Diffusion in Multicomponent Solids
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Lecture 08 - Regular Solution Model: Application to Ternary System

Welcome back to the eighth lecture of open course on Diffusion in Multicomponent Solids. In this lecture, we will go over the statistical model for evaluating the enthalpy of mixing for regular solution. And, again to give a flavor of multicomponent thermodynamics I have treated ternary solution in this lecture.

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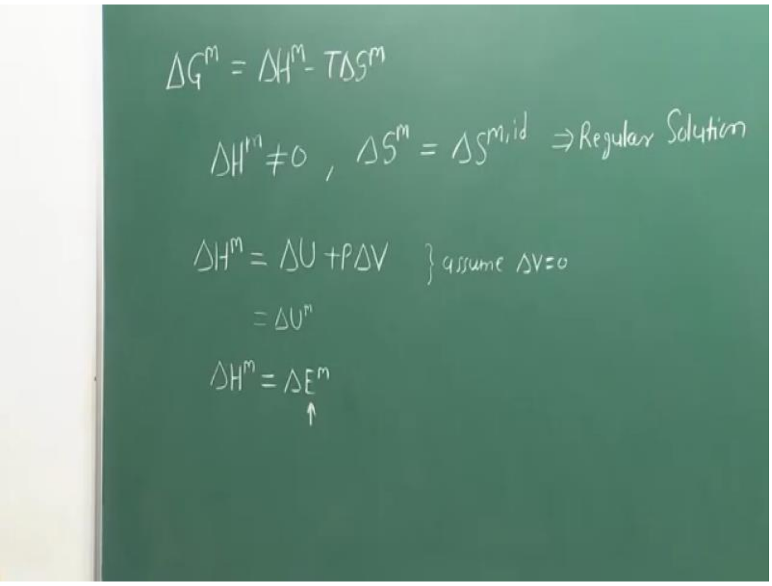

$$\Delta G^m = \Delta H^m - T\Delta S^m$$

$$\Delta H^m \neq 0 \;,\; \Delta S^m = \Delta S^{m,id} \Rightarrow \text{Regular Solution}$$

$$\Delta H^m = \Delta U + P\Delta V \quad \Big\} \text{ assume } \Delta V = 0$$

$$= \Delta U^m$$

$$\Delta H^m = \Delta E^m$$

$$\uparrow$$

in last class we analyzed ideal solutions. Today, we will try to analyze Gibbs free energy of mixing for non-ideal solutions. So:

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

Unlike an ideal solution, for a non-ideal solution delta:

$$\Delta H^m \neq 0$$

heat is either evolved or heat is absorbed during the process of mixing. Why it would happen? Because of the interactions, because A-A, B-B and A-B interactions are different and when we replace some of the A-A and B-B pairs with A-B pairs in the solution, there is a heat effect resulting into potential energy change. the enthalpy changes.

Now when A-A, B-B and A-B interactions are not same then the mixing will not be random like in real solutions. Because there will be some preference for the nearest neighbor pairs. For example, if A-B bonds are stronger than A-A and B-B bonds, then there will be a tendency to form or maximize A-B bonds. On the other hand, if A-B bonds are weaker, there will be a tendency to form A-A and B-B bonds and minimize the number of A-B bonds. There will be a kind of short range order associated with the difference in the interactions. And, the mixing process will not be completely random.

And, ΔS mixing will not be same as that for an ideal mixing where we assume random mixing. But, in order to understand this interaction effect let us try to simplify the model. Let us assume that:

$$\Delta H^m \neq 0$$

But,

$$\Delta S^m = \Delta S^{m,\ ideal}$$

This is the regular solution model. We now need to evaluate the enthalpy of mixing. ΔH^m at constant temperature and pressure is:

$$\Delta H^m = \Delta U + P\Delta V$$

We make further assumption that ΔV is negligible. And so:

$$\Delta H^m = \Delta U^m$$

ΔH^m just becomes equal to the change in internal energy.

Further the temperature is constant, we do not need to consider the changes in kinetic energy, therefore:

$$\Delta H^m = \Delta E^m$$

Where E denotes the potential energy part. And, the change in potential energy is only because of the changes in the types of pairs or changes in the number of particular bonds A-A, B-B or A-B in a binary solution.

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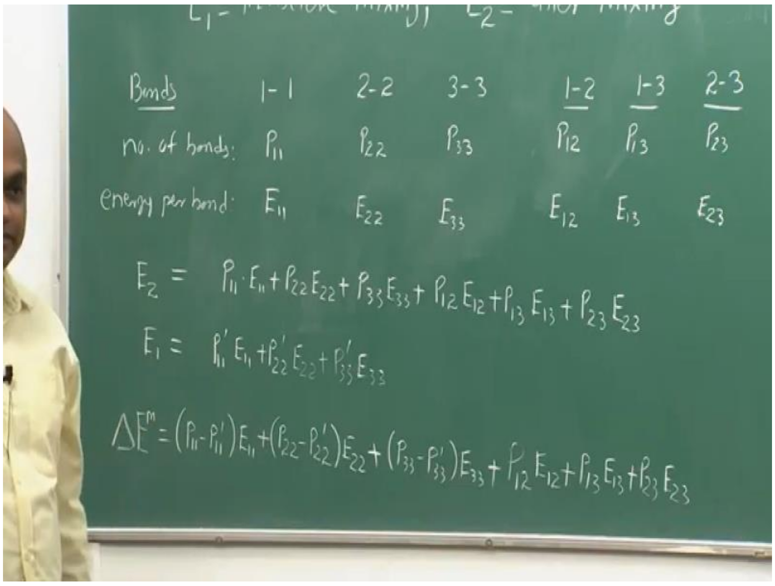

Bonds	1-1	2-2	3-3	1-2	1-3	2-3
no. of bonds:	P_{11}	P_{22}	P_{33}	P_{12}	P_{13}	P_{23}
energy per bond:	E_{11}	E_{22}	E_{33}	E_{12}	E_{13}	E_{23}

$$E_2 = P_{11} \cdot E_{11} + P_{22}E_{22} + P_{33}E_{33} + P_{12}E_{12} + P_{13}E_{13} + P_{23}E_{23}$$

$$E_1 = P'_{11}E_{11} + P'_{22}E_{22} + P'_{33}E_{33}$$

$$\Delta E^m = (P_{11} - P'_{11})E_{11} + (P_{22} - P'_{22})E_{22} + (P_{33} - P'_{33})E_{33} + P_{12}E_{12} + P_{13}E_{13} + P_{23}E_{23}$$

Let us try to evaluate change in potential energy and let us consider a ternary solution, for example, 1 mole of solution formed by mixing of N_1 atoms of 1, N_2 atoms of 2 and N_3 atoms of 3. Let us denote their potential energy before mixing as E_1, potential energy after mixing as E_2.

Now if we consider the solution after mixing, how many different types of bonds will be there? There will be of course 1-1, 2-2 and 3-3 type of bonds. Then there will also be dissimilar atom interactions or bonds, 1-2, 1-3, 2-3. So in total 6 types of bonds. Let us say there are P_{11} number of 1-1 type of bonds, and each bond has an energy E_{11}.

Similarly, P_{22} number of 2-2 bonds each having energy E_{22}, P_{33} number of 3-3 bonds each having energy E_{33}, P_{12} bonds with energy E_{12} per bond, P_{13} bonds with energy E_{13} and P_{23} bonds with energy E_{23}. So, what will be the total energy after mixing?

$$E_2 = P_{11}E_{11} + P_{22}E_{22} + P_{33}E_{33} + P_{12}E_{12} + P_{13}E_{13} + P_{23}E_{23}$$

And what will be the energy before mixing? Before mixing there will be no dissimilar bonds, only 1-1, 2-2 and 3-3 bonds and their numbers will be obviously different. Let us assume they are P'_{11}, $P'_{22}$and P'_{33} respectively. In that case total potential energy before mixing will be:

$$E_1 = P'_{11}E_{11} + P'_{22}E_{22} + P'_{33}E_{33}$$

And:

$$\Delta E_m = E_2 - E_1$$

$$\Delta E_m = (P_{11} - P'_{11})E_{11} + (P_{22} - P'_{22})E_{22} + (P_{33} - P'_{33})E_{33} + P_{12}E_{12} + P_{13}E_{13} + P_{23}E_{23}$$

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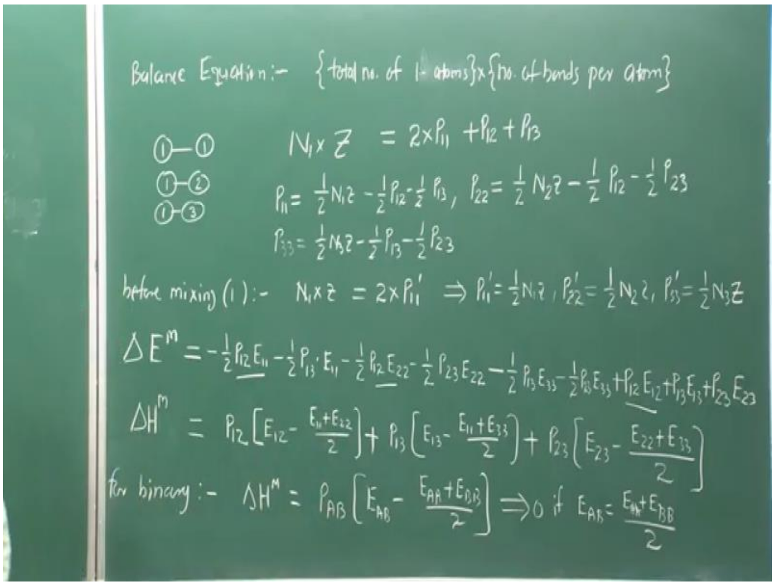

Balance Equation:- {total no. of 1- atoms}×{no. of bonds per atom}

①—① $N_1 \times Z = 2\times P_{11} + P_{12} + P_{13}$

①—②

①—③

$P_{11} = \frac{1}{2} N_1 Z - \frac{1}{2} P_{12} - \frac{1}{2} P_{13}$, $P_{22} = \frac{1}{2} N_2 Z - \frac{1}{2} P_{12} - \frac{1}{2} P_{23}$

$P_{33} = \frac{1}{2} N_3 Z - \frac{1}{2} P_{13} - \frac{1}{2} P_{23}$

before mixing (1):- $N_1 \times Z = 2\times P'_{11} \Rightarrow P'_{11} = \frac{1}{2} N_1 Z,\ P'_{22} = \frac{1}{2} N_2 Z,\ P'_{33} = \frac{1}{2} N_3 Z$

$\Delta E^m = -\frac{1}{2}\underline{P_{12}E_{11}} - \frac{1}{2}P_{13}\cdot E_{11} - \frac{1}{2}\underline{P_{12}}E_{22} - \frac{1}{2}P_{23}E_{22} - \frac{1}{2}P_{13}E_{33} - \frac{1}{2}P_{23}E_{33} + \underline{P_{12}E_{12}} + P_{13}E_{13} + P_{23}E_{23}$

$\Delta H^m = P_{12}\left[E_{12} - \frac{E_{11}+E_{22}}{2}\right] + P_{13}\left(E_{13} - \frac{E_{11}+E_{33}}{2}\right) + P_{23}\left(E_{23} - \frac{E_{22}+E_{33}}{2}\right]$

for binary:- $\Delta H^m = P_{AB}\left[E_{AB} - \frac{E_{AA}+E_{BB}}{2}\right] \Rightarrow 0$ if $E_{AB} = \frac{E_{AA}+E_{BB}}{2}$

Now all we need to do is evaluate this number of bonds. To do that let us apply the balance equation for number of bonds. First we have to find the total number of bonds in which, for example, atoms of type 1 are involved. They will be either 1-1 or 1-2 or 1-3 and there are N_1 number of 1 atoms. So each atom 1 will bond with Z number of atoms which is the coordination number of 1. It can be written as:

$$N_1 Z = 2P_{11} + P_{12} + P_{13}$$

For 1-1 type of bond we have to count twice as this bond is shared by two 1 atoms. For the dissimilar type of bonds we have to count only once. Or we can write:

$$P_{11} = \frac{1}{2}N_1 Z - \frac{1}{2}P_{12} - \frac{1}{2}P_{13}$$

Similarly, we can apply this for atoms of type 2 and also atoms of type 3 and we will get:

$$P_{22} = \frac{1}{2}N_2 Z - \frac{1}{2}P_{12} - \frac{1}{2}P_{23}$$

$$P_{33} = \frac{1}{2}N_3 Z - \frac{1}{2}P_{13} - \frac{1}{2}P_{23}$$

Now if we apply this equation before mixing, where we essentially have pure 1, pure 2 and pure 3 then we get :

$$N_1 Z = 2P'_{11}$$

Or

$$P'_{11} = \frac{1}{2} N_1 Z$$

as there are no dissimilar bonds. Similarly:

$$P'_{22} = \frac{1}{2} N_2 Z$$

$$P'_{33} = \frac{1}{2} N_3 Z$$

Now if we substitute for P_{11} and P'_{11} in this equation, we can find ΔE_m as:

$$\Delta E_m = -\frac{1}{2} P_{12} E_{11} - \frac{1}{2} P_{13} E_{11} - \frac{1}{2} P_{12} E_{22} - \frac{1}{2} P_{23} E_{22} - \frac{1}{2} P_{13} E_{33} - \frac{1}{2} P_{23} E_{33} + P_{12} E_{12} + P_{13} E_{13} + P_{23} E_{23}$$

Essentially we have found here ΔH_m.

Student: Sir, how can we assume that the coordination number for the all the three type of atoms can be same?

Professor: Okay. That is a good question. There is an assumption that we are making here. We are starting with same crystal structure as the crystal structure of the solution.

That is how we systematically form a thermodynamic solution. For example, in a binary if we want to form a solution between A and B which is FCC, we first bring pure A to FCC structure, we bring pure B to FCC structure and then mix the two to form the final FCC solution. If A and B are stable as FCC, then we just have to consider A and B in stable phases.

But suppose B is not stable as FCC, B is stable as HCP, we first have to covert HCP to FCC. There will be some Gibbs free energy change associated with it. And, then we mix the two to form the final solution which is FCC. And that is why we are considering the coordination number here as the same.

If we rearrange the previous equation we get:

$$\Delta E_m = P_{12} \left[E_{12} - \frac{E_{11} + E_{22}}{2} \right] + P_{13} \left[E_{13} - \frac{E_{11} + E_{33}}{2} \right] + P_{23} \left[E_{23} - \frac{E_{33} + E_{22}}{2} \right]$$

We are multiplying the number of dissimilar bonds with the difference between the energy of that dissimilar bond and the average of the similar type of bonds.

If write this for binary solution A-B, for example, this will be:

$$\Delta H_m = P_{AB}\left[E_{AB} - \frac{E_{AA} + E_{BB}}{2}\right]$$

And,

$$\Delta H_m = 0 \;\; if \; E_{AB} = \frac{E_{AA} + E_{BB}}{2}$$

This will be 0 if E_{AB} is equal to average of A-A and B-B bond energy. If:

$$E_{AB} = \frac{E_{AA} + E_{BB}}{2}$$

ΔH_m is 0 and then it is an ideal solution. So, for solution to be an ideal solution we initially said that the interactions have to be same. But it can be little more relaxed. As long as the A-B bond energy is equal to the average of A-A and B-B bond energies, we can still get an ideal solution. If we have a ternary solution then that has to be true for each of the dissimilar pair. Then solution is an ideal solution. Even if for 1 of the pair, it is not true then you will have some non-zero value of ΔH_m. And the solution will be non-ideal.

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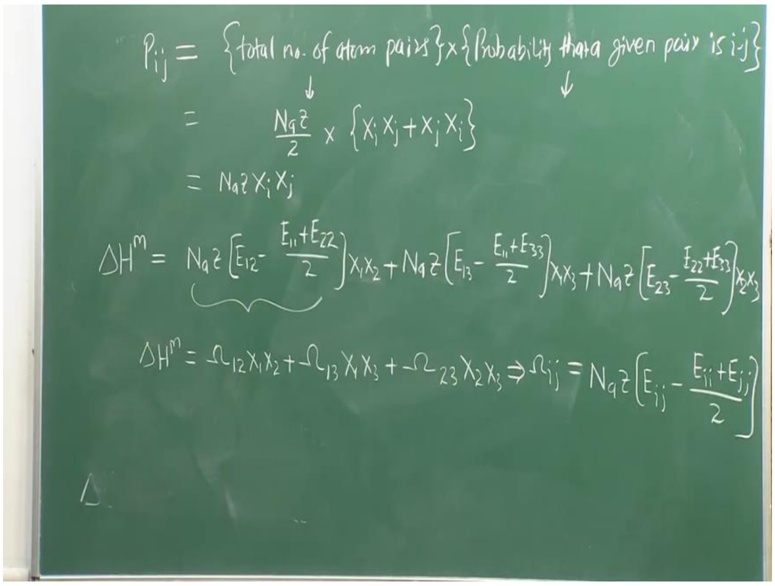

$$P_{ij} = \{\text{total no. of atom pairs}\} \times \{\text{Probability that a given pair is i-j}\}$$

$$= \frac{N_a z}{2} \times \{X_i X_j + X_j X_i\}$$

$$= N_a z X_i X_j$$

$$\Delta H^m = \underbrace{N_a z\left[E_{12} - \frac{E_{11}+E_{22}}{2}\right]} X_1X_2 + N_a z\left[E_{13} - \frac{E_{11}+E_{33}}{2}\right]X_1X_3 + N_a z\left[E_{23} - \frac{E_{22}+E_{33}}{2}\right]X_2X_3$$

$$\Delta H^m = \Omega_{12}X_1X_2 + \Omega_{13}X_1X_3 + \Omega_{23}X_2X_3 \Rightarrow \Omega_{ij} = N_a z\left[E_{ij} - \frac{E_{ii}+E_{jj}}{2}\right]$$

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Now to look into this further we need to evaluate $P_{ij}'s$, where i and j are different types of atoms. So how do we evaluate P_{ij}? Number of $i-j$ pairs. If we know the total number of pairs and multiply it by the probability that a particular pair is an $i-j$ pair, we will get P_{ij}.

This first term will be how many total number of atoms pairs are there. This will be simply $\frac{N_aZ}{2}$. It is total number of atoms × number of bonds per atom and since we are counting each bond twice we divide by 2. Now if we have a crystal structure with given number of atom pairs, what is the probability that a selected pair let us say this one is an $i-j$ pair.

We select the first atom and then the next nearest neighbor. What is the probability that the first atom is an i atom? If we consider random solution which we are considering here, this probability is nothing but the mole fraction of i atom. It is then multiplied by the probability that the next atom is a j atom which is X_j. This will be $X_i \times X_j$. We can also select first atom to be a j atom and the next one to be an i atom. In that case it will be $X_j \times X_i$. So,

$$P_{ij} = \frac{N_aZ}{2}\left(X_iX_j + X_jX_i\right) = N_aZX_iX_j$$

For ternary we get:

$$\Delta H_m = N_aZ\left[E_{12} - \frac{E_{11}+E_{22}}{2}\right]X_1X_2 + N_aZ\left[E_{13} - \frac{E_{11}+E_{33}}{2}\right]X\quad X_3 + N_aZ\left[E_{23} - \frac{E_{33}+E_{22}}{2}\right]X_2X_3$$

Or,

$$\Delta H_m = \Omega_{12}X_1X_2 + \Omega_{13}X\quad X_3 + \Omega_{23}X_2X_3$$

Where,

$$\Omega_{ij} = N_aZ\left[E_{ij} - \frac{E_{ii}+E_{jj}}{2}\right]$$

Clear? So, we have the expression for molar enthalpy of mixing in terms of bond energies of different types in the solution.

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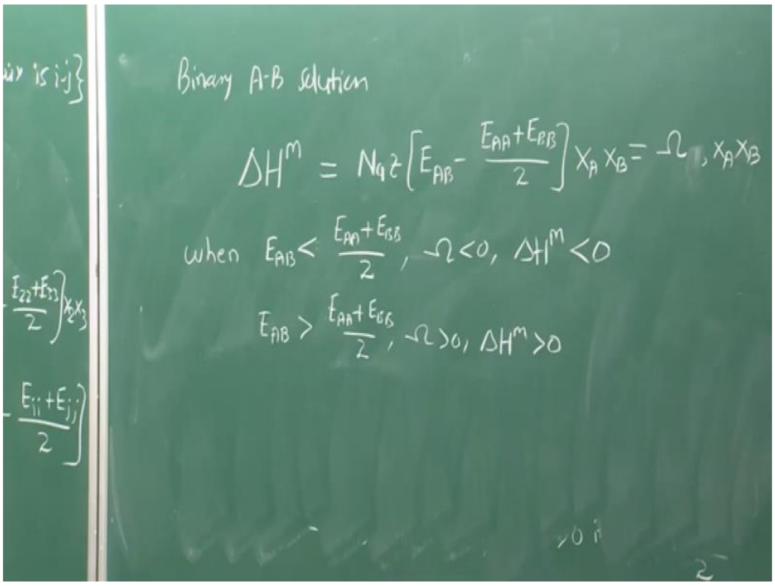

If we consider the binary solution then:

$$\Delta H_m = N_a Z\left[E_{AB} - \frac{E_{AA}+E_{BB}}{2}\right] X \quad X_B$$

Since there is only one term, we can just call it Ω:

$$\Delta H_m = \Omega X \quad X_B$$

where

$$\Omega = N_a Z\left[E_{AB} - \frac{E_{AA}+E_{BB}}{2}\right]$$

Now when A-B bond energy is same as or is equal to the average of A-A and B-B bond energies then $\Delta H_m = 0$ and the solution is ideal. But, when:

$$E_{AB} < \frac{E_{AA}+E_{BB}}{2}, \quad \Omega < 0, \qquad \Delta H_m < 0$$

Essentially, what this means is if A-B bonds are stronger or have lesser bond energy than average of A-A and B-B bonds, then the enthalpy of mixing is negative. Which means heat will be released during the process of mixing. We have seen this when we studied the Raoult's law and the Henry’s law, or how the vapor pressures vary with composition.

If you remember we said that if A-B bonds are stronger than A-A or B-B bonds, the evaporation rate or the intrinsic evaporation rate of A will come down by going into the solution from pure state. That corresponded to the negative deviation from ideality. Negative deviation of ideality also means that ΔH_m mixing is negative. Similarly, if A-B bonds are stronger than A-A or B-B, which means in this case if:

$$E_{AB} > \frac{E_{AA} + E_{BB}}{2} \;\; then \quad \Omega > 0, \qquad \Delta H_m > 0$$

It means heat will be absorbed during the process of mixing. If A-B bonds are weaker it means A-B bonds will have higher energy than average of A-A and B-B. And by forming solution you are replacing some A-A and some B-B bonds with A-B bonds. So, you are replacing stronger bonds with weaker bonds, you are replacing bonds with lower energy with bonds with higher energy, which means energy has to be provided to form the solution. And, that is why ΔH_m will be positive. This is important, so we went over this model in little bit details because it is important to understand how the interactions between the atoms give rise to the changes in the Gibbs free energy or basically changes in the enthalpies and entropies They also affect the diffusion, especially the cross-effects.

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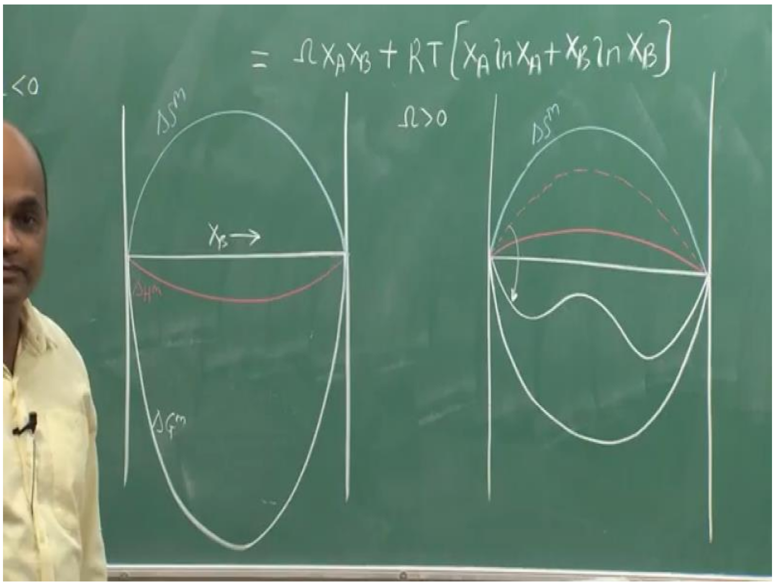

Because of these different interactions the atom jumps will be biased in a multicomponent system. And it is important to understand this, how this atom interactions affect the Gibbs free energy changes. Now if we plot for an A-B solution, for regular solution:

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

For binary solution:

$$\Delta G^{m,reg} = \Omega X \quad X_B + RT(X_A ln\, X_A + X_B ln\, X_A)$$

Now if we try to plot ΔH_m, $\Delta S_m$and ΔG_m for a regular solution, when let us say $\Omega < 0$ delta:

$$\Delta H_m < 0$$

$\Omega X \quad X_B$ have a shape something like this which is ΔH_m .

$$\Delta S^{m,\ reg} = \Delta S^{m,\ id}$$

We know it will be positive always. And if we evaluate ΔG_m at each of the composition, it will be negative everywhere.

What if Ω is positive? ΔS_m will still be positive everywhere. Now ΔH_m is positive and we will see that the magnitudes of ΔG_mwill be would be lesser than what it will be for negative Ω. As Ω becomes more and more positive, what happens? This curve will increase, it will also affect the curvature of ΔG_m. And when $\Delta H_m$is very high, you will see there will be a negative curvature developed on the ΔG_mcurve. This delta ΔG_m curve corresponds to this ΔH_m. We are still assuming ideal or random mixing, so ΔS_mwill not change for assumption of random mixing. But then because ΔH_m is becoming more and more positive, it will affect the curvature and at beyond certain value of ΔH_m, ΔG_m curve will just develop a negative curvature in between. Now this is very important because it will affect the stability of the solution. And how it will affect, we will see in the next class. Any question so far? All clear? Okay. Thank you.