Diffusion in Multicomponent Solids
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Lecture - 40
Atomic Mobility, Diffusivity and Diffusion Under External Driving Force

Welcome to the 40th lecture in this open course on diffusion in multicomponent solids. In this lecture, I shall derive the relation between atomic mobility and diffusivity. In this process we will be introduced to thermodynamic factor. In the later part of this lecture, I will talk about diffusion under external driving force and derive the Nernst-Einstein equation. I shall also illustrate the application of this equation to the process of electromigration, that is, the process of diffusion under electric potential gradient.

In last class, we discussed why chemical potential gradient is the fundamental driving force for diffusion. We also derived the equation for diffusion flux in terms of chemical potential gradient of a component and the chemical potential gradient of vacancies. So, flux of a component is related to the chemical potential gradient of different components through the kinetic coefficients L_{ij}.

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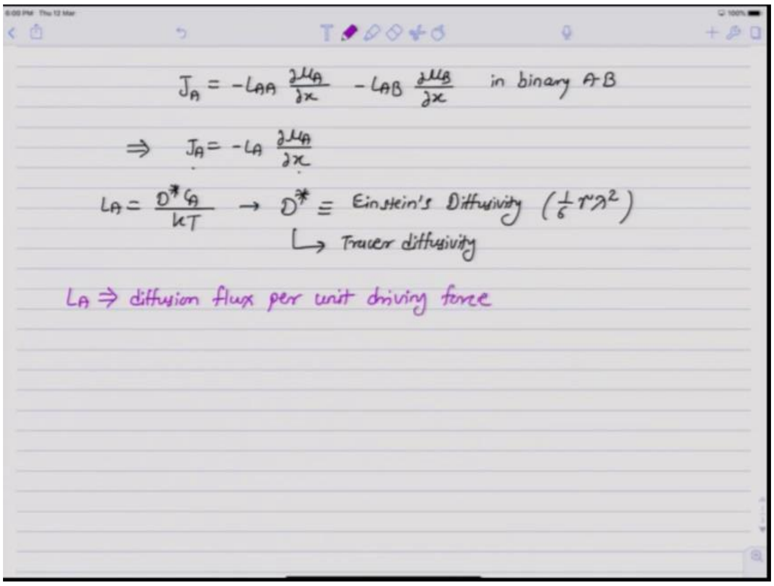

$J_A = -L_{AA}\frac{\partial \mu_A}{\partial x} - L_{AB}\frac{\partial \mu_B}{\partial x}$ in binary A-B

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

$L_A = \frac{D^* C_A}{kT} \rightarrow D^* \equiv$ Einstein's Diffusivity $\left(\frac{1}{6}\Gamma\lambda^2\right)$

$\hookrightarrow$ Tracer diffusivity

$L_A \Rightarrow$ diffusion flux per unit driving force

For example, in binary, we can write:

$$J_A = -L_{AA}\frac{\partial \mu_A}{\partial x} - L_{AB}\frac{\partial \mu_B}{\partial x} \quad in\ \ binary\ A-B\ solution$$

If the chemical potential gradient of vacancies is assumed to be zero or in other terms if there is no net vacancy flow then this cross kinetic coefficient term L_{AB} is absent and we can write:

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

L_A here is the kinetic coefficient that relates the flux of component A with the chemical potential gradient of A. We have seen that L_A can be given as:

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

Here D^* is the Einstein's diffusivity which was given by:

$$D^* = \left(\frac{1}{6}\gamma\lambda^2\right) = Tracer\ diffusivity$$

this is also commonly known as tracer diffusivity and D^* essentially characterises self-diffusion or impurity diffusion under no concentration ingredient or a very minute concentration gradient respectively. Now, what is the physical significance of the kinetic coefficient L_A. It can be understood if we again take a look at the equation for flux and if we rearrange the term L_A is nothing but:

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

and $-\frac{\partial \mu_A}{\partial x}$here is the driving force. The physical significance of L_A is that it is nothing but the diffusion flux of a component per unit driving force.

Many times we come across the term, atomic mobility, what is this atomic mobility? And what is its relation with the kinetic coefficient? Let us try to look into it now.

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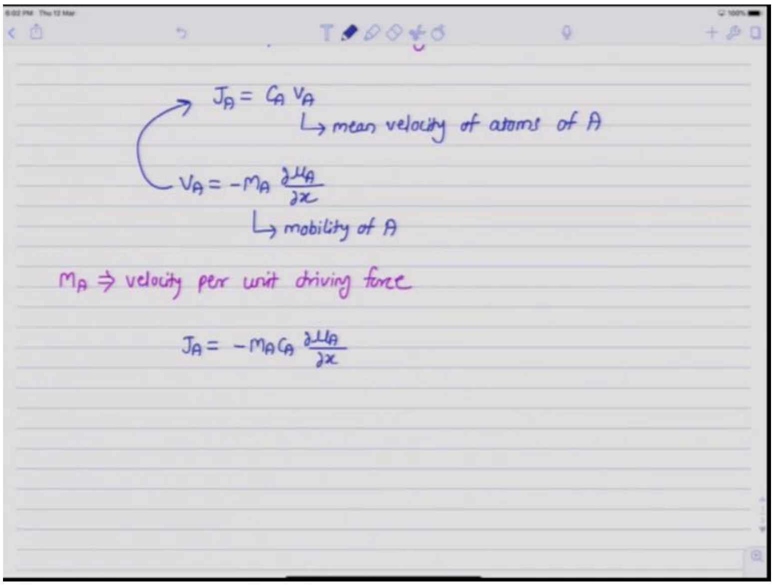


$J_A = C_A V_A$

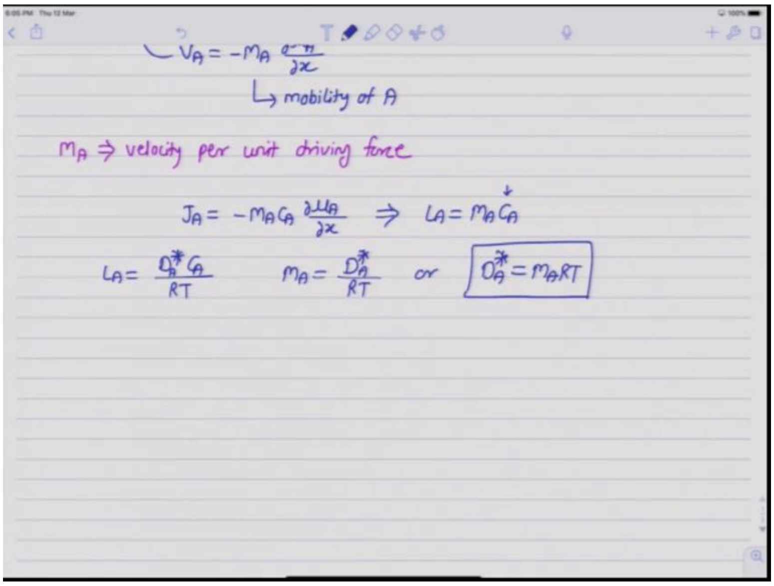
↳ mean velocity of atoms of A

$V_A = -M_A \frac{\partial \mu_A}{\partial x}$

↳ mobility of A

$M_A \Rightarrow$ velocity per unit driving force

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



$V_A = -M_A \frac{\partial \mu_A}{\partial x}$

↳ mobility of A

$M_A \Rightarrow$ velocity per unit driving force

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

$L_A = \frac{D_A^* C_A}{RT}$ $\quad M_A = \frac{D_A^*}{RT}$ or $\boxed{D_A^* = M_A RT}$

A few classes back if you remember we have seen the flux can be given as:

$$J_A = C_A V_A$$

where C_A is the concentration of A and V_A represents the mean velocity of atoms of A. Now, this velocity can be considered to be proportional to the driving force and it is related to the driving force through the term called mobility. We can write:

$$V_A = -M_A \frac{\partial \mu_A}{\partial x}$$

$-\frac{\partial \mu_A}{\partial x}$ is the driving force here and M_A is the constant of the proportionality which is called as atomic mobility of A. Similar to the kinetic coefficient, if we rearrange, we know the physical significance of the term mobility. Just like kinetic coefficient was the diffusion flux per unit driving force, mobility is the velocity per unit driving force. M_A is nothing but the velocity per unit driving force. If we substitute back for V_A in the equation for J_A, we get:

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

On comparing with a previous equation for flux we get:

$$L_A = M_A C_A$$

So, the atomic mobility or kinetic coefficients represent essentially the same quantities. They are related through the concentration C_A. But the mobility is more general term and mobilities are also used to store the databases for interdiffusivities and diffusivities. Let us try to establish the relation between the mobility and the diffusivity terms that we use. Since we know:

$$L_A = \frac{D^* C_A}{RT}$$

If we consider a mole, then we can replace K with R and we can write:

$$M_A = \frac{D^*}{RT}$$

The tracer diffusivity of A is related to the atomic mobility of A through the simple relation:

$$D^* = M_A RT$$

Again, this relation is applicable if we are considering a binary system and we are neglecting the net vacancy flow because if the net vacancy flow exists then we also have to consider the cross kinetic coefficient terms which means we also need to consider the cross mobility terms. Since we are using a single mobility to represent a single component here this is valid when there is no net vacancy flow or the chemical potential of vacancies is zero. D_A^* is the diffusion coefficient in negligible concentration gradient.

What happens when there is concentration gradient present? In that case, we talk about interdiffusion or intrinsic diffusion or commonly it is also referred to as chemical diffusion which is characterised by chemical diffusion coefficients. Let us see the relation of mobilities and the chemical diffusion coefficient terms.

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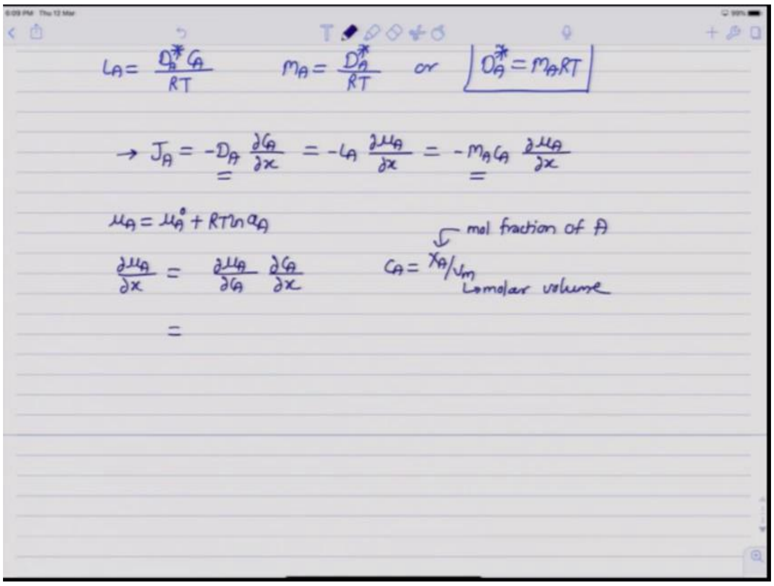


$$L_A = \frac{D_A^* C_A}{RT} \qquad M_A = \frac{D_A^*}{RT} \quad \text{or} \quad \boxed{D_A^* = M_A RT}$$

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

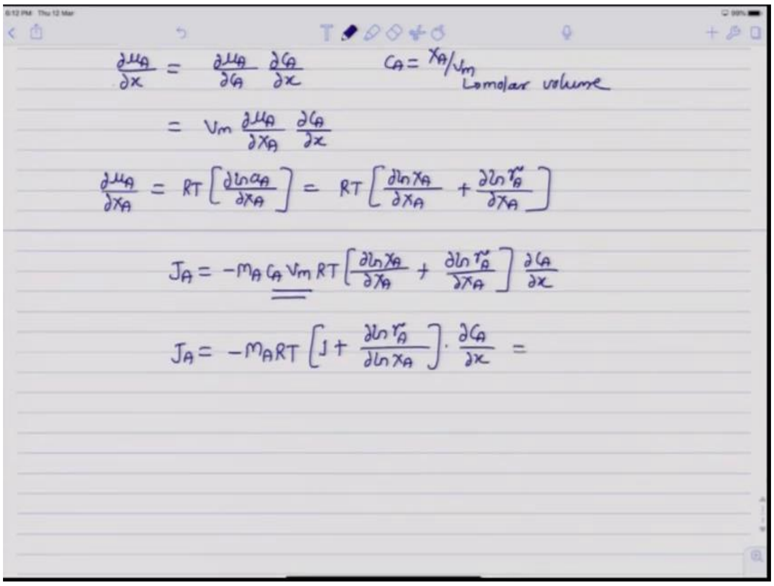
$$\mu_A = \mu_A^o + RT\ln a_A$$

mol fraction of A

$$\frac{\partial \mu_A}{\partial x} = \frac{\partial \mu_A}{\partial C_A} \frac{\partial C_A}{\partial x} \qquad C_A = X_A / V_m$$

molar volume

$$=$$



$$\frac{\partial \mu_A}{\partial x} = \frac{\partial \mu_A}{\partial C_A} \frac{\partial C_A}{\partial x} \qquad C_A = X_A / V_m$$

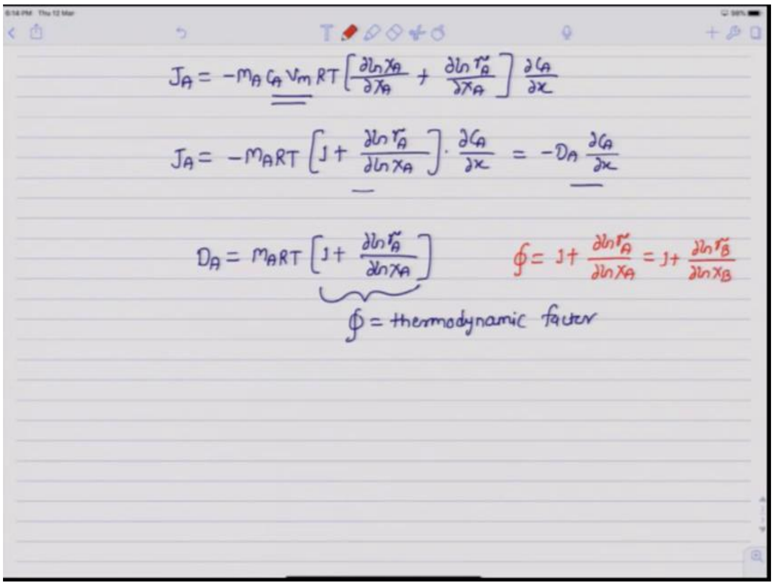
molar volume

$$= V_m \frac{\partial \mu_A}{\partial X_A} \frac{\partial C_A}{\partial x}$$

$$\frac{\partial \mu_A}{\partial X_A} = RT\left[\frac{\partial \ln a_A}{\partial X_A}\right] = RT\left[\frac{\partial \ln X_A}{\partial X_A} + \frac{\partial \ln \gamma_A}{\partial X_A}\right]$$

$$J_A = -M_A \underline{\underline{C_A V_m}} RT\left[\frac{\partial \ln X_A}{\partial X_A} + \frac{\partial \ln \gamma_A}{\partial X_A}\right] \frac{\partial C_A}{\partial x}$$

$$J_A = -M_A RT\left[1 + \frac{\partial \ln \gamma_A}{\partial \ln X_A}\right] \cdot \frac{\partial C_A}{\partial x} =$$



$$J_A = -M_A \underline{\underline{C_A V_m}} RT\left[\frac{\partial \ln X_A}{\partial X_A} + \frac{\partial \ln \gamma_A}{\partial X_A}\right] \frac{\partial C_A}{\partial x}$$

$$J_A = -M_A RT\left[1 + \frac{\partial \ln \gamma_A}{\underline{\partial \ln X_A}}\right] \cdot \frac{\partial C_A}{\partial x} = -D_A \frac{\partial C_A}{\underline{\partial x}}$$

$$D_A = M_A RT \underbrace{\left[1 + \frac{\partial \ln \gamma_A}{\partial \ln X_A}\right]}_{\phi = \text{thermodynamic factor}} \qquad \phi = 1 + \frac{\partial \ln \gamma_A}{\partial \ln X_A} = 1 + \frac{\partial \ln \gamma_B}{\partial \ln X_B}$$

In presence of concentration gradient, we can write the equation for flux as:

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

which in terms of chemical potential gradient is written as:

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

or in terms of the atomic mobility, it is written as:

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

Now, I need to relate the interdiffusivity term D_A with the mobility M_A, which means I need to express $\frac{\partial \mu_A}{\partial x}$ term in terms of $\frac{\partial C_A}{\partial x}$. One point to be noted when I am writing this equation here is I am considering the diffusion flux with respect to a frame of reference which is fixed to a lattice plane. This is also referred to as Kirkendall frame of reference and we will talk about this frame of reference in more detail later. But at this point, remember that I am talking about the frame of reference which is fixed to a lattice plane. Diffusion is then referred to as intrinsic diffusion and this diffusivity D_A is the intrinsic diffusivity of A. We know μ_A can be written as:

$$\mu_A = \mu_A^o + RT \ln a_A$$

where μ_A^o is the chemical potential of A in its standard state and typically, the standard state is taken as pure A and μ_A^o refers to the molar Gibbs free energy of pure A in its stable state at the given temperature which should be constant. a_A is the thermodynamic activity of A at the given composition. Now:

$$\frac{\partial \mu_A}{\partial x} = \frac{\partial \mu_A}{\partial C_A} \frac{\partial C_A}{\partial x}$$

and we know:

$$C_A = \frac{X_A}{V_m}$$

where V_m is the molar volume and X_A is the mole fraction of A in the solution. If we assume molar volume to be constant, this can be written as:

$$\frac{\partial \mu_A}{\partial x} = V_m \frac{\partial \mu_A}{\partial X_A} \frac{\partial C_A}{\partial x}$$

If you differentiate μ_A with respect to X_A here, we get:

$$\frac{\partial \mu_A}{\partial X_A} = RT\left[\frac{\partial \ln a_A}{\partial X_A}\right]$$

and a_A is nothing but:

$$a_A = \gamma_A X_A$$

where γ_A is the thermodynamic activity coefficient of A and X_A is the mole fraction of A. This can be written as:

$$\frac{\partial \mu_A}{\partial X_A} = RT\left[\frac{\partial \ln a_A}{\partial X_A}\right] = RT\left[\frac{\partial \ln X_A}{\partial X_A} + \frac{\partial \ln \gamma_A}{\partial X_A}\right]$$

and if we substitute back for $\frac{\partial \mu_A}{\partial x}$ in the equation for J_A we get:

$$J_A = -M_A C_A V_m RT\left[\frac{\partial \ln X_A}{\partial X_A} + \frac{\partial \ln \gamma_A}{\partial X_A}\right]\frac{\partial C_A}{\partial x}$$

Now:

$$C_A V_m = X_A$$

and using this along with taking X_A inside the derivatives we can write:

$$J_A = -M_A RT\left[\frac{\partial \ln X_A}{\partial \ln X_A} + \frac{\partial \ln \gamma_A}{\partial \ln X_A}\right]\frac{\partial C_A}{\partial x} = -M_A RT\left[1 + \frac{\partial \ln \gamma_A}{\partial \ln X_A}\right]\frac{\partial C_A}{\partial x}$$

This is nothing but simply:

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

We compare the previous two equations to get the expression for intrinsic diffusivity D_A in terms of the atomic mobility M_A and they are related as:

$$D_A = M_A RT\left[1 + \frac{\partial \ln \gamma_A}{\partial \ln X_A}\right]$$

The intrinsic diffusivity is related to atomic mobility through this factor $\left[1 + \frac{\partial \ln \gamma_A}{\partial \ln X_A}\right]$. When the solution is ideal, $\gamma_A = 1$ and then D_A is simply:

$$D_A = M_A RT$$

but in case of non-ideal solution $\frac{\partial \ln \gamma_A}{\partial \ln X_A}$ will have value other than 1 and we need to take into account this factor. This factor is commonly referred to as thermodynamic factor denoted as Φ. So Φ is equal to:

$$\Phi = 1 + \frac{\partial \ln \gamma_A}{\partial \ln X_A}$$

Based on Gibbs Duhem equation it is also easy to show in a binary system that:

$$\Phi = 1 + \frac{\partial \ln \gamma_A}{\partial \ln X_A} = 1 + \frac{\partial \ln \gamma_B}{\partial \ln X_B}$$

and D_A can be written as:

$$D_A = M_A RT\Phi$$

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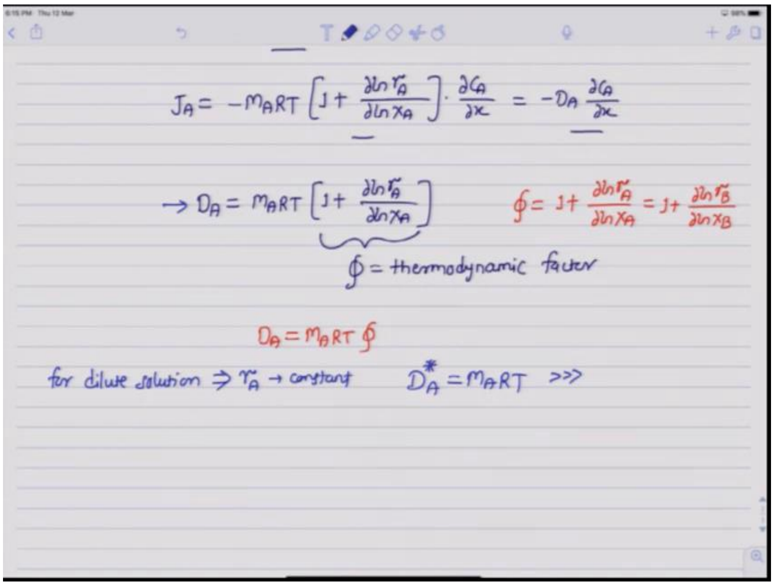

$$J_A = -M_A RT\left[1 + \frac{\partial \ln \gamma_A}{\partial \ln X_A}\right] \cdot \frac{\partial C_A}{\partial x} = -D_A \frac{\partial C_A}{\partial x}$$

$$\rightarrow D_A = M_A RT \underbrace{\left[1 + \frac{\partial \ln \gamma_A}{\partial \ln X_A}\right]}_{\phi = \text{thermodynamic factor}}$$

$$\phi = 1 + \frac{\partial \ln \gamma_A}{\partial \ln X_A} = 1 + \frac{\partial \ln \gamma_B}{\partial \ln X_B}$$

$$D_A = M_A RT \phi$$

for dilute solution $\Rightarrow \gamma_A \rightarrow$ constant $\quad D_A^* = M_A RT \quad >>>$

Now, if we are considering a dilute solution we know Henry's law will be followed and:

For dilute solution: $\gamma_A \rightarrow constant$

and when I am considering dilute solution D_A is nothing but D_A^*:

$$D_A^* = M_A RT$$

The tracer diffusion coefficient is simply equal to $M_A RT$, this is what we have already derived. Again, this equation we have derived for a binary system. If we consider multicomponent system and if we consider net vacancy flow which is also called as vacancy wind effect then we have to take into account the cross mobility term and the relations will be more complicated. Let us now restrict our discussion only for binary and in absence of net vacancy flow.

So, these relations give us the inter relations between the chemical diffusivity terms and more fundamental atomic mobility terms and these relations are important because they help us to relate the information that we obtain experimentally which is most of the time the tracer diffusivity or chemical diffusion coefficient to the more fundamental coefficients which are the atomic mobilities or the kinetic coefficients.

We have considered the diffusion under chemical potential gradients. We will now look into what happens if there is an external driving force present and the diffusion is occurring in presence of an external driving force. What type of external driving forces can be present? It can be an electric field which is nothing but the gradient of electric potential or it can be a stress field which is nothing but the gradient of strain energy. It can be the gradient in temperature and on. Let us try to look into the diffusion when external driving force is present.

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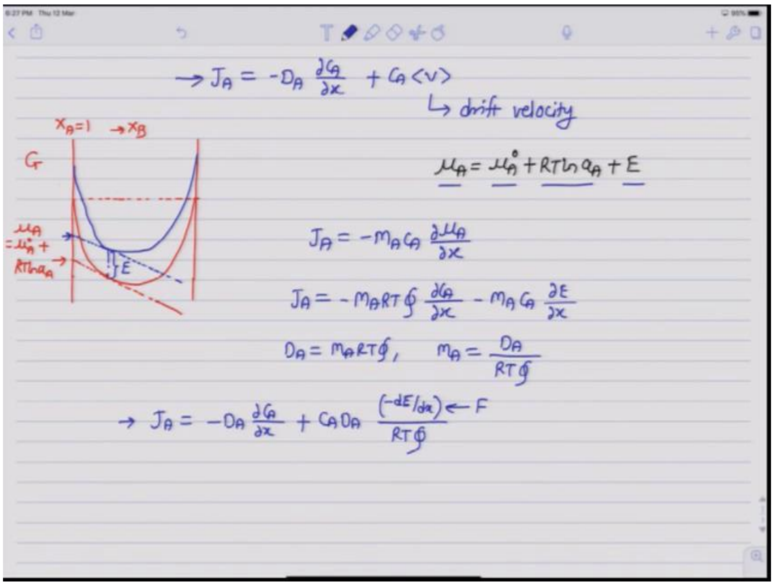


$$\rightarrow J_A = -D_A \frac{\partial C_A}{\partial x} + C_A \langle v \rangle$$

↳ drift velocity

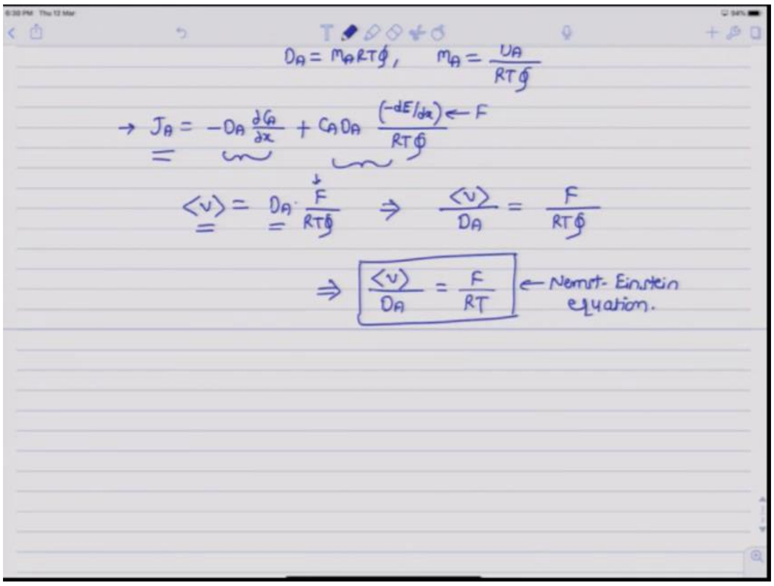
$$\underline{\mu_A} = \underline{\mu_A^\circ} + \underline{RT\ln a_A} + \underline{E}$$

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

$$J_A = -m_A RT\phi \frac{\partial C_A}{\partial x} - m_A C_A \frac{\partial E}{\partial x}$$

$$D_A = m_A RT\phi, \quad m_A = \frac{D_A}{RT\phi}$$

$$\rightarrow J_A = -D_A \frac{\partial C_A}{\partial x} + C_A D_A \frac{(-dE/dx) \leftarrow F}{RT\phi}$$



$$D_A = M_A RT\phi, \quad M_A = \frac{D_A}{RT\phi}$$

$$\rightarrow \underline{\underline{J_A}} = -\underbrace{D_A \frac{\partial C_A}{\partial x}} + \underbrace{C_A D_A} \frac{(-dE/dx) \leftarrow F}{RT\phi}$$

$$\underline{\underline{\langle v \rangle}} = \underline{\underline{D_A}} \cdot \frac{\overset{\downarrow}{F}}{RT\phi} \Rightarrow \frac{\langle v \rangle}{D_A} = \frac{F}{RT\phi}$$

$$\Rightarrow \boxed{\frac{\langle v \rangle}{D_A} = \frac{F}{RT}} \leftarrow \text{Nernst- Einstein equation.}$$

Earlier we have seen there are two contributions to any diffusion flux term. If we write J_A as"

$$J_A = -D_A \frac{\partial C_A}{\partial x} + C_A \langle v \rangle$$

the first contribution is from the Fickian term which is nothing but $-D_A \frac{\partial C_A}{\partial x}$ and the second contribution is from the drift which is written as $C_A \langle v \rangle$. C_A is the concentration of A and this v refers to the drift velocity. Now, let us consider the strain energy driving force which may be present. For example, consider the diffusion when strain energy exist in the alloy. We have to increase the Gibbs free energy of the alloy by appropriate amount equal to the strain energy and we can write:

$$\mu_A = \mu_A^o + RT \ln a_A + E$$

This can be easily seen if we draw the Gibbs free energy of a solution versus composition curve. Let us say on X axis we have X_B, left Y axis is $X_A = 1$, Y axis we are denoting Gibbs free energy of solution and the curve may have a nature something like this.

In the absence of strain energy if we want to find out the chemical potential we draw tangent to the curve at the desired composition and the intercept on $X_A = 1$ axis yields the chemical potential of A which is nothing but $\mu_A^o + RT \ln a_A$. Now, in presence of the strain energy, this curve will be shifted up and at the same composition the difference would be E. If we determine the chemical potential now, it has increased by amount E and we can write:

$$\mu_A = \mu_A^o + RT \ln a_A + E$$

If we write the equation for J_A now, it will be:

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

On following the previous steps it will be easy to show that:

$$J_A = -M_A RT\Phi \frac{\partial C_A}{\partial x} - M_A C_A \frac{\partial E}{\partial x}$$

If we substitute for M_A using:

$$D_A = M_A RT\Phi \quad , \quad M_A = \frac{D_A}{RT\Phi}$$

we can write:

$$J_A = -D_A \frac{\partial C_A}{\partial x} + C_A D_A \frac{(-dE/dx)}{RT\Phi}$$

This $(-dE/dx)$ is the gradient in strain energy is nothing but the driving force which we denote as F:

$$F = -dE/dx$$

Now, if we compare this equation with the equation that we wrote earlier, we can see the drift velocity is nothing but:

$$\langle v \rangle = D_A \frac{F}{RT\Phi}$$

In general we can write:

$$\frac{\langle v \rangle}{D_A} = \frac{F}{RT\Phi}$$

If we consider a dilute solution or an ideal solution, this takes the form:

$$\frac{\langle v \rangle}{D_A} = \frac{F}{RT}$$

This is the well-known Nernst - Einstein equation. What is the significance of this Nernst - Einstein equation? If you go back to the equation for flux, for defining the Fickian term, of course we need the diffusivity D_A but to get the drift term also we need the diffusivity term D_A. In other words, or in terms of Nernst – Einstein equation, the drift velocity is also governed by the diffusivity D_A or the mobility M_A in addition to the nature of the driving force F. It is obvious because both the Fickian flux as well as the drift will be fundamentally driven by the atomic jumps and atomic mobility would essentially occur in both of them. Again, I would like to point out when we derive this equation, I am considering the binary system and I am neglecting the net vacancy flow that is μ_V the chemical potential of vacancy is assumed to be zero. Now, let us look into the diffusion that occurs under a specific type of driving force which is industrially very important and it is the diffusion under electric potential gradient. It is also referred to as electromigration.

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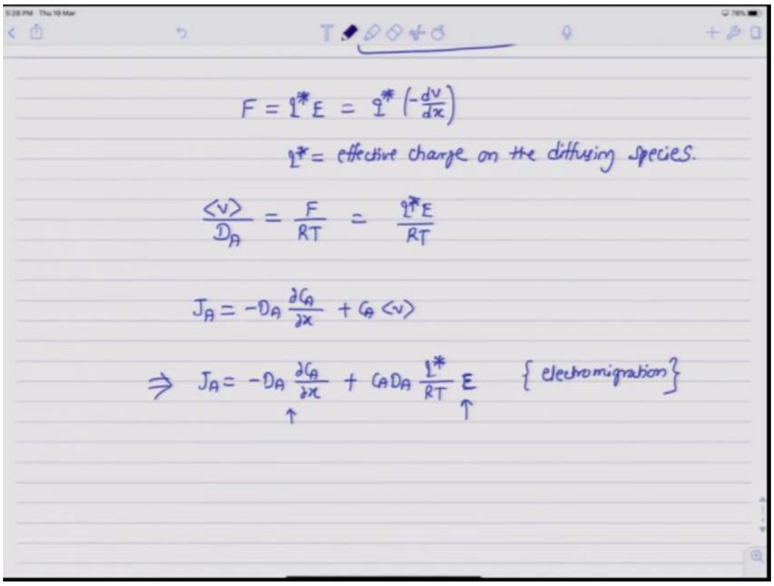

$$F = q^* E = q^* \left(-\frac{dV}{dx}\right)$$

q^* = effective charge on the diffusing species.

$$\frac{\langle v \rangle}{D_A} = \frac{F}{RT} = \frac{q^* E}{RT}$$

$$J_A = -D_A \frac{\partial C_A}{\partial x} + C_A \langle v \rangle$$

$$\Rightarrow J_A = -D_A \underset{\uparrow}{\frac{\partial C_A}{\partial x}} + C_A D_A \frac{q^*}{RT} \underset{\uparrow}{E} \quad \{\text{electromigration}\}$$

When I talk about electric field as the external driving force, F is essentially:

$$F = q^* E$$

The electric field is nothing but the gradient of electric potential $\left(-\frac{dV}{dx}\right)$ and:

$$\mathrm{q}^* = \text{effective charge on the diffusing species}$$

For ionic compounds, this effective charge will be essentially a charge on the ions but in metals it is not actually the charge on the metal ions but it has to be determined experimentally. If we want to find out the drift velocity in presence of electric field or drift velocity for electromigration, we can use the Nernst – Einstein equation which tells me:

$$\frac{\langle v \rangle}{D_A} = \frac{F}{RT} = \frac{q^* E}{RT}$$

Once I derive the equation for J_A which is:

$$J_A = -D_A \frac{\partial C_A}{\partial x} + C_A \langle v \rangle$$

Or

$$J_A = -D_A \frac{\partial C_A}{\partial x} + C_A D_A \frac{q^* E}{RT}$$

This tells me that the diffusion flux of A is governed not only by the concentration gradient but also by the electric field E and it also tells me that in absence of any concentration gradient the species can experience large diffusion flux if the electric field is high. Now, this is very important. In most of the semiconductor chips, pure copper or pure aluminium is used as interconnect material. With ever decreasing feature sizes this interconnecting parts of copper or aluminium are having very small dimensions in nano meters, at which the electric field is very high and there will be the flux of atoms even in pure copper or pure aluminium.

Now this is not desired, because if the atoms diffuse from one end to the other of the conductor, there will be accumulation of vacancies on one end which will lead to formation of voids and subsequently to the failure of the connector. On the other hand, the atoms are accumulating on the other side of the conductor and if may lead to undesired growth and it may lead to short circuiting. So, it is very important to control this electromigration in semiconductor chips. And there it is essential to work with flux equations like this.

So, we have seen the equation for diffusion flux when both the concentration gradient and electric potential gradient exist. Now, let us try to look at what happens physically? Why there is a diffusion flux even when there is no concentration gradient or when both concentration gradient and electric potential gradients are present? Why there is a drift term associated with the electric potential gradient.

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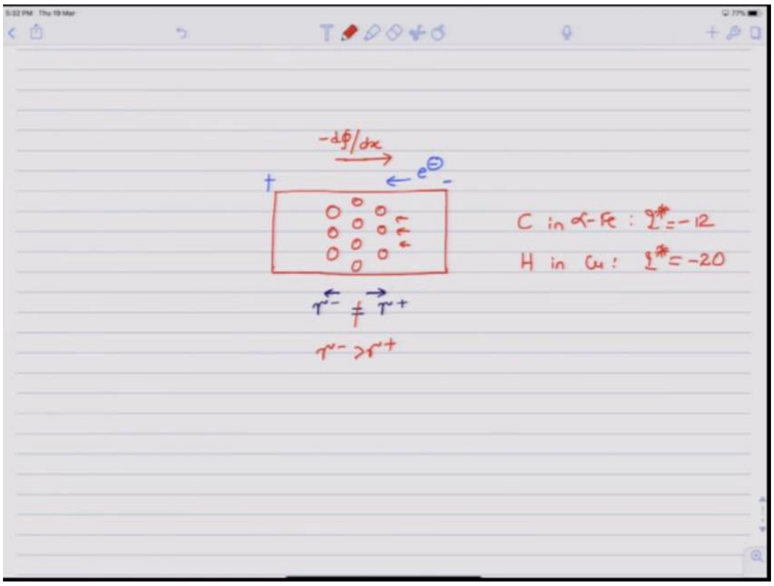

Let us try to look at it. Consider this sample in which I have shown different atomic planes here. In the absence of any electric potential gradient or any external driving force, these atoms are continuously vibrating and their jump frequency in forward or reverse direction are same. $\gamma^+$and γ^- are same. Now, consider if there is an electric potential gradient existing from left to right as shown here and the electrons are flowing from right to left.

Now, as the electrons are flowing, they are colliding with the atoms and in this process, the electrons are transferring their momentum to the atoms. Because of this the jumps of atoms are biased in the direction of flow of electrons, so there will be more jumps per unit time from right to left as compared to from left to right even when there is no concentration gradient. Because of this γ^- that is the jump frequency towards left is not same as γ^+, that is the jump frequency towards the right.

$$\gamma^- \neq \gamma^+$$

And infact:

$$\gamma^- > \gamma^+$$

Of course, there will be also an effect because of the interaction between the charges because electrons have negative charge and the ions will have positive or negative charge, but the effect because of momentum transfer from the electron is much more significant especially in metals.

In ionic compounds, the momentum transfer is less and the effect because of the charge interaction is more, but in metals the effect because of the momentum transfer from electron is more. And because of this, the effective charge q^* is not exactly same as the valance of the atom. In fact, it comes out to be much higher than the valance.

For example, effective charge for carbon diffusion in alpha iron is minus 12, whereas for hydrogen in copper it is -20 :

$$C\ in\ \alpha - Fe: \quad q^* = -12$$

$$H\ in\ Cu\ : \quad q^* = -20$$

You can see this effective charge is much higher compared to the valance and that is because of this bias in the jumps because of the momentum transfer from the electrons. So. this is the nature of electromigration and why there is a drift as we understand physically. Now, there are various other driving forces also, we will not talk about all of those. In the next class, I will talk about non ideality as a driving force. For this class we will stop here. Thank you.