Diffusion in Multicomponent Solids
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Lecture 07
Entropy of Mixing of Multicomponent Ideal Solution

Welcome to the seventh lecture of open course on Diffusion in Multicomponent Solids. In this lecture, we will derive the expression for entropy of mixing for an ideal solution. In order to give you a flavor of the multicomponent thermodynamics, we will apply this treatment to an n component solution. We will go over solution thermodynamics.

Last class, we evaluated partial molar Gibbs free energy of mixing of constituent atoms or elements based upon assuming the process of forming solution to be equivalent to evaporation of one mole of the constituent from the pure element at constant temperature and pressure P_i^o, then reducing the pressure of the vapor from P_i^o to P_i, which is the vapor pressure of i over the solution and then condensing that one mole of i from the vapor phase into the solution.

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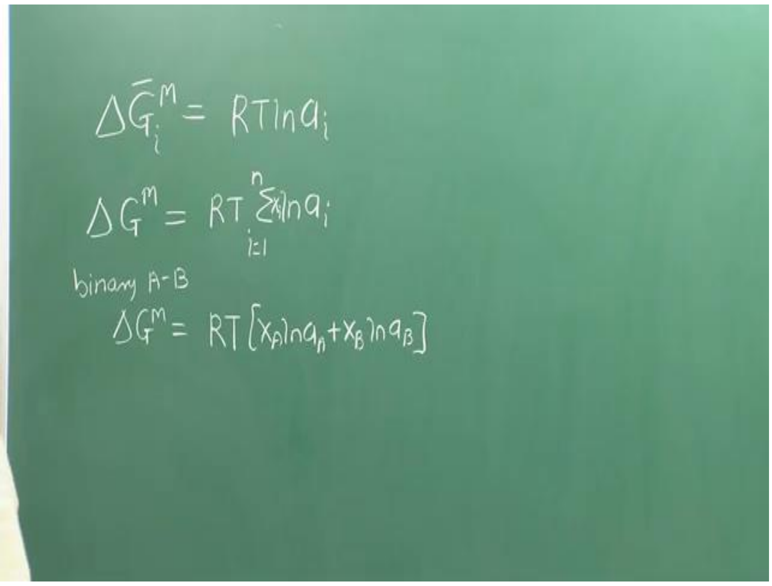

$$\Delta \bar{G}_i^M = RT \ln a_i$$

$$\Delta G^m = RT \sum_{i=1}^{n} x_i \ln a_i$$

binary A-B

$$\Delta G^m = RT [x_A \ln a_A + x_B \ln a_B]$$

With this we got the expression for partial molar Gibbs free energy of mixing components i as:

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

where a_i is the thermodynamic activity of component i in the solution. And molar Gibbs free energy of mixing to form an n component solution is:

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

For a binary solution of A and B we will get:

$$\Delta G^m = RT(X_A ln\, a_A + X_B ln\, a_A)$$

Now we will go over couple of models of forming the solution of condensed phases. We will talk particularly about solids to understand how the process occurs physically.

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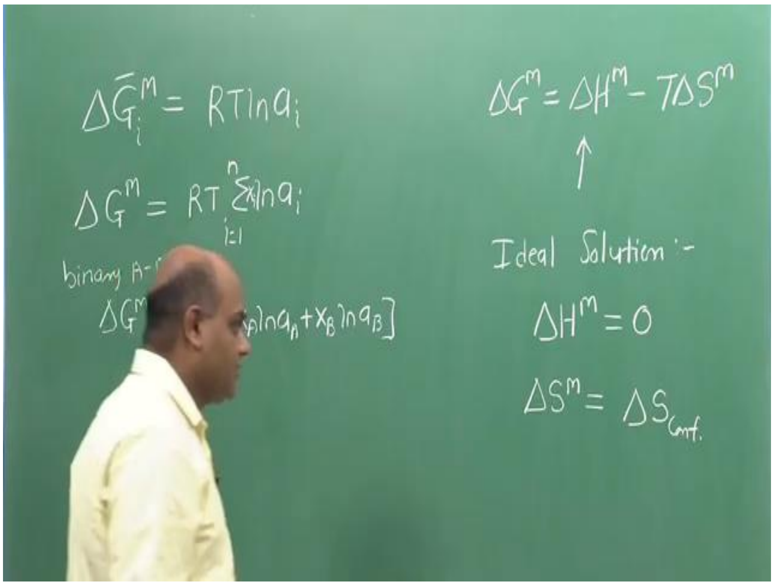

ΔG^m or the molar Gibbs free of mixing can also be written as:

$$\Delta G^m = \Delta H^m - T\Delta S^m$$

This is at constant temperature and pressure where ΔH^m is the molar enthalpy of mixing and ΔS^m is the molar entropy of mixing. The contribution to ΔH^m or the change in enthalpy associated with the process of mixing is mainly from the changes in the types of bonds.

So, we have to form A-B solution from pure A and pure B. In pure A and pure B there are only A-A and B-B pairs. When we form the solution, some of the similar atom pairs will be replaced by A-B pairs. Now, A-A, B-B and A-B interactions are not same. As a result, it causes changes in the potential energy which will lead to change in the enthalpy. That is the change in enthalpy.

Obviously, when you form a solution from pure elements, in the solution there are more special configurations available. So there is a change in entropy. We will first look at the ideal solution model. In an ideal solution, essentially the enthalpy of mixing is 0, which means there exist no interactions between the atoms or if there are interactions, they are all the same no matter what pair we are looking at A-A, B-B or A B. The interactions are all same. And the entropy of mixing is coming from the change in configurational entropy. Let us try to evaluate $\Delta S_{conf.}$ for the process of mixing.

$$\Delta S^{m} = \Delta S_{conf.}$$

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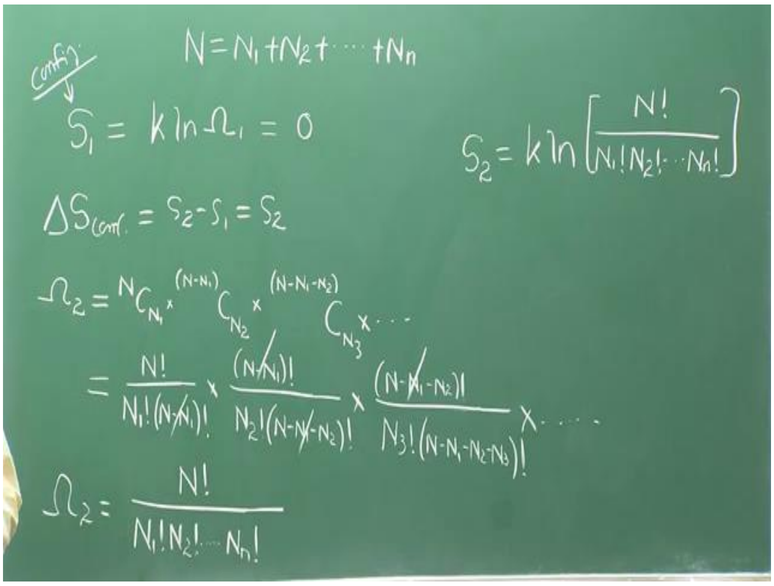

$$N = N_1 + N_2 + \cdots + N_n$$

config.

$$S_1 = k \ln \Omega_1 = 0 \qquad S_2 = k \ln \left[\frac{N!}{N_1! N_2! \cdots N_n!} \right]$$

$$\Delta S_{conf.} = S_2 - S_1 = S_2$$

$$\Omega_2 = {}^{N}C_{N_1} \times {}^{(N-N_1)}C_{N_2} \times {}^{(N-N_1-N_2)}C_{N_3} \times \cdots$$

$$= \frac{N!}{N_1!\,\cancel{(N-N_1)!}} \times \frac{\cancel{(N-N_1)!}}{N_2!\,\cancel{(N-N_1-N_2)!}} \times \frac{\cancel{(N-N_1-N_2)!}}{N_3!\,(N-N_1-N_2-N_3)!} \times \cdots$$

$$\Omega_2 = \frac{N!}{N_1! N_2! \cdots N_n!}$$

Suppose, we form an n component solution by mixing N_1 atoms of element 1, N_2 atoms of element 2 and so on. We have N_1 atoms of 1, N_2 atoms of 2, N_n atoms of n and so on. The total number of items will be the summation of all the atoms.

$$N = N_1 + N_2 + \cdots + N_n$$

Before mixing it is called the entropy of the system before mixing. We are talking here about only the configurational entropy. What should be the entropy of the system before mixing?

Student: 0, sir.

Professor: 0, right. How many configurations are available?

Student: 1.

Professor: Right, all 1 atoms are on lattice of one, all two atoms are on lattice of two and so on, right and all 1 atoms are identical, all 2 atoms are identical and all 3 atoms are identical. So, there is only one possible way in which these atoms can be arranged before mixing.

By Boltzmann’s equation we know:

$$S_1 = kln\Omega_1 = 0$$

Ω is the number of configurations possible. And Ω_1 here is 1, so S_1 is 0. Furthermore:

$$\Delta S_{conf.} = S_2 - S_1 = S_2$$

where S_2 is the configurational entropy after mixing. Let us try to evaluate S_2. For that we need to evaluate the number of possible configuration after mixing. Let us call this Ω_2. How do we evaluate that? here we are talking about random solution, which means there is a random mixing. All N_1, N_2.. atoms are distributed randomly on the available n sites.

In that case how many number of different ways we can arrange N_1 atoms on n sites. That will be ${}^{N}C_{N_1}$. Now once we arrange N_1 atoms, there are only $N - N_1$ sites left. We select N_2 atoms and arrange them on the available $N - N_1$ sites. There are ${}^{(N-N_1)}C_{N_2}$ number of ways possible in which N_2 atoms can be arranged.

After we arrange N_1 and N_2, number of sites left are $N - N_1 - N_2$ and N_3 atoms can be arranged on these many sites in ${}^{(N-N_1-N_2)}C_{N_3}$ number of ways, and on. Let us write the formula for ${}^{N}C_{N_1}$, it should be:

$${}^{N}C_{N_1} = \frac{N!}{N_1!\,(N-N_1)!}$$

So:

$$\begin{aligned}\Omega_2 &= {}^{N}C_{N_1}\,{}^{(N-N_1)}C_{N_2}\,{}^{(N-N_1-N_2)}C_{N_3} \ldots \\ &= \frac{N!}{N_1!\,(N-N_1)!} \times \frac{N-N_1}{N_2!\,(N-N_1-N_2)!} \times \frac{N-N_1-N_2}{N_3!\,(N-N_1-N_2-N_3)!} \times \ldots\end{aligned}$$

We can simplify this. These cross terms will just keep getting canceled. And finally, we have the expression for Ω_2 :

$$\Omega_2 = \frac{N!}{N_1!\,N_2!\,\ldots N_n!}$$

We can write S_2 is equal to:

$$S_2 = kln\Omega_2$$

So, how do we simplify this further? Each number here is typically a very large number, right? When we talk about one mole of solution that N is going to be 6.023×10^{23} number of atoms. If we are dealing with large numbers, we can use Sterling's approximation.

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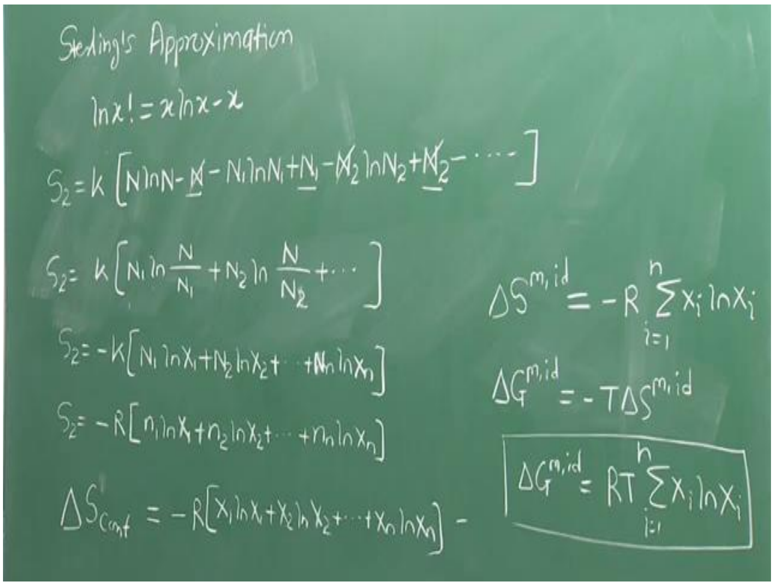

Sterling's Approximation

$$\ln x! = x\ln x - x$$

$$S_2 = k\left[N\ln N - \cancel{N} - N_1\ln N_1 + \underline{N_1} - \cancel{N_2}\ln N_2 + \underline{\cancel{N_2}} - \cdots\right]$$

$$S_2 = k\left[N_1\ln\frac{N}{N_1} + N_2\ln\frac{N}{N_2} + \cdots\right]$$

$$S_2 = -k\left[N_1\ln X_1 + N_2\ln X_2 + \cdots + N_n\ln X_n\right]$$

$$S_2 = -R\left[n_1\ln X_1 + n_2\ln X_2 + \cdots + n_n\ln X_n\right]$$

$$\Delta S_{Conf} = -R\left[X_1\ln X_1 + X_2\ln X_2 + \cdots + X_n\ln X_n\right] -$$

$$\Delta S^{m,id} = -R\sum_{i=1}^{n} X_i\ln X_i$$

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

$$\boxed{\Delta G^{m,id} = RT\sum_{i=1}^{n} X_i\ln X_i}$$

It says:

$$ln x! = x ln x - x$$

If we use this approximation, you can write:

$$S_2 = k(N ln N - N - N_1 ln N_1 + N_1 - N_2 ln N_2 + N_2 - \cdots)$$

$$S_2 = k\left(N_1 ln\frac{N}{N_1} + N_2 ln\frac{N}{N_2} + \cdots\right)$$

$\frac{N}{N_1}$ is the atom fraction of 1 or mole fraction of 1, which we call as X_1. So, we can write this as:

$$S_2 = -k(N_1 ln X_1 + N_2 ln X_2 + \cdots N_n ln X_n)$$

If we multiply and divide the equation by the Avogadro's number we get:

$$S_2 = -R(n_1 ln X_1 + n_2 ln X_2 + \cdots n_n ln X_n)$$

Where R is gas constant and n_i is the number of moles of i component also written as $\frac{N_1}{N_{Av}}$. Basically $\Delta S_{conf.}$ in this case should be equal to S_2, this should be more appropriately $\Delta S'$ because we are talking about the entire system. If we say per mole, we have to divide the equation by the total number of moles, so we can get rid of this prime sign.

So, the molar configurational entropy of mixing is obtained by dividing the previous eq. by total number of moles:

$$\Delta S_{conf.} = -R(X_1 lnX_1 + X_2 lnX_2 + \cdots X_n lnX_n)$$

Basically ΔS^{mixing} for ideal solution, which is all because of the change in configurational entropy should be equal to:

$$\Delta S^{m,id} = -R\sum_{i=1}^{n} X_i ln\, X_i$$

Obviously, since $\Delta H^{m,id} = 0$, delta G m ideal should be equal to:

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

$$\Delta G^{m,id} = RT\sum_{i=1}^{n} X_i ln\, X_i$$

This is the expression we got for the Gibbs free energy of mixing for an ideal solution. If you remember we also derived an expression for Gibbs free energy of mixing for ideal gases, and they have come out to be the same.

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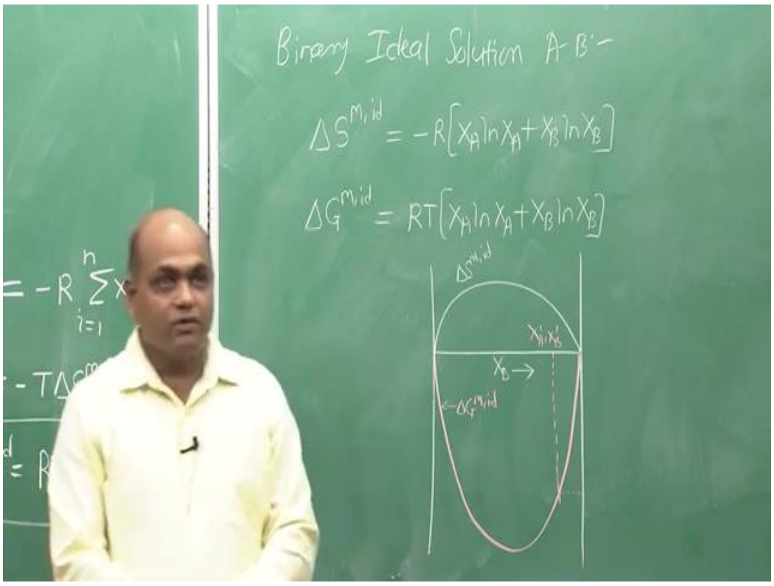

So, let us plot this as a function of composition for just a binary solution of, say components A and B. For binary ideal solution of A and B, we can write:

$$\Delta S^{m,id} = -R(X_A lnX_A + X_B lnX_B)$$

$$\Delta G^{m,id} = RT(X_A lnX_A + X_B lnX_B)$$

Let us plot both these quantities as a function of composition say X_B. X_A and X_B are fractions. The logarithmic terms are negative which means $\Delta S^{m,id}$ has to be positive while $\Delta G^{m,id}$ will be negative.

How do we interpret this curve? Obviously, you see a minimum somewhere. But do not interpret it as the composition corresponding to this minimum is the most stable solution. The way it has to be interpreted is at a given composition, let say X_A^1-X_B^1 $\Delta G^{m,id}$ for ideal solution of A and B is negative. It means if we mix A and B in this proportions, there will be a negative change in Gibbs free energy or this mixing process is an irreversible process. That is the way it has to be interpreted. So, this was for an ideal solution. We will now look into the non-ideal solution that will be in the next class.