Diffusion in Multicomponent Solids

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Lecture 06 - Thermodynamic Activity & Gibbs Free Energy of Mixing

Welcome to the second week of open course on Diffusion in Multicomponent Solids. This is the sixth lecture in the series and in this lecture, we will start with solution thermodynamics. I will first explain the concept of thermodynamic activity and later, I will derive the equation for Gibbs free energy of mixing in terms of activities of the components.

Interdiffusion is a process of intermixing that drives many transformations, that is, the transformation from non-stable state to a stable state. And so it is important for us to understand the Gibbs free energy changes associated with the process of mixing. In next couple of classes, we will talk about solution thermodynamics or the process of intermixing and Gibbs free energy changes associated with it.

When we talk about solutions, thermodynamic activity is an important parameter. As you all know, diffusion is driven down the gradient of chemical potentials or equivalently down the gradient of thermodynamic activities. Let us try to understand what is thermodynamic activity and what is the physical significance of thermodynamic activity parameter.

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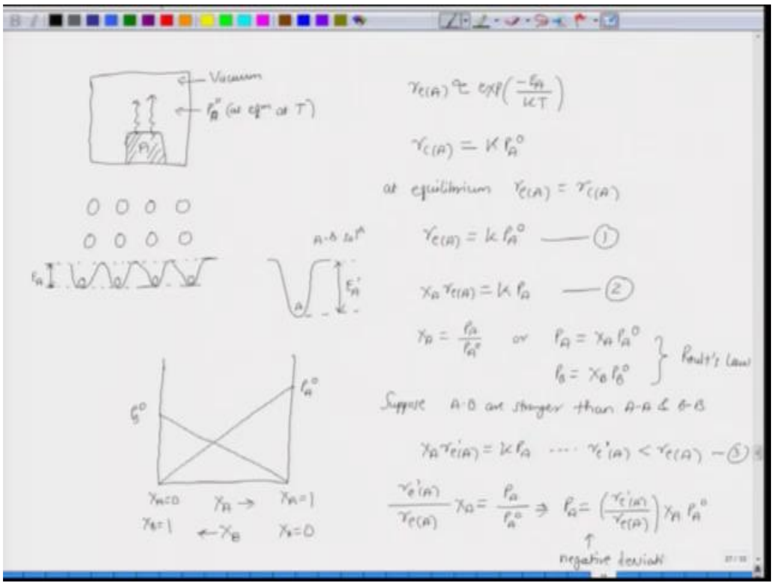

$r_{e(A)} \propto \exp\left(\frac{-E_A}{kT}\right)$

$r_{c(A)} = K p_A^0$

at equilibrium $r_{e(A)} = r_{c(A)}$

$r_{e(A)} = k p_A^0$ —— ①

$X_A r_{e(A)} = k p_A$ —— ②

$X_A = \frac{p_A}{p_A^0}$ or $p_A = X_A p_A^0$, $p_B = X_B p_B^0$ } Rault's Law

Suppose A-B are stronger than A-A & B-B

$X_A r'_{e(A)} = k p_A$ ···· $r'_{e(A)} < r_{e(A)}$ — ③

$\frac{r'_{e(A)}}{r_{e(A)}} X_A = \frac{p_A}{p_A^0} \Rightarrow p_A = \left(\frac{r'_{e(A)}}{r_{e(A)}}\right) X_A p_A^0$

↑ negative deviation

As you all know, any condensed phase, that is, a solid or a liquid builds up an equilibrium vapor pressure above its surface. Consider, for example, a solid which is contained in a container. Let us say this solid is a pure element A and let us say initially the chamber was evacuated. This is a non-equilibrium state. Now, A has to exert an equilibrium vapor pressure and since the chamber was evacuated - what happens? Some of the A atoms will go into the vapor phase that will build up the vapor pressure and this process will continue until the pressure becomes equal to the pressure at equilibrium at temperature T. P^o or let say P_A^o to be precise is the equilibrium vapor pressure of A at temperature T.

The evaporation will stop when the pressure inside the chamber reaches P_A^o, but on the atomistic scale, the process of evaporation is still going on, but it is counterbalanced by the reverse process of condensation. So, what is happening at the atomistic level is that there is a continuous evaporation of some atoms of A from solid into the vapor phase, but at the same time, some atoms of A are hitting back on the solid surface and they are getting condensed. At equilibrium, the rate of condensation is equal to the rate of evaporation and so, we do not see any net evaporation or condensation when the equilibrium is established.

Let us try to analyze how these rates are affected with the composition. Initially, let us say the rate of evaporation is $r_{e(A)}$. How the evaporation process occurs? Basically, what we are doing is plucking out an A atom from the solid surface and putting it into the vapor phase. Now all of us know that in solid all the atoms are in their equilibrium positions, right? They are continuously vibrating about their equilibrium positions. If we consider this atomic arrangement, essentially each atom is located at what we call as potential energy well. These are the equilibrium positions, which means at these positions or at the regular lattice sites, the forces are balanced. There are interactions between the atoms, but at the equilibrium positions, these interactions are balanced. Essentially, those are the minimum energy positions which are called the potential energy wells. If all the atoms are identical, the depth of this potential energy wells are same. Let us call it as E_A. In order to remove one atom from the surface, there has to be some work done. The atom has to gain enough energy, it has to overcome this activation barrier E_A and obviously rate of evaporation will be proportional to $exp^{\left(\frac{-E_A}{kT}\right)}$. This is the Arrhenius equation.

Now what about the condensation? For condensation to occur some of the A atom have to hit on the surface and become part of A. We know in the vapor phase, the A atoms are continuously undergoing the translational motion and some of the A atoms will hit solid A and become part of A, which is the condensation process. Essentially the rate of condensation $r_{c(A)}$ will be proportional to the vapor pressure. If it is pure A, $r_{c(A)}$ will be proportional to P_A^o because pressure quantifies how many atoms are hitting the wall per unit time. We can write $r_{c(A)}$ as:

$$r_{c(A)} = kP_A^o$$

And we know at equilibrium, the rate of evaporation is the same as rate of condensation. And we can write:

$$r_{e(A)} = kP_A^o \qquad (1)$$

Let us call this equation 1. Now suppose, instead of pure A we initially had a solution of A and another component B, then what difference it will make? We know when A is inside the solution instead of pure A, we need to consider the equilibrium partial vapor pressure. And obviously, the vapor pressure P_A exerted by element A when it is inside the solution will be less than P_A^o. Now how the rate of condensation and rate of evaporation will change? Evaporation of A atoms can occur only from the sites of A. So, we have to reduce the intrinsic rate of evaporation of A by the factor X_A, that is, the mole fraction of A assuming that the concentration of the surface is same as the bulk concentration. We need to apply the factor X_A to the intrinsic rate of evaporation. Now, on the other side, rate of condensation will be proportional to P_A because the new equilibrium partial vapor pressure is P_A.

$$X_A r_{e(A)} = kP_A \qquad (2)$$

This is our equation 2. If we divide Eq. 2 by 1, we get:

$$X_A = \frac{P_A}{P_A^o}$$

Similarly, for B we can write:

$$X_B = \frac{P_B}{P_B^o}$$

Where, P_B^o is the equilibrium vapor pressure exerted by pure B at temperature T. We are considering all these processes at the same temperature T.

This basically is called Raoult's law. We can plot how the equilibrium partial pressure P_A varies with composition, X_A. Y-axis is the partial vapour pressure of A and x axis is X_A. At X_A A equal to 0, P_A is equal to 0, and when X_A is equal to 1, P_A will be P_A^o.

Raoult's law tells that the plot will be a straight line as this is a straight line relation. Similarly, if we plot P_B as a function of X_B, $X_B$will be in the opposite direction. At $X_B = 1$, P_B will be equal to P_B^o and $X_B = 0$, P_B will be 0.

When the solution follows Raoult's law, we say it is an ideal solution. Now there is an assumption that we have made here which we did not express earlier. See when we wrote this equation 1 and 2 for pure element as well as for the solution, we are assuming $r_{e(A)}$ is same, that is, intrinsic rate of evaporation is not changing for A whether it is pure A or whether A is inside a solution. This can happen when either there are no interactions between A and B or the interactions between A and B are same as that between A and A or between B and B.

In this case we call it an ideal solution or Raoultian solution. Basically, ideal solutions are characterized by no interactions between the atoms or all the interactions are same. Let us see how the situation changes when we have the interactions between A-A and B-B and A-B, which are different.

What will happen in that case? Suppose A-B interactions are stronger than A-A and B-B, what will happen? If you are considering the solution of A and B, what will happen to the potential well? Obviously, there will be some A-B bonds, which are stronger than A-A bonds. And the A atom which is surrounded by B atom will lie at a deeper potential energy well, right. Let us call this E'_A, which means that to pluck one atom of A out of the solution, more work will be required to be done as against pure A. Obviously, the intrinsic rate of evaporation will change. We can write this equation 2 for the solution case as:

$$X_A r'_{e(A)} = kP_A \qquad (3)$$

And we know that for this case, when A-B interactions are stronger than A-A and B-B:

$$r'_{e(A)} < r_{e(A)}$$

Now if we divide equation three by one, what we get:

$$\frac{r'_{e(A)}}{r_{e(A)}} X_A = \frac{P_A}{P_A^o}$$

And since:

$$r'_{e(A)} < r_{e(A)}$$

So,

$$P_A < X_A P_A^o$$

If we plot the relation between P_A and X_A, it will lie below the Raoultian line. This is called as negative deviation from ideality.

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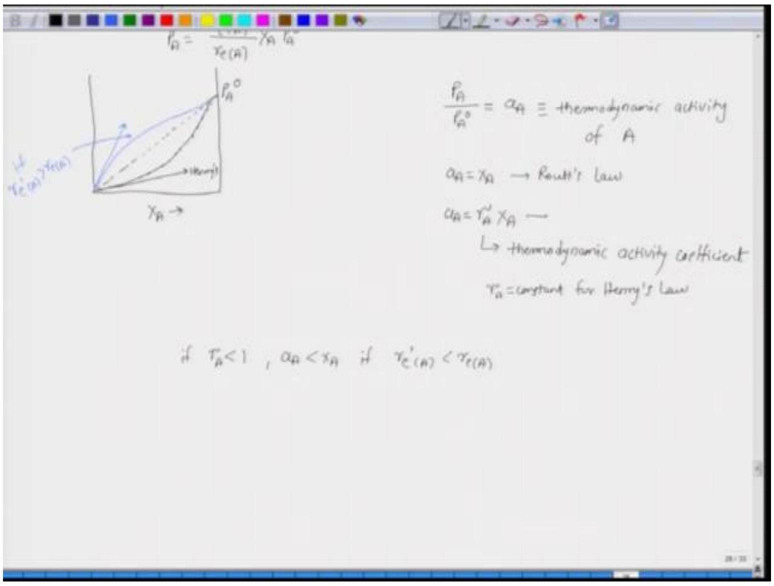

$\frac{P_A}{P_A^o} = a_A \equiv$ thermodynamic activity of A

$a_A = X_A \rightarrow$ Raoult's law

$a_A = \gamma_A X_A$ —

↳ thermodynamic activity coefficient

γ_A = constant for Henry's Law

if $\gamma_A < 1$, $a_A < X_A$ if $r'_{e(A)} < r_{e(A)}$

If we try to plot the relation between P_A and X_A obviously, this is the Raoult law line and since,

$$r'_{e(A)} < r_{e(A)}$$

there will be a negative deviation. Now, here we are considering a dilute solution of A in B, what does that mean? That means that most of the A atoms are surrounded only by B atoms. Most of the bonds that A is involved in are A-B type of bonds, which means $r'_{e(A)}$ is basically constant as a function of concentration as long as the concentration is very low.

Initially, there will be a linear relation between P_A and X_A. This is called Henry's law. Now, what happens as we increase the concentration of A? With the increasing concentration of A, probability of forming A-A bonds is more and since A-A bonds are weaker than A-B, it will raise the overall potential energy well. The potential energy well will be lesser and lesser deeper as X_A increases, which means that there will be deviation from the Henry's law line at higher concentrations.

And what happens, as X_A tends to 1. As X_A tends to 1, Again all A atoms will be mostly surrounded by only A atoms, the intrinsic rate of evaporation will be similar to the intrinsic rate of evaporation of pure A. And as X_A tends to 1, this will follow the Raoult's law line.

This is basically for a negative deviation from ideality. Now, what happens if $r'_{e(A)} > r_{e(A)}$, which means A-B bonds are weaker than A-A and B-B bonds. With the similar logic we can show that in that case there will be a positive deviation.

Okay, now we can define the quantity thermodynamic activity of A as:

$$\frac{P_A}{P_A^o} = a_A$$

In terms of thermodynamic activity we can state Raoult's law as:

$$a_A = X_A$$

This is the Raoult's law and we can define:

$$\gamma_A = \frac{r'_{e(A)}}{r_{e(A)}}$$

where γ_A is called the thermodynamic activity coefficient. When we have dilute concentration, we know there is a linear relation between a_A and $X_A$and γ_A is constant. This is the Henry's law. This gives us the physical significance of the term thermodynamic activity. What is it?

Activity is a ratio of equilibrium partial vapor pressure of A exerted by the solution to the equilibrium vapor pressure exerted by pure A at a given temperature T. And we know if $\gamma_A < 1$ that means, $a_A < X_A$ and this occurs when $r'_{e(A)} < r_{e(A)}$. The intrinsic rate of evaporation in solution is less than intrinsic rate of evaporation in pure A, which means, the intrinsic evaporation tendency of A is reduced when it goes from pure state to the solution. What is evaporation? The atom is trying to escape from the solid. Basically that defines the escaping tendency of the component, in this case A. If:

$$a_A < X_A$$

it denotes negative deviation, which means, the intrinsic escaping tendency of A is reduced by going into the solution.

On the other hand, if we have:

$$a_A > X_A$$

in that case the intrinsic escaping tendency of A increases by going into the solution. Here, we are comparing the intrinsic escaping tendency in solution with that in the pure state. Basically, here we are taking this pure state as a reference state or the standard state. This is the significance of thermodynamic activity.

Now, when we are analyzing the intermixing process, we need to see what are the Gibbs free energy changes associated with it based upon which we can decide the equilibrium or stability criteria. We will see how the Gibbs free energy changes are calculated for the mixing process.

Before that, it is first important to define the contribution from individual element to the total property of the system. For example, Gibbs free energy or volume, which are also extensive property.

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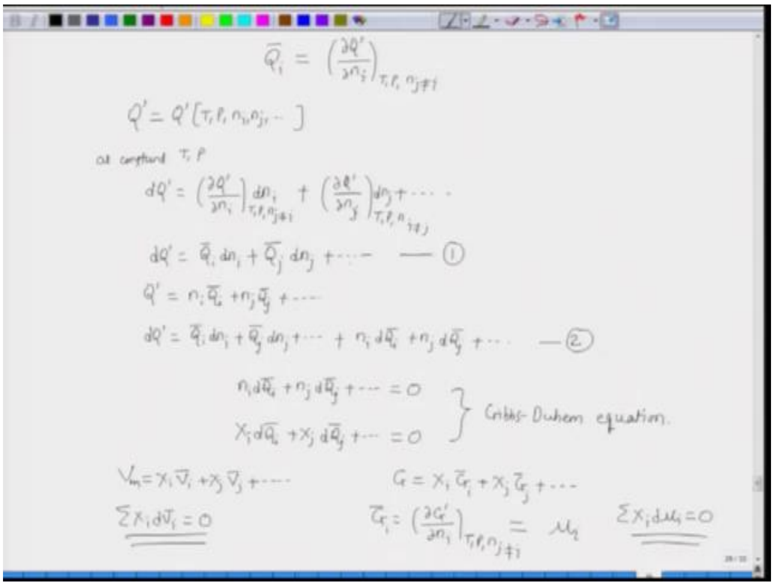

$$\bar{Q}_i = \left(\frac{\partial Q'}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

$$Q' = Q'[T, P, n_i, n_j, \cdots]$$

at constant T, P

$$dQ' = \left(\frac{\partial Q'}{\partial n_i}\right)_{T,P,n_{j\neq i}} dn_i + \left(\frac{\partial Q'}{\partial n_j}\right)_{T,P,n_{i\neq j}} dn_j + \cdots$$

$$dQ' = \bar{Q}_i\, dn_i + \bar{Q}_j\, dn_j + \cdots \quad — ①$$

$$Q' = n_i \bar{Q}_i + n_j \bar{Q}_j + \cdots$$

$$dQ' = \bar{Q}_i\, dn_i + \bar{Q}_j\, dn_j + \cdots + n_i\, d\bar{Q}_i + n_j\, d\bar{Q}_j + \cdots \quad — ②$$

$$\left.\begin{aligned} n_i\, d\bar{Q}_i + n_j\, d\bar{Q}_j + \cdots &= 0 \\ X_i\, d\bar{Q}_i + X_j\, d\bar{Q}_j + \cdots &= 0 \end{aligned}\right\} \text{Gibbs-Duhem equation.}$$

$$V_m = X_i \bar{V}_i + X_j \bar{V}_j + \cdots$$

$$\underline{\underline{\Sigma X_i\, d\bar{V}_i = 0}}$$

$$G = X_i \bar{G}_i + X_j \bar{G}_j + \cdots$$

$$\bar{G}_i = \left(\frac{\partial G'}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \mu_i \qquad \underline{\underline{\Sigma X_i\, d\mu_i = 0}}$$

The contribution per mole from the individual component to the total property of the system is referred to as the partial molar quantity. Partial molar property is denoted by $\bar{Q}_i$ and it is defined as:

$$\bar{Q}_i = \left(\frac{\partial Q'}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

partial of Q' with respect to number of moles of $i,\ n_i$, at constant temperature, pressure and constant number of moles of other components. It is basically the change in property Q' by the addition of one mole of *i* when we keep temperature, pressure and other numbers of moles constant. Again, this has to be done at constant composition, because then $\bar{Q}_i$ will also change with composition. When we add this one mole to the system to define $\bar{Q}_i$, it has to be added to a large amount of the system, that addition of one mole of i does not affect the composition significantly.

Okay now, we know then Q' is a function of temperature, pressure and number of moles of all the species. So, let us consider n component system and Q' basically is a state function. So, it has an exact differential. At constant temperature and pressure, we can define its differential as:

$$dQ' = \left(\frac{\partial Q'}{\partial n_i}\right)_{T,P,n_{j\neq i}} dn_i + \left(\frac{\partial Q'}{\partial n_j}\right)_{T,P,n_{i\neq j}} dn_j + \cdots$$

And we can see these partials are nothing but the partial molar quantities which results in:

$$dQ' = \bar{Q}_i dn_i + \bar{Q}_j dn_j + \cdots \qquad (1)$$

Let us denote this by equation one. As I said, a partial molar property is basically the contribution per mole of species i to the total property Q'. We can mention Q' :

$$Q' = \bar{Q}_i n_i + \bar{Q}_j n_j + \cdots$$

If we take a differential of this we get:

$$dQ' = \bar{Q}_i dn_i + \bar{Q}_j dn_j + \cdots \quad + n_i d\bar{Q}_i + n_j d\bar{Q}_j + \cdots \qquad (2)$$

Let us denote this by equation 2 and if we compare equation 1 with equation 2, we see that:

$$n_i d\bar{Q}_i + n_j d\bar{Q}_j + \cdots \qquad = 0 \qquad (3)$$

Or if we divide this equation by the total number of moles of the system and we can write:

$$X_i d\bar{Q}_i + X_j d\bar{Q}_j + \cdots \qquad = 0 \qquad (4)$$

where X_i is the mole fraction of i. Both equations (3) and (4) are equivalent and they are called Gibbs-Duhem equation. These are very important equations. The Gibbs-Duhem equation will be very important for our class, we will keep using it as we go along, but what is the physical significance of this? It essentially tells me that not all partial molar quantities are independent. And practically why it is important? Because, for example if we are considering a binary system, many times we find that it is possible to measure the property of only one component and measuring property of second component is not practical. But this equation tells me that if I can measure the property of one component as a function of composition, then from the Gibbs-Duhem equation I can get to the other property. That is the physical significance of this Gibbs Duhem equation and this is very important.

For example, we will often talk about molar volumes when we study diffusion because the analysis of diffusion profiles is considerably affected by the changes in molar volumes. Volume is an extensive property; obviously we have a partial molar volume, which is the contribution per mole by individual species to the total volume of the system. In terms of mole fractions we can write molar volume as:

$$V_m = X_i \bar{V}_i + X_j \bar{V}_j + \cdots$$

Where $\bar{V}_i$ and $\bar{V}_j$ are the partial molar volumes and we can write the Gibbs-Duhem equation as:

$$\sum X_i d\bar{V}_i = 0$$

Similarly, if we consider molar Gibbs free energy, we can write:

$$G = X_i \bar{G}_i + X_j \bar{G}_j + \cdots$$

Where by the definition of partial molar quantities $\bar{G}_i$ is defined as:

$$\bar{G}_i = \left(\frac{\partial G'}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \mu_i$$

This looks familiar? This is equivalent to the chemical potential. The partial molar Gibbs free energy of i in a solution is same as its chemical potential μ_i in the solution. We can write the Gibbs Duhem equation for chemical potential as:

$$\sum X_i d\mu_i = 0$$

These two equations are very important and we will use them in the later part of the class.

Okay, now how do we analyze the Gibbs free energy changes associated with the mixing process? If we mix A and B to form a solution, what is the Gibbs free energy change associated with mixing A and B? et us carry out that mixing process systematically.

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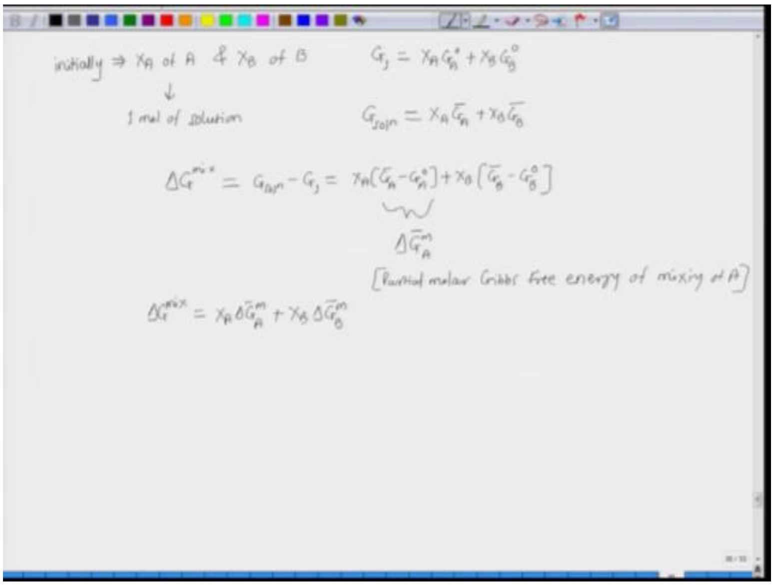

initially ⇒ X_A of A & X_B of B

↓

1 mol of solution

$$G_1 = X_A G_A^o + X_B G_B^o$$

$$G_{soln} = X_A \bar{G}_A + X_B \bar{G}_B$$

$$\Delta G^{mix} = G_{soln} - G_1 = \underbrace{X_A(\bar{G}_A - G_A^o)}_{\Delta \bar{G}_A^m} + X_B[\bar{G}_B - G_B^o]$$

[Partial molar Gibbs free energy of mixing of A]

$$\Delta G^{mix} = X_A \Delta \bar{G}_A^m + X_B \Delta \bar{G}_B^m$$

Suppose, initially we take X_A moles of A and X_B moles of B and we form one mole of solution, what will be the initial Gibbs free energy of the system? Let us call it G_1:

$$G_1 = X_A G_A^o + X_B G_B^o$$

where G_A^o and G_B^o are the molar Gibbs free energies of A and B. What will be the Gibbs free energy after formation of solution? Let us call this $G_{solution}$. In terms of partial molar Gibbs free energy it will be:

$$G_{solution} = X_A \bar{G}_A + X_B \bar{G}_B$$

The Gibbs free energy associated with the mixing process is molar Gibbs free energy because we are forming one mole of solution from X_A moles of A and X_B moles of B. That will be:

$$\Delta G_{mix} = G_{solution} - G_1$$

the final Gibbs free energy minus initial Gibbs free energy.

And, from these two equations, we can write it as:

$$\Delta G_{mix} = X_A(\bar{G}_A - G_A^o) + X_B(\bar{G}_B - G_B^o)$$

What is this quantity, $\bar{G}_A - G_A^o$? It is basically the change in Gibbs free energy associated with A when it goes from pure state into the solution. We can call it as $\Delta\bar{G}_A^m$ or partial molar Gibbs free energy of mixing of A. We can write ΔG_{mix} as:

$$\Delta G_{mix} = X_A \Delta\bar{G}_A^m + X_B \Delta\bar{G}_B^m$$

Now, we need to evaluate $\Delta\bar{G}_A^m$ and $\Delta\bar{G}_B^m$. Let us see what happens to the individual species to form a solution from the pure state.

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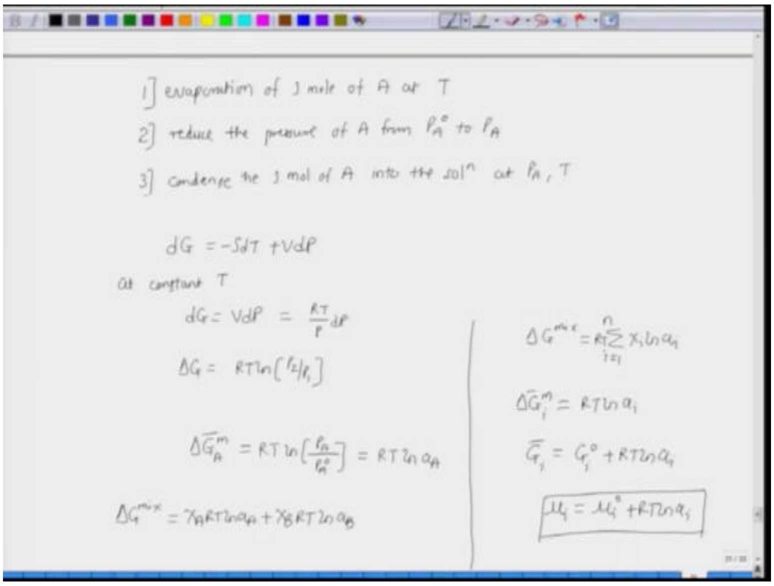

1] evaporation of 1 mole of A at T

2] reduce the pressure of A from P_A^o to P_A

3] condense the 1 mol of A into the soln at P_A, T

$$dG = -SdT + VdP$$

at constant T

$$dG = VdP = \frac{RT}{P}dP$$

$$\Delta G = RT\ln[P_2/P_1]$$

$$\Delta\bar{G}_A^m = RT\ln\left[\frac{P_A}{P_A^o}\right] = RT\ln a_A$$

$$\Delta G^{mix} = X_A RT\ln a_A + X_B RT\ln a_B$$

$$\Delta G^{mix} = RT\sum_{i=1}^{n} X_i \ln a_i$$

$$\Delta\bar{G}_i^m = RT\ln a_i$$

$$\bar{G}_i = G_i^o + RT\ln a_i$$

$$\boxed{\mu_i = \mu_i^o + RT\ln a_i}$$

What we are doing here is we are taking X_A moles of A from pure A and putting it into a solution. Now, when I had pure A, the partial pressure exerted by A was P_A^o. When I have A in solution partial pressure exerted by A is P_A. Essentially, we are changing the vapor pressure of A from P_A^o to P_A. This solution process can be considered as is composed of three steps. The first step is, evaporation of one mole of A at temperature T. Suppose pure A is at equilibrium and we evaporate one mole of A at constant temperature, pressure from solid state to the vapor state. Then, reduce the pressure of A from P_A^o to P_A and then third step as condense the one mole of A into the solution at P_A and temperature T. The steps one and three are essentially the reversible processes, evaporation of one mole of A at T and P_A^o is reversible. Similarly, step three is reversible, but step two is an irreversible process. There will be the Gibbs free energy change associated with step two. Now, this we can replace with a reversible process and find out what is the Gibbs free energy change associated with it. We are trying to see what is dG.

We know it should be:

$$dG = -SdT + VdP$$

and at constant temperature you know dG is equal to VdP. Now, if we consider ideal gas, we are considering vapors and the vapor pressures are typically really low pressures. We know at low pressure we can consider a real gas as close to an ideal gas. So, we can apply the ideal gas equation here. We can replace V with $\frac{RT}{P}$.

So, if you make a state change from pressure 1 to pressure 2, you know:

$$dG = VdP = \frac{RT}{P}dP$$

$$\Delta G = RTln\left(\frac{P_2}{P_1}\right)$$

In this case, when we carry out these three steps ΔG is equivalent to $\Delta\bar{G}_A^m$ and we are changing the pressure from P_A^o to P_A :

$$\Delta\bar{G}_A^m = RTln\left(\frac{P_A}{P_A^o}\right)$$

And $\left(\frac{P_A}{P_A^o}\right)$ is nothing but thermodynamic activity of A, so:

$$\Delta\bar{G}_A^m = RTln\, a_A$$

So, the Gibbs free energy of mixing should be equal to:

$$\Delta G_{mix} = X_A RTln\, a_A + X_B RTln\, a_A$$

In general for an n component system, we can write the molar Gibbs free energy of mixing as:

$$\Delta G_{mix} = RT\sum_{i=1}^{n} X_i ln\ a_i$$

We know $\Delta\bar{G}_i^m$ was:

$$\Delta\bar{G}_i^m = \bar{G}_i - G_i^o = RTln\ a_i$$

Again this equation you all are familiar with, I suppose, because $\bar{G}_i$ bar is nothing but μ_i. we can write this as:

$$\mu_i - \mu_i^o = RTln\ a_i \qquad (5)$$

Now we know the Gibbs free energy change associated with mixing process or when we form a solution from pure components, what should be ΔG_{mix} and the standard equation for chemical potentials, i.e. Eq. (5). In this case μ_i^o is nothing but the chemical potential of i in its standard state. You can define any state as standard state. In this case, our standard state was pure i. More specifically, the standard state conventionally is defined as pure component i in its stable state at the temperature being considered.

Essentially the solution thermodynamics boils down to the study of temperature, composition, vapor pressure interrelationship. We studied that when we form the solution, how the pressure of vapor above the surface of the solid or liquid (the condensed phase) changes and this vapor pressure will of course be a function of temperature and vapor pressure. Intrinsic rate of evaporation also changes with composition. The solution thermodynamics essentially deals with interrelationship between temperature, composition and vapor pressure.