Phase Diagrams in Material Science Engineering.

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Module - 06
Lecture – 23
Quasichemical Theory ll

So, students we are going to continue on our discussion on the quasi chemical approach of genesis of different phase diagrams. As I told you that, in this approach we are basically using thermodynamical techniques to analyze the genesis of different phase diagrams. As you know the formation of different phases depends on the free energy.

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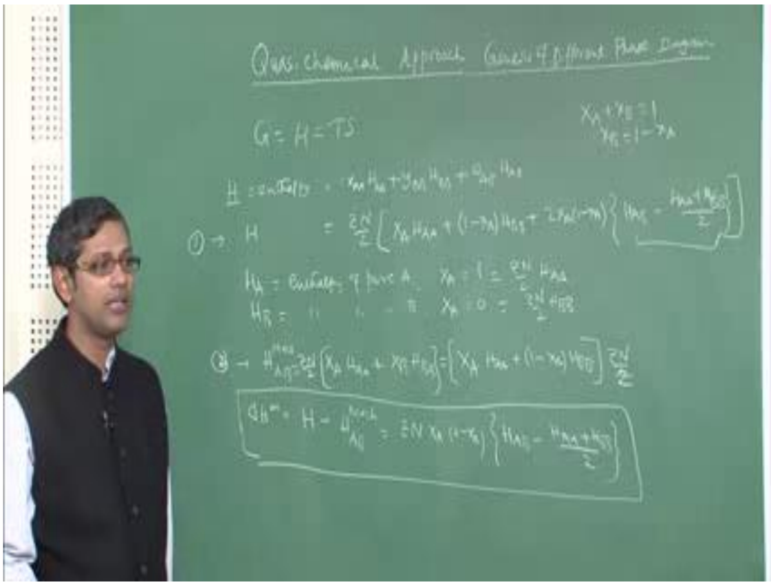

And in material science we use more frequently the Gibbs free energy as a measure of stability of different phases, which is given by g equals h minus t s, where g is the Gibbs free energy, h is the enthalpy t is the temperature s is the entropy. So, by using quasichemical approach, we basically calculate the expression for h and s for solids and liquids solutions, and then see how different parameters of that expression affect the phase diagrams.

So, I discussed with you how we calculate h, h is the enthalpy term, and enthalpy can be calculated using bond energies of different pairs, and for that I assume the two elements a and b, and therefore, there are two types of atoms in the solid solution and liquid solution a and b, and different bonds which can form are a a type b b type or a b type. So, therefore, depending on the bond energies, the enthalpy is given by the term like x a a number of bonds of a a h a a is the bonds energy of a a type bonds, y b b h b b where y b b is the number of bonds of b b type and h b b is a bond energy of b b plus w a b multiplied by h a b, where w a b is the number of bonds of a b type, and h is the bond energies of a b. So, am using the formulas which I have discussed in the last class.

You can get this expression as like this, you can write down, this is equal to z n by 2 into x a h a a plus x 1 minus x a h b b plus twice x a 1 minus x a h a b minus h a plus h b b h b b by 2 like this correct. So, this is what we can get; z is the coordination number, n is the number of atoms present in the system, x is the mole fraction of a x, and h a is the bond strength of a b h a a is the bond strength of a a type bond and h b b is the bond strength of b b type bonds. And I hope in last class I have discussed this expression and you have already got idea how to derive It, because I left some steps behind. So, that you can work out and get the expression correctly. So, now this is the expression of enthalpy as the function of mole fractions; z is the now coordination number and the bond energies as you can clearly see. And in this case as I told you z is positive, n is positive, x a is positive.

So, therefore, the value of h depends on, the sign of h depends on, sign of these term, or difference of the bond energy of a b minus average of bond energies of a a and b b type atoms. So, therefore, this is the prime factor controlling the sin of h in this term. Now let us look at, whether can I get h a, h a is the enthalpy of pure a, and it corresponding to x a equal to one, because pure a x a will be 1 x b will be zero and therefore, I get this is equal to z n by 2 h a a, can clearly see this is equal to z n by 2 multiplied by h a a. So, similarly h a h b enthalpy of pure b can be obtained when x a equal to zero, then x b equal to 1, because we know that the solid solution liquid solution x a plus x b equals 1. So, for pure b x a equal to 1 for pure a x b equal to zero or x a equal to 1 whatever it is, and this equal to z n by 2 multiplied by h b b correct.

So, therefore, if we have a physical mixture of 2 elements a and b, in which the mole fraction of a is x a, mole fraction of b is 1 minus x a, then because x b is equal to 1 minus x a right that is why. So, in a solid solution or liquid solution, if in a physical mixture, not a solid in a physical mixture, if you have x a fraction of a and x b fraction of b, then the enthalpy of the system, enthalpy of mechanical mixture I write mechanical mixture, enthalpy of mechanical mixture of a b will be equal to 1, would be equal to x a multiplied by h a a right x a multiplied by h a a and x b multiplied by h b b that is correct, and x b multiplied by h b b.

So, that is equal to x a multiplied by h a a plus 1 minus x a multiplied by h b b. So, as you clearly see that is actually. So, and that will be multiple x, sorry this will be multiplied by z n by 2 this is the number of bonds z n by 2 correct. Because this is the total number of bonds present in the system. So, now, as I clearly see this term, is exactly equal to the first two terms of this expression; expression number one, for you can see in the expression number two, this term or expression number two is equivalent to the first two terms of the equation one, you can clearly see that.

So, therefore, any change of the enthalpy because of solution liquid solution formation is, given by the third term very clearly, because this is the enthalpy of the mechanical mixture of a b. So, therefore, any change of enthalpy, because of solid solution liquid solution must be equal to this term; third term. So, I can write down delta h m which is the enthalpy change because of solid solution or liquid solution formation, is equal to h minus h a b mechanical mixture and that is equal to z n x a minus into 1 minus x a. You can clearly see this 2 and this 2 would get canceled multiplied by h a b minus h a a plus h b b by 2. So, this is the enthalpy change, because of the solid solution formation; this is the term given by. As you can clearly see in this term this is a function of x a square. So; that means, this term is.

It will be nature of this term, if the temperature is constant that the z and n are constant, another fix temperature a b (Refer Time: 08:44) energies of a b and b b and a a are constant. So, that for that will be the parabolic nature, because its x square h is proportional to x square fine. So, that is why I told in the many times in the class, that why the free energy equations g is basically parabolic, it is must parabolic in nature. Now as you know this is for h that is fine we calculated. So, we need to also calculate the s entropy, and I would like to tell you here that we have already done these calculations, in the some other classes, but I will do it again. So, I will keep this term, I will write it at the top, and rest of the thing I will erase. So, I keep these three things here; one is g other one is delta h m. So, delta h m is z n x a multiplied by 1 minus x a h a b minus h a a plus h b b by 2.

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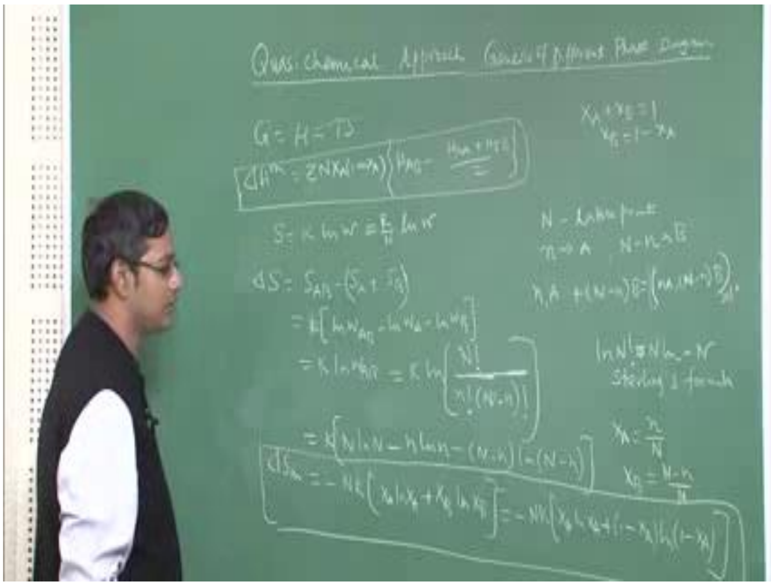

I erase everything else, because I need to derive the expression of s entropy, but at this point I would like to tell you, that you know we are more interested more in the delta terms not in the absent value of h and s, the change, because of the formation of the solid solution. As you know, entropy in a statistical mechanics way is determined by the number of ways you can arrange the atom in a lattice for a solid solution that I have already told you right. So, as Boltzmann told the entropy is given by this expression k l n w, where k is Boltzmann constant; that is nothing, but r by n r is the universal gas constant n is the Avogadro number a log of w is this, where w is what, w is the probability of distribution of the atoms on the lattice side; that is the thing. This tells you the probability of distribution, now, to cut the things short, because I have already discussed.

I will not going on to detail about that, but to cut other things short, suppose in a solid solution you have n number of lattice points, n number of lattice points that are suppose, and you have small n number of a atoms and capital n minus small n number of b atoms to be arranged on the n lattice points this is what is the task. So, suppose you have a lattice points and you need to arrange small n number of a atoms and capital n minus small n number of b atoms in that n lattice points, and this arrangements, the most probable arrangement will give us the entropy, or the entropy change rather as you know. As you know here if you have pure a atoms, suppose you have only a atom and you want to arrange a atoms on the lattice sides.

So, there is only one vapor ranging lattice points. suppose if you have small n number of pair atoms you want to arrange on the small n number of lattice sides. So, there is only one vapor arranging them, we cannot do much. So, here if you have capital n, suppose small n number of b atoms you want to arrange them on small n number of lattice points, then arrangement will be same there is no change. So, I can write down delta s, or change of entropy, because of this arrangement can be written as s ab minus s a minus s b what is that, where thus, because of this term this is the entropy of ab solid solution. Suppose I have got n a atoms plus n minus n b atoms and I am forming a solid solution n a n minus n s b atom solution. So, to do that what is happening, if I have pure a then this is the entropy, if I have pure b then this is the entropy, and if I have solid solution this is the entropy.

So, entropy change is given by this minus this, and this can be written as l n, let me common take common k l n w a b minus l n w a minus l n w b right that is what it is. So, as you know as I told you arranging pure a atoms on lattice sides it does not change any distribution, it will have a probability of one. So, therefore, this basically equal to l n w a b am I right; that is what it is because these two terms this is log of 1 this is log of 1. So, log of 1 is zero it will get cancel, and this can be written as k l n factorial k l n factorial n minus 1 factory l n let me see whether I have done it here, yes k l n factorial n factorial like this. What is this? This is the permutation combination factorial n capital n of factorial, factorial capital n factorial small n and n minus 1 factorial or n factorial divided by small n factorial multiplied by n minus n factorial, and you know that you can apply sterling approximation; what is sterling approximation.

Log of n capital is equal to l log n this is approximation minus n, this is called sterling approximation sterling formula he has given long back. So, you can apply this finally, what you will get, you will get k I am not going to write down everything finally, what you will get; k l log n minus n log n remember this n is capital and this n is small minus n minus small n log of n minus log n this because I am just I am doing lot of (Refer Time: 15:24) that is why I am using my notes. So, finally, this can be written as; minus n k x a log of x a plus x b log of x b where x a is given by small n by capital n x b is given by n minus n by capital n this is what is, because this is the mole fraction. If you have total number of a atoms n total number of side is capital n then this is the mole fraction of a, similarly, mole fraction of b total number of b atom divided by total number of sides.

So, that is the my entropy change, you can clearly see n is positive, k is positive Boltzmann's constant is the capital Avogadro number, and these terms are negative log of x a is negative, because x a and x b are what they are all fractions. So, therefore, there negative, this can also be written like this in terms of single variable x a noise. So, this is my delta s term. I would like you to derive this yourself otherwise you will be not able to feel the mathematics, you will be you know you will be simply going by the motion, you should do yourself and get this expression on your notebook while you are listening to this lecture, switch off the lecture and then you try to derive this expression on yourself. So, I have got delta s and I have got delta h. So, now, I will erase and I will write down what is delta g, because that is what is the most important factor correct. So, delta g is the change of free energy, and change of free energy is given by delta h minus t delta s. So, what is that then that is given by let us do that. So, delta h is delta g delta h minus.

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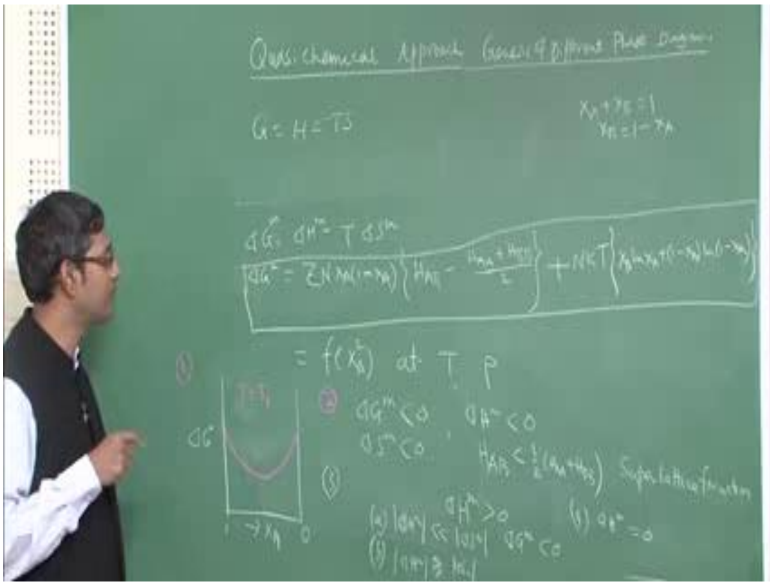

So, let us write m also, and m should be here t delta s m. So, that is given by z n x a multiplied by 1 minus x a h a b minus h a a plus h b b by 2 plus n k t this minus will become plus x a l n x a plus 1 minus x a l n 1 minus x a that is what it is, this is my delta g m expression. So, these three expressions, is what we are going to use for all our future descriptions of the solid solution or liquid solution. So, now let us analyze it; first thing you should do, point wise, let me just do point wise. So, I erase this part, this part I erase this one also, but it is there. So, we will analyze point wise one by one noise.

First point is that, this is the whole thing is the function of x a square, at constant is a function of x square at constant temperature and pressure. Delta g is a function of x square why? See that z is a constant n is a constant, and at constant temperature this one and this will also be not changing, they will be constant. So, therefore, this is I told you already, this is a 1 minus x square or is a function of x square. This one is also like that, if you expire log it will be 1 minus x a, first term if you consider. So, x a into 1 minus x is x square again 1 minus x a 1 minus x square, and n k t is also constant and constant temperature.

So, therefore, the delta g if you plot at a constant temperature delta g, if you plot this delta g curve as a constant temperature, it will look like a delta g m versus x b if I plot or x a, x a if I plot, this will be zero here one here. So, this will be a parabola, at any temperature t equal to t 1; that is clear.

So, all those free energy curves I have drawn in the different phase diagrams, are now clarified that, why this shape is present, why you draw this shape, and this is a very important lesson you must should not forget all your life, because most of the courses across different departments in India, the instructor draw this diagram, but never explain why this diagram is like this, why it will looks like a parabola, why it looks like a (Refer Time: 20:55) parabola, he never explain. This is basically, because of this mathematical expression, and which I derived from bond energy calculations. So, that is why both the terms are parabolic in nature. So, total time will be having nature. This is the first thing, first point I would like to. Second thing is that, as you see a these terms. So, delta g as I you have already learned, delta g is a change of free energy.

So, for any process to happen spontaneously delta e should be negative; that is what been told you in thermodynamics. Remember I am not teaching thermodynamics, I am teaching phase diagram course. So, these basics you must have it. So, for any process to happen spontaneously delta g must be negative. So, you know delta g has two parts; this is first part, this is second part. This is the entropy change, which is always negative why, because n is a positive, k is positive, t is positive, and this is a negative, always x a is the fraction, and therefore, 1 minus x is a fraction a log of a b fraction is a negative with a 0.5 log it will be negative 0.2 log negative 0.9 log negative.

So, any fraction if you take a log it will be negative. So, that is the thing actually; therefore, entropy terms, entropy change will be always negative and that actually; that is why you form solid solution or liquid solution easily, this is the main reason, because entropy trivializes the formation of solid or liquid solution. On the other hand delta g actually depends also on enthalpy term, and the enthalpy term positiveness or negativeness of the enthalpy term as I told you depends on the relative magnitude of these bond energies, very clearly, relative magnitude of these bond energies, this completely depends on that. So, now, so; that means what; there are three situations possible, for delta g to be negative, delta s is always negative, there is no problem. So, therefore, for delta g to be negative, delta h must be negative, when the delta g will be negative.

Before that let me clarify, you know bond energies are always negative, you know that. If something forms between two (Refer Time: 23:17) a a or b b or a b bond energies are negative. So, this is only possible when, this possible when h a b, the bond energies or enthalpy of a b does equal to the bond energy of a b, is less than or equal to half of h a a plus h b b. If this is less than the both or all are negative, if this is less negative then this term will be negative, because this is there is a negative sign there. In that case delta g m will be negative. So, therefore, a solid solution will form, when this condition will be satisfied. In fact, these condition means what, these condition means the bond energies of, formation energies of bonds for dissimilar pair between a b is lower than between a a and b b; that is the thing you should understand.

So, bond energies between a b is lower than the average bond energies of a a and b b; that means what, this similar atoms will be forming more easily bonds in the similar atoms, and these leads to super lattice formation, or ordering or formation of order compounds; like n I 3 l f e 3 f e a l all those compounds I talked about in phase diagram these conditions met, when this condition is met will have this compound formation. So, you can explain the formation of this compound by simply form quasi chemical approach, now this is the second case. Third case is what; third case was delta g sign will also depend on both these two. So, as you see here delta s m is always negative. So, therefore, whether if delta h m is positive, there are two situations possible, two sub categories are possible; one, when the relative magnitude of this one, is much lower than relative magnitude of means relative value of this one not sign, relative value of this one.

So, when relative value of delta h m is much lower than delta s m, then delta h, delta g u will be negative; obviously, because the value of delta s m will be so much small, it will super set the value of delta h, whether it is positive does not matter, but situation will be changed when delta h m value is almost similar, or greater than equal to delta s m. Then we will have different situations.

And so I would stop here, in the next class briefly I will explain the 3 b condition, what will happen. So, you have understood clearly that there are three situations t different conclusions we have done; one is set, other one is the first thing while both of them are negative, is very easy superlative forms, then third one is what will happen to the relative magnitude, and the last one which I will discuss is when delta h m is zero. So, these two things, three and four I will discuss in the next class and clarify it to you. Please practice this, when you have to take this in this lecture.