Heat Treatment and Surface Hardening - II

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Lecture – 19
Expression for ΔHmix as a function of interaction energy and mole fraction, based on the QCM (part-II)

Hello everyone. Let us start lecture 19. Today we will finish our discussion on del hmix.

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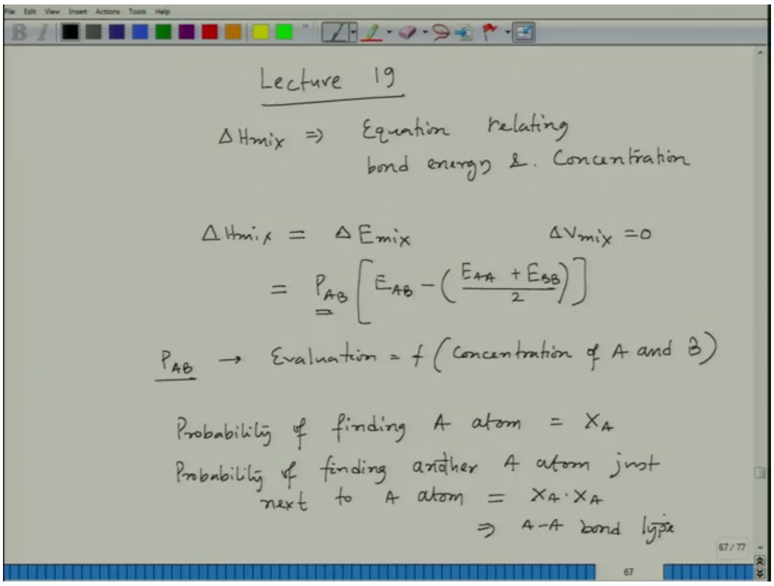

Lecture 19

$\Delta H_{mix} \Rightarrow$ Equation relating bond energy & Concentration

$\Delta H_{mix} = \Delta E_{mix}$ $\quad \Delta V_{mix} = 0$

$= \underline{\underline{P_{AB}}} \left[E_{AB} - \left(\frac{E_{AA} + E_{BB}}{2} \right) \right]$

$\underline{P_{AB}} \rightarrow$ Evaluation $= f$(Concentration of A and B)

Probability of finding A atom $= X_A$

Probability of finding another A atom just next to A atom $= X_A \cdot X_A$

$\Rightarrow$ A-A bond type

And it is equation relating bond energy and concentration. In our last lecture we have seen that del Hmix is nothing but del Emix since we have considered del vmix equal to 0, this is the assumption which is considered while constructing quasi chemical model. And then it becomes PAB, which is the number of AB bonds in a binary solution of A and B with this energy contribution.

Now, we have to find out the value of PAB. This evaluation we have to do as a function of concentration of A and B in the mixture. Now if we have some lattice and that lattice is formed by A and B atoms, then the probability of finding A atom at any site is equal to XA which is the mole fraction or the atom fraction. Now the probability of finding another A atom just next to the to A atom is nothing but XA into XA.

That means this indicating AA bond type or other way the probability of formation of AA bond.

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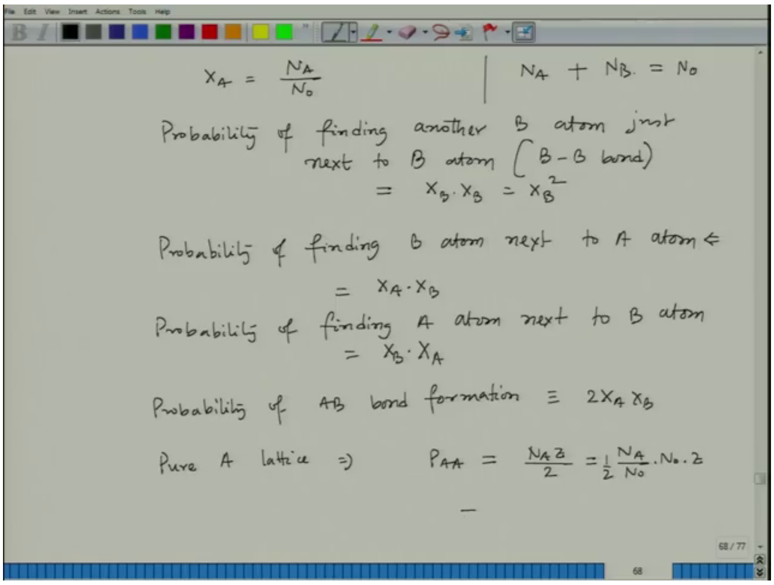

$X_A = \frac{N_A}{N_0}$ | $N_A + N_B = N_0$

Probability of finding another B atom just next to B atom (B - B bond)

$= X_B \cdot X_B = X_B^2$

Probability of finding B atom next to A atom ⇐

$= X_A \cdot X_B$

Probability of finding A atom next to B atom

$= X_B \cdot X_A$

Probability of AB bond formation $\equiv 2 X_A X_B$

Pure A lattice ⇒ $P_{AA} = \frac{N_A Z}{2} = \frac{1}{2} \frac{N_A}{N_0} . N_0 . Z$

And remember here Xa is equal to NA by n 0. Since we have considered in the beginning that any number of A atom and NB number of B atom are joined together or mixed together and that time this combination of these 2 gives us Avogadro number of atoms; that means, you are we are forming one mole of mixture or solution.

Similarly, same way the probability of finding another B atom, just next to another B atom which is nothing but the probability of finding BB bond is nothing but XB into XB which is XB square, and this also leads to XA square. So, now, we see that if in a mixture we have A and B type of atoms, then what is the probability of finding AA bond type or BB bond type, which is proportional to X square as well as XB square.

Now, we have to find out that what is the probability of finding A atom next to a B atom or finding B atom, next to AA atom that would lead to the concept of probability of finding AB type of bond. So, now, probability of finding B atom, next to A atom is nothing but first is the probability of finding A atom at any site which is XA and then the next site would be occupied by B atom. So, XB if we try to find out AB bond with reference to A atom because here we are trying to find out AB bond with reference to A atom. Where also see the possibility of AB one formation of a with ref with reference to B atom so; that means, probability of finding A atom next to B atom would be first is the probability of finding B atom at any site is XB. And then next will be the probability of finding A atom next to it.

So, hence probability of AB bond formation would be proportional to XA XB 2. So; that means, this 2 is coming because, one case we are finding it AB, one formation probability with reference to A atom. And in the second case we are finding AB bond formation with reference to B atom. Now if i try to see a pure case pure a lattice. So, that time we know that PAA that is number of a type of bond in case of pure substance is nothing but NA Z by 2, I can write it in this fashion NA by N0 n 0 into Z half.

So, it is nothing but N0 into Z into XA. Now this is the number of AA type bond in pure case, but once we consider a mixed situation; that means, we have AA A type of atom as well as B type of atom both are present in the crystal which is formed after mixing A atom as well as B atom. So, that case in case of mixture.

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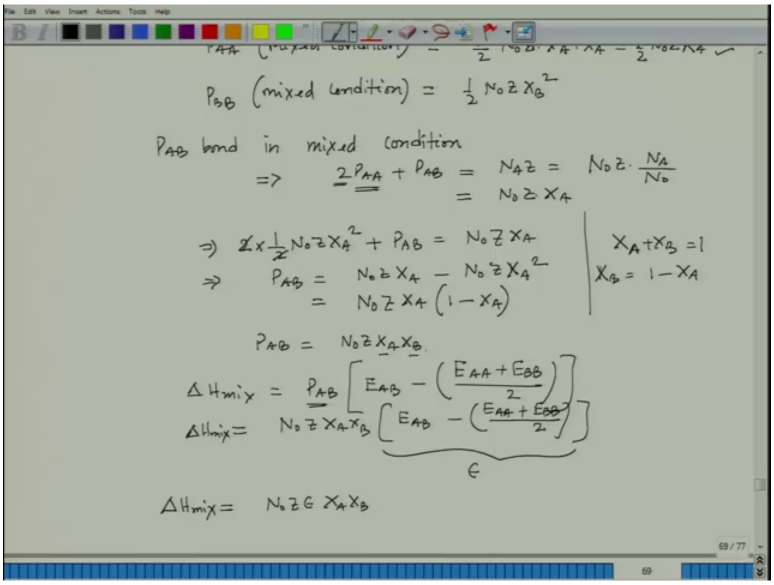

$$P_{BB}\ (\text{mixed condition}) = \frac{1}{2} N_0 Z X_B^2$$

P_{AB} bond in mixed condition

$$\Rightarrow \quad \underline{2} \underline{\underline{P_{AA}}} + P_{AB} = N_A Z = N_0 Z \cdot \frac{N_A}{N_0}$$
$$= N_0 Z X_A$$

$$\Rightarrow \cancel{2} \times \frac{1}{\cancel{2}} N_0 Z X_A^2 + P_{AB} = N_0 Z X_A$$
$$\Rightarrow \quad P_{AB} = N_0 Z X_A - N_0 Z X_A^2$$
$$= N_0 Z X_A (1 - X_A)$$

$$X_A + X_B = 1$$
$$X_B = 1 - X_A$$

$$P_{AB} = N_0 Z \underline{X_A} \underline{X_B}$$

$$\Delta H_{mix} = \underline{\underline{P_{AB}}} \left[E_{AB} - \left(\frac{E_{AA} + E_{BB}}{2} \right) \right]$$

$$\Delta H_{mix} = N_0 Z X_A X_B \underbrace{\left[E_{AB} - \left(\frac{E_{AA} + E_{BB}}{2} \right) \right]}_{\epsilon}$$

$$\Delta H_{mix} = N_0 Z \epsilon X_A X_B$$

Or solution initially if we consider the solution formation that time; I will have this concept valid z.

Now, if I try to find out pa in the mixed condition that time I have to just multiply this factor with or this factor with XA because I am trying to find out position of A next to another A atom. So, it would be half NA N0 or N0 Z XA into XA is equal to half N0 Z XA square. I can also find out BB in mixed condition is equal to half N0 Z XB square.

Now, if I try to find out PAB bond in mixed condition would be equal to 2 PAA plus PAB equal to NA Z equal to N0 Z NA by N0 Z XA. I have already found out the value of PAA in the mixed condition which is this one. So, I just replace that value half N0 Z XA square plus PAB equal to N0 Z XA. Remember this Z is coordination number.

So, now we can get PAB equal to N0 Z into 2 because here we have to consider this 2 factor. So, N0 Z XA minus N0 Z XA square; so then becomes N0 Z XA 1 minus XA we already know that XA plus XB equal 1. Hence XB equal to 1 minus XA. So, if I replace that PAB equal to N0 Z XA XB. Now I know that del h mix equal to PAB EAB minus by 2. So, then I just put the value of PAB as a function of coordination number; mole fraction of A and B in the mixture, so then N0 Z XA XB EAB minus EAA plus ebb by 2.

So, this is my final del hmix expression. Since this one we have consider as energy e. So, then I can write del hmix e XA XB. This particular term is written as omega. So, I can write it as XA XB omega.

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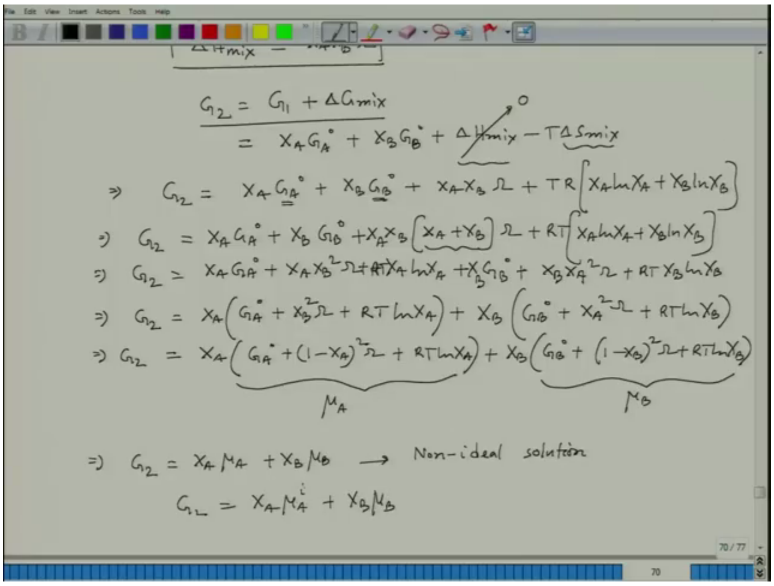

$\Delta H_{mix} =$

$$\underline{G_2 = G_1 + \Delta G_{mix}}$$
$$= X_A G_A^\circ + X_B G_B^\circ + \underbrace{\cancelto{0}{\Delta H_{mix}}} - T\underbrace{\Delta S_{mix}}$$
$$\Rightarrow G_2 = X_A \underline{G_A^\circ} + X_B \underline{G_B^\circ} + X_A X_B \Omega + TR\left[X_A \ln X_A + X_B \ln X_B\right]$$
$$\Rightarrow G_2 = X_A G_A^\circ + X_B G_B^\circ + X_A X_B \left[\underbrace{X_A + X_B}\right]\Omega + RT\left[X_A \ln X_A + X_B \ln X_B\right]$$
$$\Rightarrow G_2 = X_A G_A^\circ + X_A X_B^2 \Omega + RT X_A \ln X_A + X_B G_B^\circ + X_B X_A^2 \Omega + RT X_B \ln X_B$$
$$\Rightarrow G_2 = X_A\left(G_A^\circ + X_B^2 \Omega + RT \ln X_A\right) + X_B\left(G_B^\circ + X_A^2 \Omega + RT \ln X_B\right)$$
$$\Rightarrow G_2 = X_A \underbrace{\left(G_A^\circ + (1-X_A)^2 \Omega + RT \ln X_A\right)}_{\mu_A} + X_B \underbrace{\left(G_B^\circ + (1-X_B)^2 \Omega + RT \ln X_B\right)}_{\mu_B}$$

$$\Rightarrow G_2 = X_A \mu_A + X_B \mu_B \longrightarrow \text{Non-ideal solution}$$
$$G_2 = X_A \mu_A^i + X_B \mu_B$$

So, the final expression in terms of omega; it becomes XA XB this this is my final expression, now we started with ideal solution, where del hmix was considered as 0. Now this was minus this was my initial expression when we try to consider solution formation. So, this can be written as XA GA 0 plus XB GB 0 plus del h mix minus t del s mix during in case of ideal solution this is 0, but since we are considering non ideal case where del hmix can have positive or a negative value depending on the value of this quantity, it can be positive or it can be negative.

So, then we have to consider this del h mix value in our calculation of G2 or the free energy of mixed solution phase it can be liquid it can be solid; so this particular G2 as we have understood that this is indicating free energy of a particular phase in the mixed condition or solution condition. Now we can do little bit of adjustment here XA GA 0 plus XB, GB 0. See this 0 superscript 0 is indicating the standard value and every time this is indicating a particular phase when that pure metal is in that particular phase, let us say if it is a solid. So, both the standard values are indicative of pure solid A and pure solid B at one atmosphere pressure at of course the temperature what where we are considering that solution formation.

Plus, XA XB minus t now I can replace this del hmix expression XA ln XA plus XB ln XB. Then G2 equal to XA GA 0 plus XB GB 0, plus I can write this one as XA plus XB. Now this is nothing but one. So, I can just make a mention of this plus RT XA ln XA plus XB ln XB G2 would be equal to XA GA 0, plus XA XB square plus XA ln XA plus G XB GB 0 plus XB X square plus RT XB ln XB. I just redistribute the entire expression. So, I can write G2 equal to XA GA 0 plus XB plus sorry I just missed 1 RT term here RT ln XA plus XB GB 0 plus XA s square plus RT ln XB.

Then I can write it as XA, 1 minus XA if I convert everything in terms of XA because one side would be all XA and another side would be all XB plus RT ln XA plus XB GB 0 plus 1 minus XB square plus RT ln XB. Now this entire term can be written in the form of chemical potential, which is the chemical potential of A and this one is nothing but chemical potential of B in that particular phase.

So, G2 equal to XA mu A plus XB mu B this is in case of non ideal solution. Now here the only difference if I try to find out the expression for G2 in case of ideal situation G2 equal to XA mu A plus XB mu B. I simply put id in case of ideal solution, that time the only extra part is this quantity or in this case this is quantity; so the difference between chemical potential in case of non ideal solution and chemical potential of that particular element or component in that solution.

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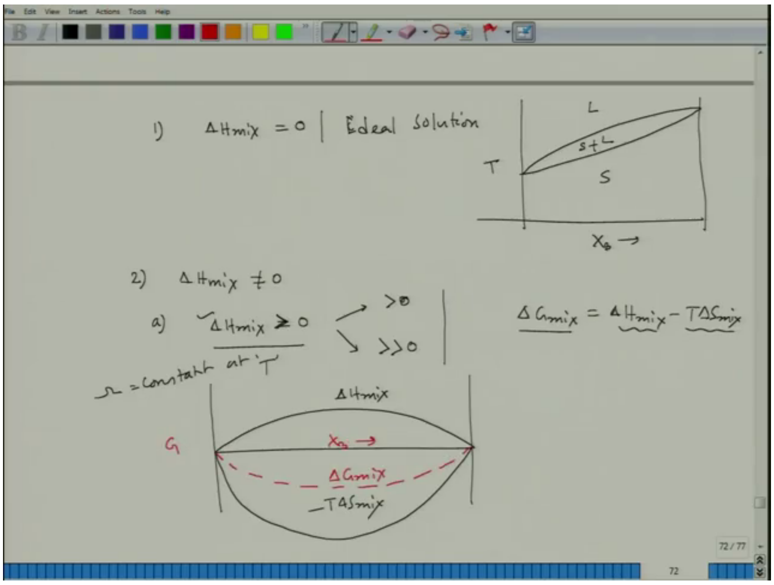

In case of ideal case the difference is in case of mu A and 1 minus XB square in case of mu B. This is the difference mu A and mu B with mu A ideal and mu B ideal.

And just to mention mu A ideal is equal to GA 0 plus RT ln XA. And mu B ideal is equal to GB 0 plus RT ln XP. So, these has been shown in previous lectures. So, the final expression for in case of non ideal situation is nothing but XA mu A plus XB mu B. This is the expression for non ideal situation. At any concentration if I try to find out the free energy of the mixture, we have to just put a tangent at that particular composition on that free energy line G2 line and see their intersection point on 2 pure metal site.

So, for example, if I try to see this particular free energy composition diagram, let us see if this is g this is XB. And in case of non ideal situation if my free energy line is this this is G2, let us say some phase some phase this p means phase. So, then let us say if I try to find out at X 0 what would be my chemical potential in case of non ideal situation, I just need to draw a tangent on that particular point over that free energy line. And this would be my mu B and this would be my mu A of that phase of that phase.

So, it is exactly the similar trend, but only thing is our free energy calculation needs to take care of del hmix or this omega term. Now we have seen situation, 3 see one situation we have already seen which is del h mix is equal to 0. And accordingly we have done all sort of calculations in order to find out phase diagram because that time, to solve that mixture that particular those particular situations who was little easy because we did not have to consider del hmix. And for example, in this case which is absolute ideal situation ideal solution and we have drawn an isomorphous phase diagram. And in that case we have taken a solid liquid isomorphous situation.

But if it is non 0 value, then situation would be little complicated. Let us consider a situation where del hmix is equal to is greater than 0. When we are considering greater than 0 it can have 2 more situations, one is del hmix greater than 0 or greater than greater than0. So, this 2 situation can arise, but simply if we try to consider if it is greater than 0 what would be it is effect on the free energy line of the solution of a particular phase. So, in order to do that we have to draw free energy composition diagram, along with the plot of del hmix as well as plot of minus t del hmix. So; that means, del g mix would have effect from both del h mix as well as minus t del s mix.

Since this is slightly positive, I can write it like this. And that time we are considering this is constant at temperature t where we are considering this particular plot this is del h mix. And minus t del s mix would be always negative. So, minus t del s mix. So, del g mix would be in between. So, this would be my del g mix. And here g and this is XB. So, this is a situation because this is a combination of both. So, that is what you are getting in between, but this situation would be different if in the center position this value is greater than this value, if we take the mod value of both the cases and this that time situation would be little different and we will get entirely different plots.

So, we will discuss it in our next lecture.

Thank you.