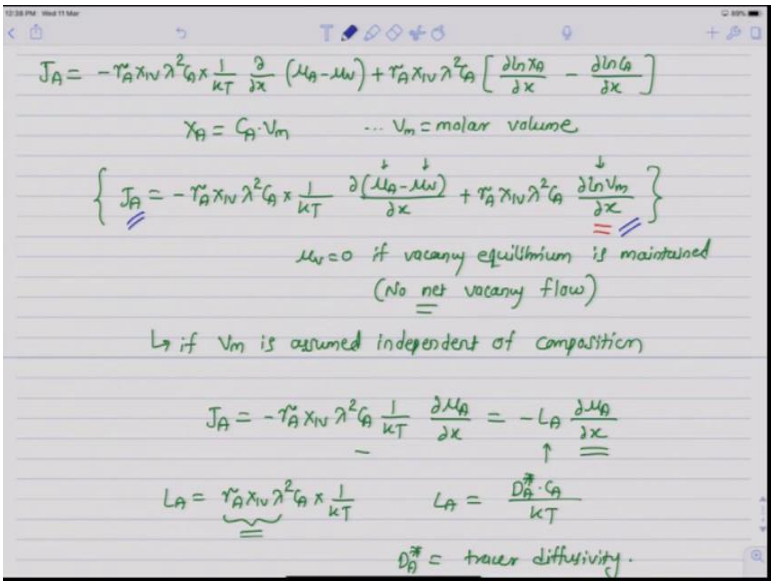

$$J_A = -\tilde{r}_A x_{1V} \lambda^2 C_A \times \frac{1}{kT} \frac{\partial}{\partial x}(\mu_A - \mu_V) + \tilde{r}_A x_{1V} \lambda^2 C_A \left[\frac{\partial \ln x_A}{\partial x} - \frac{\partial \ln C_A}{\partial x} \right]$$

$$x_A = C_A \cdot V_m \qquad \ldots V_m = \text{molar volume}$$

$$\left\{ \underset{/\!/}{J_A} = -\tilde{r}_A x_{1V} \lambda^2 C_A \times \frac{1}{kT} \frac{\partial(\overset{\downarrow}{\mu_A} - \overset{\downarrow}{\mu_V})}{\partial x} + \tilde{r}_A x_{1V} \lambda^2 C_A \underset{= /\!/}{\overset{\downarrow}{\frac{\partial \ln V_m}{\partial x}}} \right\}$$

$\mu_V = 0$ if vacancy equilibrium is maintained
(No $\underline{\underline{\text{net}}}$ vacancy flow)

↳ if V_m is assumed independent of composition

$$J_A = -\underset{\sim}{\tilde{r}_A} x_{1V} \lambda^2 C_A \frac{1}{kT} \frac{\partial \mu_A}{\partial x} = -\underset{\uparrow}{L_A} \underline{\underline{\frac{\partial \mu_A}{\partial x}}}$$

$$L_A = \underline{\underline{\underbrace{\tilde{r}_A x_{1V}}}} \lambda^2 C_A \times \frac{1}{kT} \qquad L_A = \frac{D_A^* \cdot C_A}{kT}$$

D_A^* = tracer diffusivity.

One more point that I would like you to note here is that, the dependence of molar volume on composition will also give rise to a contribution to the flux of A and it comes through the term $\frac{\partial \ln V_m}{\partial x}$. Only when we assume that the molar volume is independent of composition, we can ignore the drift associated with the diffusion and that is why we define the volume fixed frame of reference.

All right, so we derived the relation that expresses the diffusion flux of a component in terms of its own chemical potential gradient and when there is a net vacancy flow, that is, when there is a difference in the tracer diffusivities of different diffusing species. In that case the contribution will also come from the chemical potential gradients of other components and in general, the flux can be expressed by the Onsager type of relation. Thank you.