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Phase field modelling: the materials science, mathematics and computational aspects

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Module No.1
Lecture No.1
Tutorial – 3

Welcome this tutorial is related to the regular solution model. In the regular solution model we wrote that the change in enthalpy ΔH or in our case that is the same as ΔU is some regular solution parameter Ω times XA, XB where XA and XB are the mole fractions of A and B atoms. So we want to know what is the relationship of this Ω the regular solution parameter to the crystal structure and the bond energy.

So that is what we are going to derive in this tutorial. Again this is taken from introduction to thermodynamics of materials gas kill. This derivation is not given in porter and a sterling this derivation is not given it just refers to gas kill. So from gas kill we are going to do this derivation. So we are going to assume that the Avogadro number, so I am going to take a mole of material.

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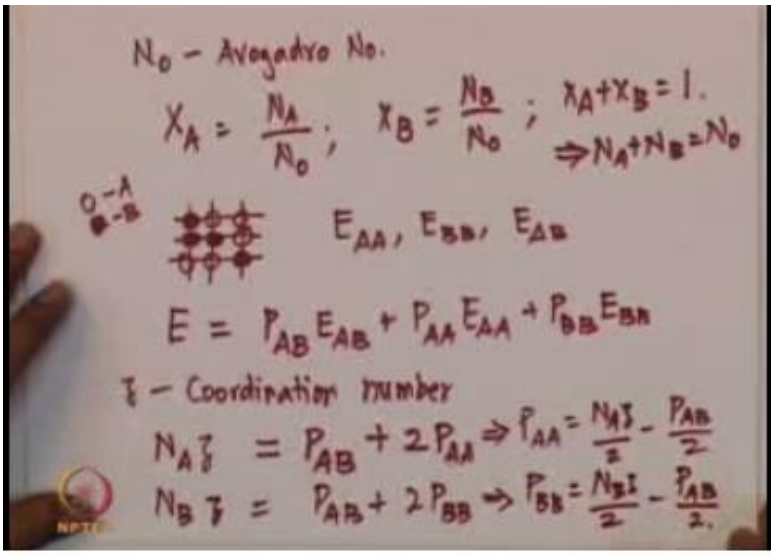

So the Avogadro number I am going to denote by n not. So EA which is the mole fraction of A I am going to say is given by NA/N0 and XB which is the mole fraction of B is going to be given by NB/N0 and I am going to assume that XA + XB = 1 which implies basically that NA+NB=N. In other words we have only A and B species nothing else is there so the lattice is either occupied by an A atom or occupied by a B atom.

Now let us say that suppose I have a lattice and I have this A, B atoms okay. So this is A, so this B okay. So I have this distribution then I want to know what is the energy and I am assuming that all the contribution to the energy is coming from the bond energy, so that is the approximation we are making. So let us say that all this is coming from EAA, EBB and EAB, these are the bond energy.

Suppose if I take two A atoms and from infinity if I bring them together they are going to form a bond and that bond strength is A, and if I take two B atoms and bring them together from infinity towards each other then they form a bond and that bond energy is BB and AB atoms form the bond AB. So what is the total energy then that energy E is nothing but probability of finding an AB bond AB+ number of EAA bonds plus number of BB bonds right.

So if I take the total number of BB bonds multiplied by the BB bond energy total number of AA bonds and multiplied by the AA bond energy total number of AB bonds and multiplied by the AB bond energy of course I will get the total energy okay. Now let us say that in my crystal structure Z is the coordination number, that is the number of nearest neighbors that are there in my structure.

So this is 6 for cubic, and 8 for body centered cubic, and 12 for face centered cubic and so on and so forth okay. So these are the total number of nearest neighbors and in terms of their bond energies we know. So if I want to know how many bonds are associated with A atoms of course, there are NAA atoms and Z is the coordination number, so that will be the total number of A bonds because if I am having A atom here and if I have four neighbors so it will have four bonds and so on and so forth right.

And that will be equal to total number of AB bonds because in each there will be an A atom associated and 2 times AA bonds, because, you know if I have A atom here I will count and if that also happens to be an A atom for that also I will count towards this bond. So there are twice the number of bonds when there are AA right.

So this will be, so how did we get this? So we said the total number of A atoms and their coordination number at every side so that should be the total number of A bonds and some of them are made with B and some of them are made with A itself, so that is how we got it. In a similar fashion so from here you can get that what is PAA, PAA is nothing but NAZ/2-PAB/2.

In a similar fashion you can write NB times Z will be equal to PAB+ 2PB why because there are total number of B atoms NB and if Z is the coordination number there should be NBZ total B bonds, B atoms associated with these bonds and they are some of them are AB bonds some of them are BB bonds. So that implies PBB is again NBZ/2- PAB/2 okay. Now we can write the total energy E in terms of these bond energy.

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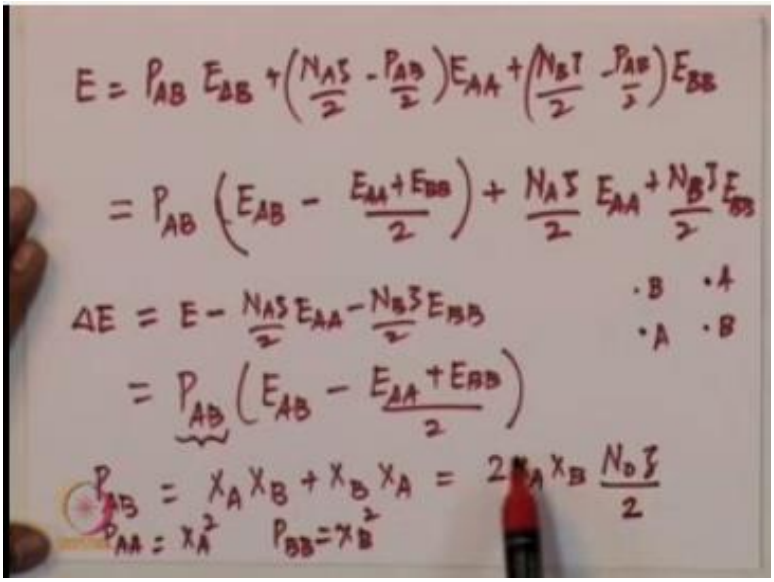

So what do I get, I get E=PAB EAB + PAA can be replaced by (NAZ/2-PAB/2)EAA+(NBZ/2-PAB/2)EBB. So let us expand and so we will have PAB EAB and – PAA/2 EAA-PAB/2EBB, so we can write that as PAB (EAB-EAA+EBB/2). So this is all the terms and then of course, there are these +NAZ/2 EAA+NBZ/2 EBB okay. Now NAZ/2 EAA and NBZ/2 EBB are nothing but the energy of the pure A pure B.

So if we are interested in ΔE which is the E- whatever energy you had for the pure material that you have taken together and put to form this mixture, then we know that should be this quantity subtracted. So NAZ/2 EAA-NBZ/2 EBB, so that is basically gives you PAB EAB-EAA+EBB/2 okay. Now so if we can write PAB then we have ΔE which is what was written as **ω** XA XB.

So we need to calculate PAB then we are through, so we can get an expression. So how do we get our PAB? For getting PAB they are going to assume that the sides are occupied randomly okay. Now if suppose you have only A atoms the probability of occupancy of any site is 100% for A, if you have only B atoms of course it is 100% for B, if you have any fraction suppose 50% of the atoms are A atoms then there is 50% probability that any given site will be occupied by A atoms.

In other words if I want to know what is the probability that a given site is going to form a bond of the type AB PAB, so what do I do I take two sides and then I find out the probability of this is A and this is B that will form a AB bond or this is A and this is B what is the probability of this is A that is given by XA, what is the probability that this is B that is given by XB plus this is XA in other words two times XA XB is the probability that any given site is actually occupied any given pair of sites will actually have a bond PAB.

In a similar fashion you can show that PAA is nothing but XA^2 and PBB is actually XB^2 so you add all these probabilities XA^2+XB^2+2XA takes XB which is nothing but $(XA + XB)^2$ XA+XB is 1, so that is equal to one. So the total probability becomes 1, so our probability calculation is okay. So we are going to take that this is the probability that the occupancy is that quantity, but that is not the only thing we also have to, so there are going to be N Avogadro number of sites okay.

So this is the probability and for each side there are Z bonds and then we are considering pairs, so we have to divide by 2. So this quantity is basically the total number of AB bonds okay. So this 2 is going to go away.

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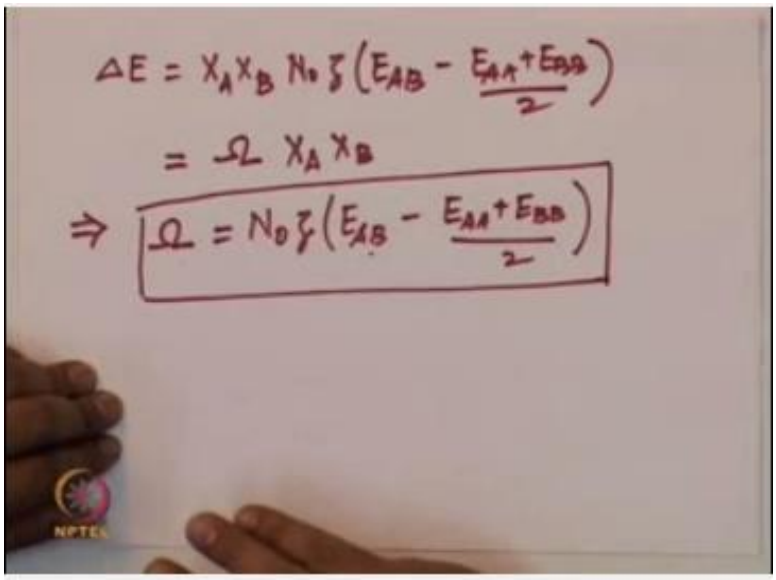

So let us substitute then we get the expression that ΔE is nothing but the number of AB bonds which is given by XA XB N0 Z times EAB-EAA+EBB/2 is basically the change in energy ΔE is what how we defined and this was written as Ω XA XB which implies that Ω the regular solution parameter is nothing but N0 times Z times EAB-EAA+EBB/2 okay. So this is how the regular solution parameter is related to the Avogadro number the number of nearest neighbors in the given crystal structure.

So which could be 6 or 8 or 12 depending on what type of cubic system for example you are assuming and this is nothing but on the average how costly or cheap is an AB bond with respect to AA BB bonds, that is if you break one AA one BB and make two EAB bonds then how much is the change in energy. So this is zero then that is ideal solution **ω** is zero, if this is a positive or negative then the system would prefer phase separation or order. So this is what we looked at so this is how one derives the regular solution parameter in terms of these basic quantities, thank you.

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