Phase Diagrams in Material Science Engineering
Prof. Krishanu Biswas
Department of Material Science and Engineering
Indian Institute of Technology, Kanpur

Lecture – 22
Quasichemical Theory l

So, far I have discussed with you different types of binary phase diagrams, in which liquid phase is present, and then, I am in the subsequent lectures I would discuss about solid state phase diagrams, binary phase diagrams, but in between I want to let you know that the genesis of these kind of different phase diagrams.

So, there are lot of study, studying for the (Refer Time: 00:43) calculations to thermodynamic calculations, why different kind of phase diagrams evolved or forms and like why you have isomorphic systems, eutectic systems, peritectic phase diagrams, and monotectic phase diagrams or syntectic type phase diagrams. Why this different type of phase diagram at all formed in the real systems? And this can be answered from different angles. The easiest one is the thermodynamics approach. You can use the thermos-dynamical concepts and come up with this with an explanation for that. And you can also use kinetic approach and to explain that, but that now no time I am not going to do that.

And finally, one can also use (Refer Time: 01:32) approach; that is, you can take two atoms and using their pair potentials you can calculate the phase diagram. That is very, you know, generic and very complex also, because you need to know the pair potentials not only that, you also need to have a good compositional facility to do that.

But for your understanding, for a course like this, we need to consider the thermos-dynamical approach and that is what it is known as quasichemical approach in the actual thermo-dynamical sense. So, we will consider atoms when you talk about this approach. Let me first explain what will happen. Let us suppose we have a system with two atoms A and B.

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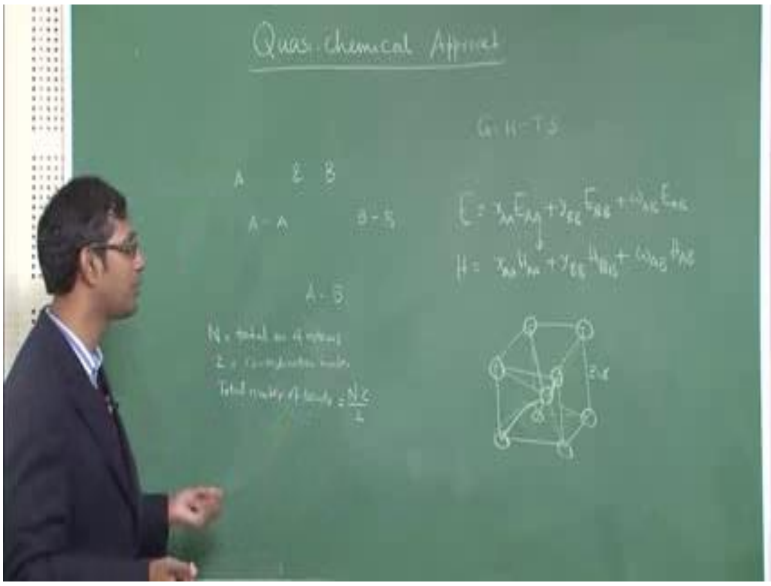

There are two atoms A and B, correct? So, this talks about interaction between A and B. I know that if I have two atoms A and B, there are three types of bond possible: one is A-A; type other one is B-B type; and third one is a A-B type; there are only three types of bond possible. You can have bond between A and A, bond between B and B, and bond between A and B - there are three different types of bond possible.

Now, if you have a system in which all kinds of when two atoms represent, and these three different types of bonds can form and total energy of system can be given number of bonds of A-A type; suppose this is x AA and multiplied by bond strength of A-A bonds, right? This is the energy total energy of the A-A bonds in the system. If I, if you know the number of bonds of A-A type, and if you know the strength of the A-A bond, then these two multiplication will give you the total energy of the A-A bonds. Similarly, for B-B bonds, if this is the number of B-B bonds y B-B, and this is the strength of B-B bonds, this is what is the energy of the total B-B bonds.

And finally, this is the number of A-B bonds, when w, small w, A-B into energy of A-B, total summation will give you the energy of the system. That is clear. (Refer Time: 03:53) steel what is happening. Now, this is nothing but enthalpy of the system. Why? Because enthalpy of the system is connected to the bond energies; if I have two atoms, then this is what will give me the enthalpy. So, sometime, we write total enthalpy of the system is x A-A multiplied by enthalpy between two A-A bonds plus B-B number of B-B bonds multiplied by enthalpy of B-B plus total number of bonds of A-B multiplied by bond enthalpy of A-B, correct.

So, from here to there, when it transpose, from here to there, difference is that I have replaced bond energies by enthalpy. This is almost similar; that is not my difference between (Refer Time: 04:44) a and a e a in quasichemical theory. So, now, question is that this is enthalpy. So, as you know, the free energy of the system is given by enthalpy minus Ts. So, I need to also calculate entropy, but in the first class, in today's class lecture, I am going to tell you how we can get enthalpy. Enthalpy is very important parameter and that is what actually most of this phase diagram variations depends on. So, the enthalpy can be calculated using this approach. And how I am going to do that - that is what I am going to show you in today's class.

In the next class, I will discuss how you can get entropy. In fact, that is what I have already done in the very beginning of this semester. So, I am not only going to borrow that formula for entropy and discuss further. I am not going to derive it again but for enthalpy I need to derive the full relationship so that you understand. But what I suggest you that when I am doing this formulation, you must follow step by step, take a paper and pen, and follow my step. Then only you can calculate and get an proper understanding of this concept.

So, quasichemical approach assumes that the bond energies are equally related to the enthalpy of the defined bonds. So, now, let us suppose the system consisting of total number of system constitutional number of atoms N, and these is total number of atoms in the system, and also assume that z (s) - small z - is the coordination number of the system. I will explain what it is. What is the meaning of coordination number? Well somebody says in bcc coordination number is 8. What is the meaning of that? Very simple, you draw a bcc unit cell; this will be clear to you.

There are atoms at these corners - eight corners - and there is an atom at the center, very simple. The coordination number of this atom is 8, because it is bonded with all the eight atoms. This is the first nearest bonds which you form, correct? That is why it is z value is 8. For fcc z value will be 12; that is very clear. So, that is what is z. So, when you form solid solutions, then you are basically changing these different bonds. That suppose you form a solid solution between A and B, A might sit here and B might sit at the corners. So, therefore, AB there will be 8 AB bonds, and the coordination number will be 8.

See if I have a total number of bonds atoms in a system is n and z is the coordination number. What is the total number of bond possible? Very simple, total number of bonds is how many? That will be multiplied by n into z divide by two. Why two? Because you know for every atom there is only one bond the bond kind of only one bond is possible. Suppose, there is A atom and B atom; there is only one bond; but you are counting two atoms. So, therefore, the total number of atoms are n, total number of coordination number is z, n z by two, half of that will give you the total number of bonds presents. Is is it clear? Very simple, I have A atoms, it has eight bonds together with eight atoms, but you know number of atoms are nine. So, if I take a large number of atoms, this will be coming like this, NZ by 2.

So, if this is the total number of bonds presence, now how do I calculate number of A-A bonds, number of B-B bonds, number of A-B bonds - how we can calculate? Well that can be calculated using very simple formula; very simple concept; what is that concept? I know that in a solid solution the A and B - the amount of A and B presence - and you have probably seen all the phase diagrams, I am presenting the concentration in terms of mole fraction xb, xa, because I told you at the beginning of this semester that the mole fraction is the widely used compositional variable used in the phase diagrams.

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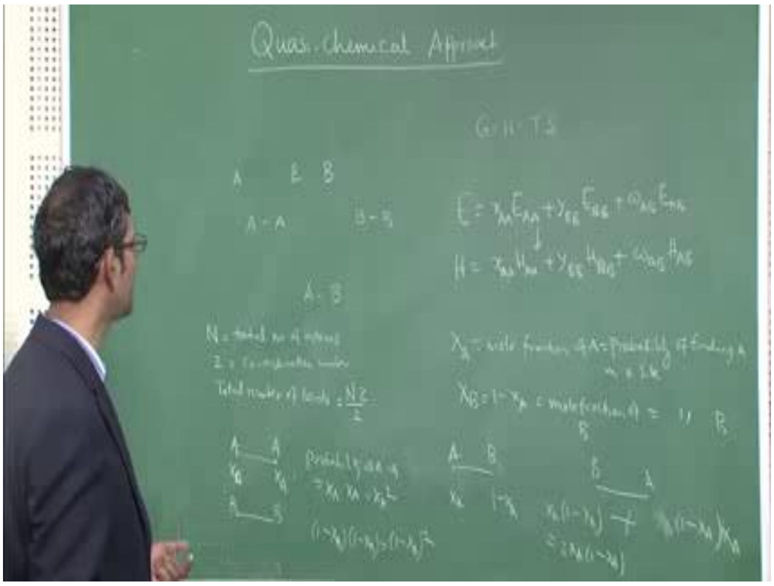

So, suppose I have in an alloy mole fraction of a is XA - this is the mole fraction of A, in the alloy, mole fraction of A - what does it mean? That means, the probability of finding an atom A in the solution is XA, because XA is the fraction and any probability will be fraction. So, if XA is the fraction and XA denotes the mole fraction of A, so that means, XA is also equal to probability of finding A, probability of finding A, in a site, correct? That is obvious, because that is the fraction, and that is the mole fraction of A. Similarly, XB, which is equal to X one minus XA is the mole fraction of B and is equal to probability of finding B in a site, correct?

So, now if I have a atom A here, and I want to find another atom A here, so that A-A bond form, this is A this is A. So, probability of finding this atom is XA. Now, probability of finding this atom is also XA nearby. So, the probability of probability of A-A bond, probability of A-A bond is what? Probability of A-A type bond formation is XA multiplied by XA; XA square. Why it is so? Well, as I told you XA is the mole fraction of A which is nothing but probability of finding A in a site. So, if I put a lattice point here, in solid solution, suppose atomic structure, the probability of finding this atom A is XA. Now, probabilities of finding another atom in the next site, a neighboring site A atom; is also XA. So, probability of forming this bond A-A type bond is XA multiplied by XA that is equal to XA square, correct?

Similarly, probability of finding B-B bond is what? 1 minus XA into 1 minus XA; that is equal to 1 minus XA whole square, correct, now, I have got these numbers, probability of finding XA, probability of finding XB bonds, A-A and A-B bonds. What is the probability of finding A-B bonds? Probability of finding A is XA, probability of finding B is one minus XA. So, probability of finding a bond A-B type of bond is XA multiplied by one minus XA.

Now, you know A-B can be looked at A-B or B-A. Bond is same whether that is between A and B or B and A; does not matter; it is a A-B type of bond. So, for these also it will be XA multiplied by one minus XA. So, therefore, probability of finding an A-B bond is this plus this that is equal to twice XA minus 1 minus XA. Is it clear? If it is not clear, try to understand. Probability of finding A-B bond is same as finding probability of B-A bond because the bond is between A and B or B and A, does not matter; it is a AB type of bond. So, now, for this case if I have this type of A sitting first, B sitting next, what will happen? Probability of finding A is XA, probability of finding B is 1 minus XA.

So, probability of finding A and B in the nearby regions, neighboring region, neighboring points is XA multiplied by one minus XA. Similarly, for B in and A like that configuration probability of finding B is one minus XA, probability of finding A in the nearby position XA. So, probability of finding B and A in the neighborhood region is XA multiplied, 1 minus XA multiplied by XA, 1 minus XA multiplied by XA. So, the probability of finding A-B bond is equal to this plus this, because both the situations are (Refer Time: 13:50). So, that is why we have to add, and if you add, we get two into XA minus XA into one minus XA, correct? That is, obviously, the way that is to be done.

Now, I rub off these things and go back to the number of bond formations. You have noted down? Otherwise, now, question is - this I have total number of bonds is NZ by two, as I told you.

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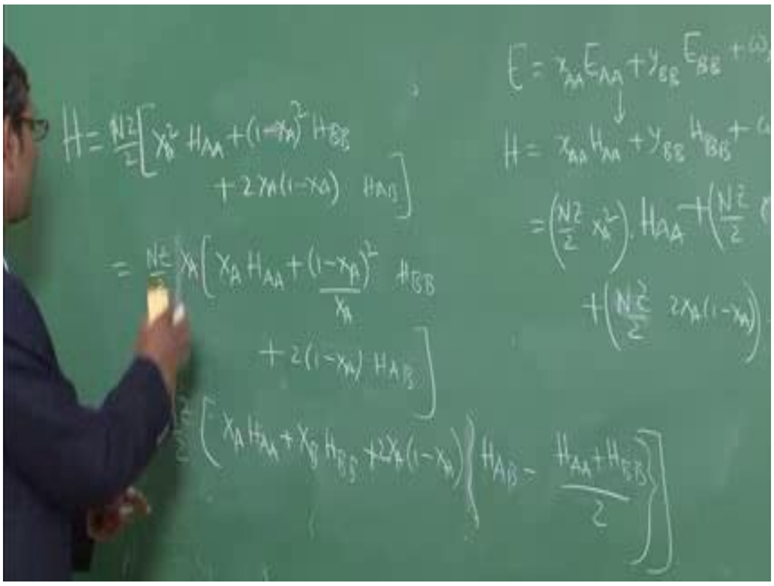

So, XA is nothing, but NZ by two multiplied by X square because that is the A-A bond XA square. So, this is what is your XA and HA is remaining the same, HAA plus number of B-B bonds is again can be calculated - NZ by two multiplied by 1 minus XA whole square into HBB plus, this is what we should write, twice XA, sorry NZ by 2 NZ by 2 going to become twice XA 1 minus XA. This is the whole thing for WAB multiplied by HAB.

So, look at this derivation. So, we have found out number of bonds of A-A type multiplied by HAA, that is given by NZ by two into XA square NZ by two is the total number of bonds of A in the system multiplied by XA square it will give you total number of A bonds. Similarly, NZ by two multiplied by one minus XA square whole square will give you total number of B-B bonds multiplied by HAB will give you the total number of total more energies of B-B bonds. Similarly, for AB bonds you can do that. So, now, once you have got this, this is a very important derivation, once you have got this, you can do lot of things.

Let us re-write the sentence little bit nicely, re-write the derivation. We can write these things in a simple manner. I do it here. HA is equal to NZ by 2, I will take common, NZ by two I will take common. So, then it is become XA square HAA plus 1 minus XA square HABB plus 2 XA 1 minus XA into HAB, right? That is what you will get. So, now, I can actually write down this sentence nicely. How we can write down? NZ by 2 this can be written a little bit different way. What is that? I need to take common XA, yes, let us do that, and if I do that, then what will happen? Yes, XA multiplied by HAA plus one minus XA whole square by XA, because I have taken common into HBB plus two one minus XA into HAB, right.

I can write this way and this can again be further modified. Whether these can be further modified like this? XA HAA plus XB HBB plus you know XA 1 minus XA common or this is like this HAB minus, yes, minus HAA plus HBB by 2, this can be written like this. So, I can remove this step; this is not required. From there I can get down. How I get down? Basically, this is simple. I add some quantity here; some quantity there which I subtract.

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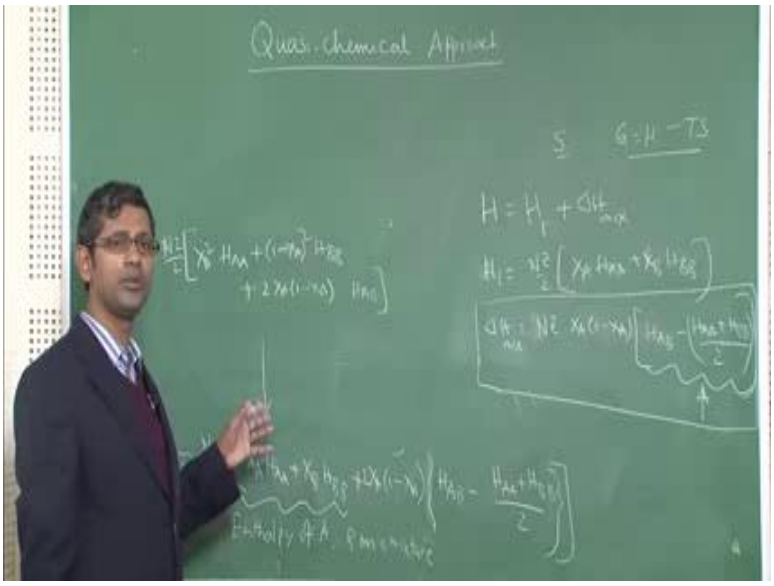

So, you can clearly see this is nothing but NZ, enthalpy of the pure system XA HAA XA XB HBB plus the enthalpy difference because of addition of, because of mixture mixing. So, what I can do is that, this part, these parts, this one, this one is nothing but enthalpy of a pure A and B in a mixture.

On the other hand, this is for the mixing, this is for the mixing. So, rather what I can do? I can write down H, this is H, H is equal to H 1 plus delta H and where H 1 is this NZ by 2 XA HAA plus XB HBB; XB is nothing but one minus XA, and delta H is given by twice, sorry not twice, NZ XA 1 minus XA, and keep it XB also, multiply it by HAB minus HAA plus HBB by two, right? So, that is my H, delta H mix. That is the enthalpy which forms because of mixing A and B atoms; that is the enthalpy. As you can clearly, see N is a positive number; Z is a positive number; N is number of atoms which will be Avogadro number; Z is the coordination number which is positive number; XA is the positive number; one minus; XA is the positive number.

So, the positive or negativeness whether it of delta H mix depends on this number in the bracket. So, there what is this number? This is nothing but enthalpy, by enthalpy of HAA minus enthalpy of HAA plus HBB divided by two, if the difference of the uneven bonds or different difference between the bonds of A-B minus average of A-A and B-B; that is it. So, the sign of this would completely depend on this parameter; sign of this completely depend on this parameter. So, we can explain formula very nicely. What is that? We can say that if in a system A-B bonds are easy to form, then this will be positive because then HAA, so, now, then this will be negative, because this will have low energy than this one. So, because this will have low energy in case of co-ordination formation it is higher than this will be negative.

So, in that case if delta H is negative, free energy system is also negative, the enthalpy is enthalpy is always negative; T minus, minus T is always negative, because entropy is always positive. So, that is why. So, but on the other hand if suppose a bond formation is more likely like for the similar pair A-A or B-B is more favorable than A-B then what will happen? These will be positive, and if this is positive, then it can create different kinds of situations in the free energy gap. So, I am just going to leave this derivation at this particular equation to you to understand in detail manner and derive the way I have done it. And once you have done, in the next class I will take from this, and add also derive entropy, and this is I have done for enthalpy, I will do for entropy. And finally, I will derive H minus Ts and show you have different kinds of free energy gaps will appear and that will lead you to different phase diagrams.

So, I just leave it with you these particular things. So that you analyze there in a book, very nicely, any phase diagram. I told you both the books have this particular derivation nicely done, even I could find on internet also the total derivations. So, we will see in the next class.