Diffusion in Multicomponent Solids
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Lecture 11 - Driving force for Diffusion, Chemical potentials and Concentrations

Hello friends and welcome to lecture 11 of this open course on Diffusion in Multicomponent Solids. In this lecture, we will make a transition from thermodynamics to diffusion. We will understand that chemical potential gradient is a driving force for diffusion but concentration gradients are practically easier to work with. Various units used for concentrations are also discussed in this lecture.

Now that we have gone through little bit of thermodynamics we will move onto studying diffusion in which we will keep referring back to many of these thermodynamic concepts. In thermodynamics we saw how to define the state of equilibrium which is the state at which the Gibbs free energy is minimized at constant temperature and pressure. Now there can be many equilibrium states but the state that has the lowest Gibbs free energy or has the global minimum in the Gibbs free energy is the stable state.

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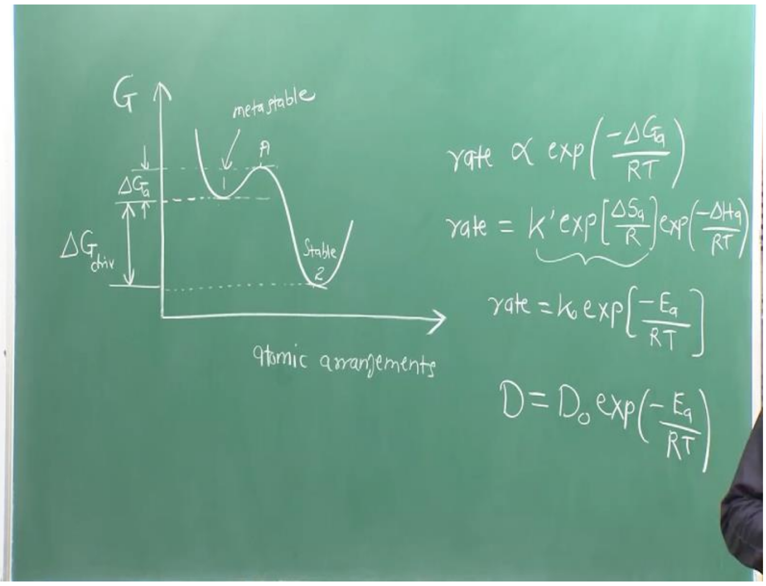
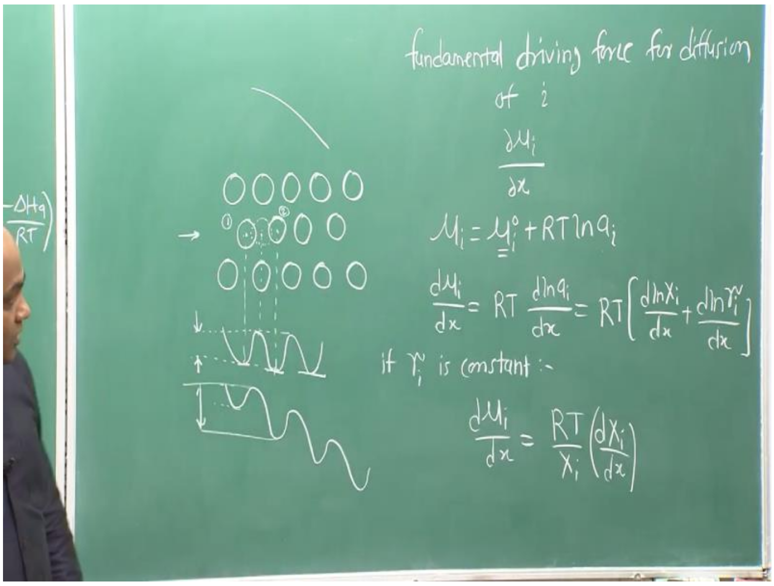


$$\text{rate} \propto \exp\left(\frac{-\Delta G_a}{RT}\right)$$

$$\text{rate} = \underbrace{k'\exp\left[\frac{\Delta S_a}{R}\right]}\exp\left(\frac{-\Delta H_a}{RT}\right)$$

$$\text{rate} = k_0\exp\left[\frac{-E_a}{RT}\right]$$

$$D = D_0\exp\left(-\frac{E_a}{RT}\right)$$



If a system exists in an unstable state, thermodynamics states that it should transform to a stable state. For example, if we plot Gibbs free energy of a system as it continuously moves through different atomic arrangements, we may get a schematic plot which looks something like shown above. Now there are two equilibrium states, let us call them state 1 and state 2 which have minimum in the Gibbs free energy. But state 2 is characterized by global minimum in the Gibbs free energy, that is, the Gibbs free energy of state 2 is the lowest of all other states. So this is the stable state. State 1 which is characterized by the local minimum in Gibbs free energy is referred to as metastable state. If by any chance, we retain the system in state 1 then the thermodynamics says that the system should move from state 1 to state 2 spontaneously. Spontaneously here means irreversibly. Also remember that spontaneity does not talk anything about speed of the process. It does not mean fast or slow, it only says it should move from state 1 to state 2. So thermodynamics only gives the direction of a process.

Now since state 2 has a lower Gibbs free energy than state 1, there is a decrease in Gibbs free energy during this process and that is why the process is irreversible. Driving force for the transformation from state 1 to state 2 is the the difference between the Gibbs free energy of the two states. However, you will notice that while going from 1 to 2, the system has to cross a hump in Gibbs free energy. It actually represents an energy barrier to the transformation. That means before the system can move from 1 to 2, it has to gain certain amount of energy which is equal to the difference between e this maximum in the Gibbs free energy. State corresponding to this maximum is called an activated state. Let us denote it by state A the difference between state A and state 1 is basically the activation energy for transformation. Until and unless system gains this activation energy it will not be able to move from state 1 to state 2. And the speed of the process depends upon this activation energy. To determine the rate of the process is in the realm of kinetics.

In this particular case:

$$rate \propto \exp\left(\frac{-\Delta G_a}{RT}\right)$$

In the simple theory of kinetics, rate is proportional to $\exp\left(\frac{-\Delta G_a}{RT}\right)$ where ΔG_a represents the energy barrier or activation energy. We can also write:

$$rate = k' \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(\frac{-\Delta H_a}{RT}\right)$$

as:

$$\Delta G_a = \Delta H_a - T\Delta S_a$$

Where k' is a constant, ΔH_a is the enthalpy of activation and ΔS_a is the entropy of activation. Temperature independent terms in the rate expression can be combined to give:

$$rate = k_o \exp\left(\frac{-\Delta H_a}{RT}\right) = k_o \exp\left(\frac{-E_a}{RT}\right)$$

Activation enthalpy is usually denoted by E_a. You can see the rate of the transformation is basically dependent upon the energy barrier that the system has to cross. And it varies exponentially the rate varies exponentially with temperature. Now, how does the system cross this energy barrier?

Student: Thermal energy…

Usually it is assisted by the thermal migration of the atoms, so these processes are usually referred to as thermally activated processes. Even diffusion is a thermally activated process and that is why diffusivity follows this relation:

$$D = D_o \exp\left(\frac{-E_a}{RT}\right)$$

Let us try to see physically the nature of this activation barrier when we talk about diffusion. Let us take an example of diffusion in solid. It is said that unit step of diffusion in solid is a single atomic jump. What is that atomic jump? Let us consider a simple two-dimensional arrangement of atoms and consider these two sites as site 1 and site 2. We know that in solid, the atoms are sitting in a potential energy well at their equilibrium lattice sites which means these equilibrium positions have minimum in energy. If we talk about this row of atoms, this is how the energy will vary with distance. Now if an atom has to move from site 1 to site 2, while doing that it crosses a position which has a maximum in the energy. Somewhere between these sites, atom has maximum energy. And once the atom crosses this maximum, then it will fall into the next potential energy well or into the next lattice site. This is one atomic jump. For this jump to happen, obviously the atom has to cross the energy barrier. What is the physical significance of this? You can see these atoms are actually touching each other. When the atom has to move from 1 to 2 site, it has to push other atoms apart. And there has to be an energy provided for that and that is this activation energy for diffusion. Specifically, this is the activation energy for migration.

But just having the enough activation energy for migration is not enough. The second condition is that the next site also has to be vacant. In diffusivity, in the activation energy term, there will also be a contribution from enthalpy of vacancy formation. That we will see in detail later, but right now it is just sufficient to understand how the activation barrier is created for this atomic jump.

Now these atoms are continuously vibrating at the any temperature above 0 Kelvin and each vibration does not have the same energy. That is, the energy distribution is continuously changing among the particle and if you consider any one particle or any one atom every vibration is with different energy. Certain vibrations may have energy greater than the energy required to cross this barrier. So that can be a potential successful jump provided the next site is vacant. This is how the thermal vibrations help the process of diffusion. Diffusion is also a thermally activated process.

Now suppose the chemical potential was uniform throughout the lattice. In that case, these potential energy well depths are same. When atom jumps from position 1 to position 2, there is no change in Gibbs free energy, that means there is really no driving force for this jump. But what if the chemical potential on site 2 is lesser than that on site 1?

Student: Atom will try to migrate from site 1 to site 2.

Professor: Right. What is the chemical potential? Chemical potential we defined as:

$$\mu_i = \frac{\partial G'}{\partial n_i}$$

This is basically the change in Gibbs free energy by adding one atom to the system. At site 1, one atom is getting removed during this jump and at site 2, one atom is getting added. If the chemical potential of site 1 is higher than that on site 2, what is going to happen? The decrease in Gibbs free energy around 1 is going to be more than increase in Gibbs free energy around 2. That means there will be a net decrease in Gibbs free energy and there will be a certain driving force for diffusion to occur. In other words, if we look at this potential energy wells, suppose there is a negative gradient in the chemical potential or the chemical potential is decreasing from left to right, it means it is equivalent to saying that the potential energy well depths are decreasing from left to right.

The atoms on the right are situated in a deeper potential energy well than those on the left. So, the activation energy for the atomic jump from left to right is lower compared to that for the jump from right to left. At any given instant the fraction of atoms jumping from left to right will be more than those jumping from right to left. And in effect there will be a net flow of atoms from left to right.

We say the gradient in chemical potential or $\frac{\partial \mu_i}{\partial x}$ is the fundamental driving force for diffusion. Now we know:

$$\mu_i = \mu_i^o + RTln\, a_i$$

where μ_i^o refers to the chemical potential of i in the standard state. Typically, the standard state is the stable state of pure i at the temperature T. This most of the time refers to the molar Gibbs free energy of pure i at temperature T. You can take any standard state. In that case μ_i^o will not be the molar Gibbs free energy of pure i, but you need to consider the chemical potential of i in that state. And a_i refers to the thermodynamic activity of i in the solution of that composition. If we take the derivative with respect to x and if we consider isothermal process, it should be:

$$\frac{d\mu_i}{dx} = RT\frac{dln\, a_i}{dx}$$

As

$$a_i = \gamma_i X_i$$

$$\frac{d\mu_i}{dx} = RT\left[\frac{dln\, X_i}{dx} + \frac{dln\, \gamma_i}{dx}\right]$$

where γ_i is the activity coefficient and X_i is the mole fraction of i. And if γ_i is constant, we can simply write:

$$\frac{d\mu_i}{dx} = \frac{RT}{X_i}\frac{dX_i}{dx}$$

$\frac{dX_i}{dx}$ is basically the gradient in concentration. Here you can see the simplest manifestation of the gradient in chemical potential is the gradient in composition. And this is good for us because it is much easier to experimentally determine the concentration than the chemical potentials and that is why you will see that most of the experimental practical formalisms of diffusion are done in terms of concentration gradients.

Once you know the diffusion quantities in terms of concentration gradients treated as driving force, you can convert them back into the diffusion quantities which treat chemical potential as driving force. Even when γ_i is not constant, we know the interrelations. By knowing the thermodynamic quantities, thermodynamic properties of the system like the thermodynamic activity coefficients and its relation with the composition, we can convert one set of diffusion parameters into the other.

And that is why we will deal with diffusion as driven by the composition gradients. Later on when we will go into the theoretical aspect, we will also treat diffusion down the chemical potential gradient and we can establish the interrelation between the diffusion quantities determined in one form with those determined in the other form.

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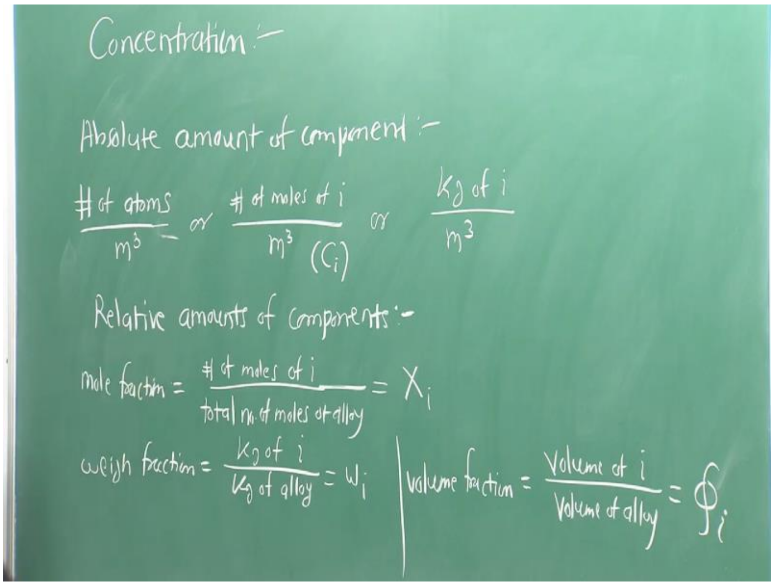

Concentration :-

Absolute amount of component :-

$\frac{\#\text{ of atoms}}{m^3}$ or $\frac{\#\text{ of moles of } i}{m^3}$ (C_i) or $\frac{\text{kg of } i}{m^3}$

Relative amounts of components :-

mole fraction = $\frac{\#\text{ of moles of } i}{\text{total no. of moles of alloy}} = X_i$

weigh fraction = $\frac{\text{kg of } i}{\text{kg of alloy}} = w_i$ | volume fraction = $\frac{\text{Volume of } i}{\text{Volume of alloy}} = \phi_i$

Concentration is important parameter here. It can be expressed in number of units. It can be either in terms of absolute amount of component, for example, number of atoms per unit volume of the alloy:

$$\frac{\#\ of\ atoms}{m^3}$$

or it can be number of moles of i per unit volume of alloy:

$$\frac{\#\ of\ mole\ of\ i}{m^3}$$

or it can be in terms of weight, weight of i per meter unit volume of alloy:

$$\frac{kg\ of\ i}{m^3}$$

or it can be in terms of relative amount of components. Relative amount of components can be mole fraction which is nothing but:

$$mole\ fraction = \frac{no.of\ mole\ of\ i}{total\ no.of\ moles\ of\ alloy} = X_i$$

It is usually referred to as X_i. This is also same as atom fraction, which is number of atoms of i divided by total number of atoms. There is only a factor of Avogadro’s number between number of atoms and number of moles. So the mole fraction is basically same as atom fraction.

Or it can be weight fraction that is:

$$weight\ fraction = \frac{kg\ of\ i}{kg\ of\ alloy} = W_i$$

or it can be volume fraction:

$$volume\ fraction = \frac{Volume\ of\ i}{Volume\ of\ alloy} = \phi_i$$

We will most of the time use the unit for concentration as number of moles of i per m^3. It is denoted usually as C_i or in terms of fractions, we will most of the time use mole fraction X_i. Now what is the advantage of using these fractions instead of the absolute quantities? For any type of fraction for example, mole fraction:

$$\sum X_i = 1$$

Which means if there is an n component system, out of n components only $n-1$ concentration variables are independent, the nth one will be dependent. If we consider binary alloy, we need to specify only one mole fraction because the second one is fixed, in ternary we need to specify two mole fractions, the third one will be fixed or dependent. That is an advantage.

How do we convert one into the other? Because most of the time when we see the flow of atoms or the fluxes of atoms, we will express those in terms of number of moles per unit area per unit time. How do we convert them back and forth? for example, how do we convert C_i to X_i?

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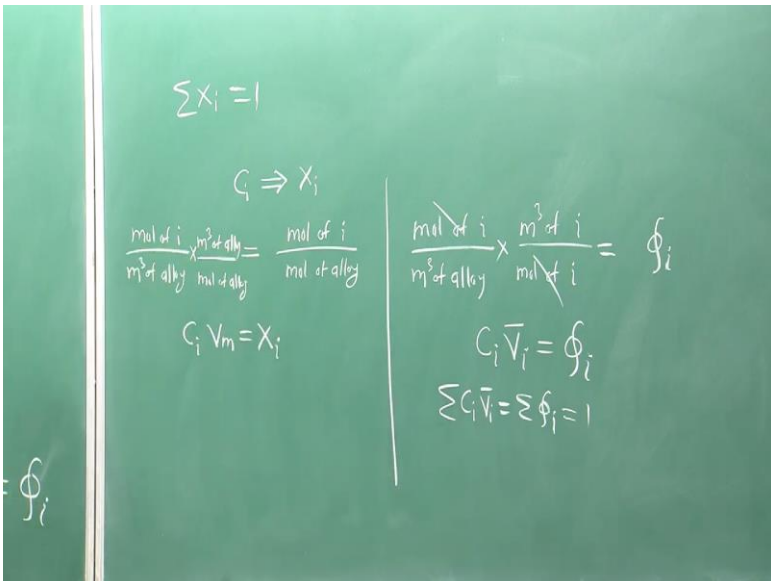

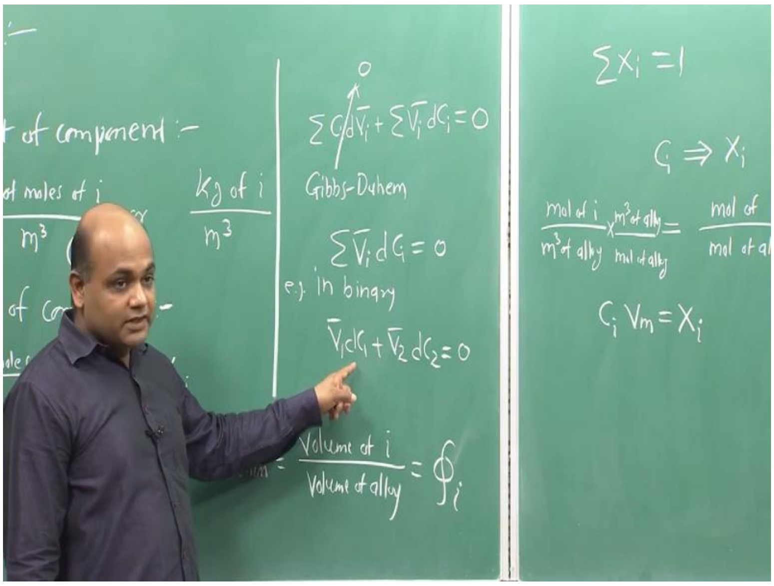

X_i is basically mole of i per mole of alloy:

$$X_i = \frac{mole\ of\ i}{total\ mole\ of\ alloy}$$

and :

$$C_i = \frac{mole\ of\ i}{m^3\ of\ alloy} \qquad (1)$$

To convert C_i to mole fraction, it can be done by:

$$\frac{mole\ of\ i}{m^3\ of\ alloy} \times \frac{m^3\ of\ alloy}{mole\ of\ alloy} = \frac{mole\ of\ i}{total\ mole\ of\ alloy}$$

Meter cube of alloy per mole of alloy is the molar volume of the alloy:

$$\frac{m^3\ of\ alloy}{mole\ of\ alloy} = V_m$$

So,

$$C_i V_m = X_i$$

If instead of multiplying Eq. (1) above by meter cube of alloy we multiply by mole of i divided by mole of i, we get:

$$\frac{mole\ of\ i}{m^3\ of\ alloy} \times \frac{m^3\ of\ i}{mole\ of\ i} = \frac{m^3\ of\ i}{m^3\ of\ alloy} = \phi_i$$

Or meter cube of i per meter cube of alloy. This is basically the volume fraction ϕ_i. And what is meter cube of i per mole of i?

Student: Partial molar volume

Professor: Partial molar volume. We can write:

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

This is important relation. If we take the summation over all n components:

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

If we differentiate both sides, we get:

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

Now, $\sum C_i d\bar{V}_i = 0$ based on Gibbs-Duhem equation. What we get is:

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

For example, in binary you can write:

$$\bar{V}_1 dC_1 + \bar{V}_2 dC_2 = 0$$

This is an important relation which we will use later on when we try to develop methodologies for analysis of diffusion and diffusion couples. There is another important point here, when we analyze diffusion in terms of concentration gradients, only one of the gradient is independent, the other one is dependent in a binary system provided we know the partial molar volumes.