Phase Diagrams in Material Science Engineering
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Lecture - 24
Quasichemical Theory_Free energy formalism

Today we are going to complete our discussions on Quasichemical approach of phase diagrams. I think in the last 2 lectures, I described you how we can derive the expression for the enthalpy and entropy from the atomistic viewpoint. So, I will just try to first correlate that thing and finally, we go ahead with the free energy formalism. So, as you know the important aspect is this parameter for any stability of failure that is called the free energy change.

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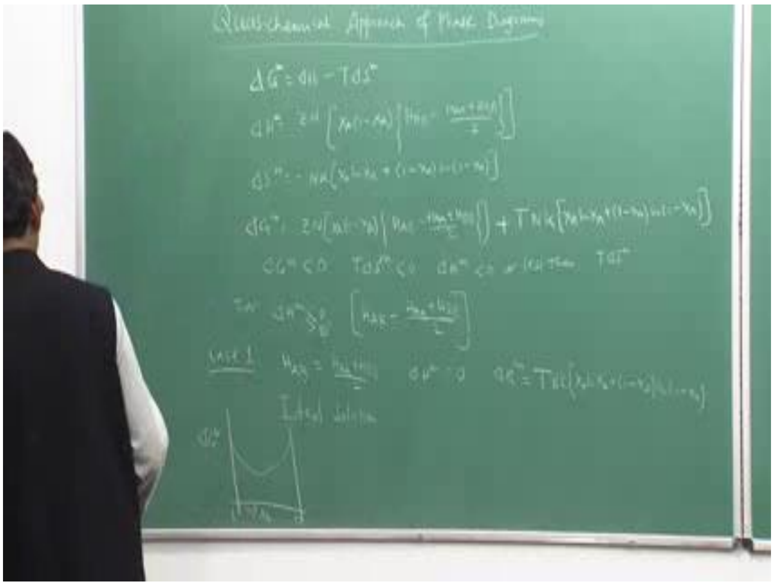

Delta g is nothing, but change of free energy. When you add 2 elements together to form a solid solutions or liquid solution and delta g is equal to delta h minus t delta s, where delta h is the enthalpy change and delta s is the entropy change. So, delta h as i derive is basically z n multiplied by x a 1 minus x a h a b minus h a plus h b b divide by 2. This is what is the expression for delta h. Sometime people write this is equal to delta h m because it is mixed.

Similarly this is h m and delta s m, but it is not important. You are going to use without the superscript also. Similarly delta s m I have derived to be minus n k x a l n x a plus 1 minus x a l n l n means log of 1 minus x a. So, thus delta g m will be equal to z n x a 1 minus x a multiplied by h a b minus h a a plus h b b by 2 plus t into n k multiplied by x a ln x a plus 1 minus x a ln 1 minus x a. That is the whole free energy change when you form salicylic 2 atoms a and b type.

So, as you can see here, this term is called entropy change and this term is called enthalpy change. So, let us first discuss 1 by 1 what will happen in situations enthalpy change entropy change that is t n k multiply. This term is always negative. Why? It is because x a is always a fraction and because x a is a fraction. So, 1 minus x a is also fractions and due to that if the both these two parameters are fractions. Then, log of a fraction is negative number like log of 0. 5 log 0. 4 is a negative number. Because of that this term is negative term. Obviously, an is the Avogadro number, k is Boltzmann constant, t is temperature and they cannot be negative.

So, this is negative means this whole thing will be negative. As you know the free energy change for any spontaneous process should be as low as possible and it is possibly negative also. So, therefore for the g m to be negative, this is already negative. If this term is negative then delta g m also will be negative. What I mean to say is that if g m has to be negative, then these terms must be negative or this term must be positive, but lower than the value of this term because this is always negative.

Let us be very clear about that as the delta s m term t delta, s m term is always negative. So, for these to be negative delta, h m has to be either negative or less than delta t delta s m term. That is very clear. If that is the case, then salicylic solution will easily form. So, now, if I take delta h m term, it depends on what it depends on again this fraction z and n and this factor now if you look at carefully, z is the correlation number. That is a positive number n is Avogadro. So, positive number x a and 1 minus x a also positive numbers. Therefore, whether delta h m will be negative or positive, that depends on the sign of this factor. Inside this, what is that for delta h them to be negative? The factor which will control is this. One factor will be controlling whether it is negative or positive this factor.

What is that factor? This is the enthalpy of a b bond or opposes a bond form by opposite atoms or the different atoms minus the average of the enthalpy of a bonds and b bonds. That is similar atom bonds. So, therefore this is nothing, but difference of the enthalpy of these dissimilar bond energies minus enthalpy corresponding to average enthalpy corresponding to similar bonds. So, therefore you know the whole sign will depend on the relative values of these factors depending on relative values of these. There are three different situations possible. The first one which is case one for your case is in which h a b is equal to h a a plus h b b by 2. That means this whole thing is 0. Why? If the bond energies of the similar bonds is equal to the average of bond energy of the dissimilar, sorry bond energies of dissimilar bond is equal to the average of the similar bonds, then these term will be 0. This will vanish. If this vanishes, delta h m will also vanish. That means delta h m will be 0.

I think I would like to clarify you one thing before I go ahead I am always correlating this h terms enthalpy terms of bond energies. As you have seen, these enthalpy terms are diluted to the bond energies and also number of bonds correct because enthalpy is related to the bond energy to the number of bonds of that type present. So, therefore I am relating these enthalpy terms with the bond energies. There is a direct correlation. This is very clear. So, the first case if the enthalpy of the dissimilar bonds is equal to the other enthalpy of the similar bonds, delta h m will be equal to 0. If delta h m is equal to 0, then delta g m is nothing, but these terms t n k x a log of a plus 1 minus x a log of 1 minus x a and this is always negative.

So, this is the case of ideal solutions. That means what for any value of temperature and x a, this is delta gm and this is x b or x a. Suppose this is 0 and this will be the curve will look like this. So, that means for any value of x a, temperature whatever may be the solid solution will be stable always. It does not matter whether you know the temperature is lower or high, the concentration of a is low or high, it does not matter at all. This is the situation for ideal solution. That is why ideal solutions are always stable at any temperature and any concentration of the elements present. So, this is the case 1. This normally does not happen in the real situation. In real situations, bond energies of these dissimilar bonds will not be always equal to the bond energies of the dissimilar bonds.

Now, let us look at the case 2. What is case 2? Case 2 is the one in which this one is less than equal to this. I put mod because normally bond energies are negative.

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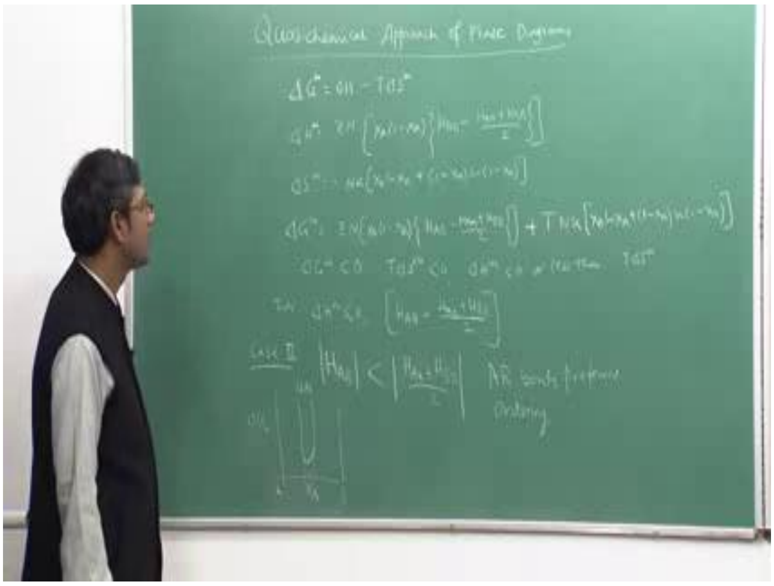

Normally or in chemistry, literature, you see bond energies are considered to be negative. So, that means if the bond form between ab atoms, the energy of the bond is always treated to be negative. So, that is why I use the mod values. So, if this is situation if suppose delta h a b energy bond energy is less than the energy bond energies of h a or b b and a b or otherwise h a b is less than equal to h a a b b by whole by 2. If this is the situation, what will happen to this term? This term will also be negative because h a b is negative as by convention bond energies are any bond energy is negative. So, that means if h a b is negative is less than this value, and then whole term will be negative. So, thus in that situation if that is the situation, what will happen in that situation, you will always have ab bonds will be preferred, but it has low energy.

If every bonds preferred means what the dissimilar bonds are preferred and dissimilar bonds preferred means you have ordering. What is the meaning of ordering? Let me clarify. You know ordering means a atom will always like to be surrounded by b atoms or b atoms will like to surrounded by a atoms. So, that is the ordering. It is never that a atom will be surrounded by a atoms or b atom will be surrounded by b atoms.

It will be always the case that a atom is surrounded by b atoms or otherwise b atom is surrounded by a atoms. That is nothing, but ordering or super lattice formation. This is the situation for the most of inter metallic compounds. We discussed intermediate compounds, we discussed like ni al ni 3 a l f e a l. There are many inter metallic compounds as discussed. For that this is the situation. The bond energies for ab is lower than the bond energies for the average values of aa and bb. Is it clear?

Whatever the situation, these will be negative and because this is negative, delta g m is also negative and delta g m negative will be giving you the stability of the phase. So, that is why actually in these case also if I plot a g m versus x a, this will be also like this, but for the most of the intermetallic phases because they are stable only for a small composition z1, the free energy curve will be like this.

Suppose this is 50-50. The situation of nickel aluminum is intermetallic compound. So, this is 50-50 compositions and it is clear that this can accommodate some of the differences. So, therefore the free energy curve will be looking like this. Similarly for a fe3al, it will be different. It will be 2 is to 3, 2 is to 1 or 3 is to 1. Therefore, position will be different. So, my real intention for this is that for formation of order compound or super lattice compounds, these conditions to be satisfied. So, this is case 2, not case 1.

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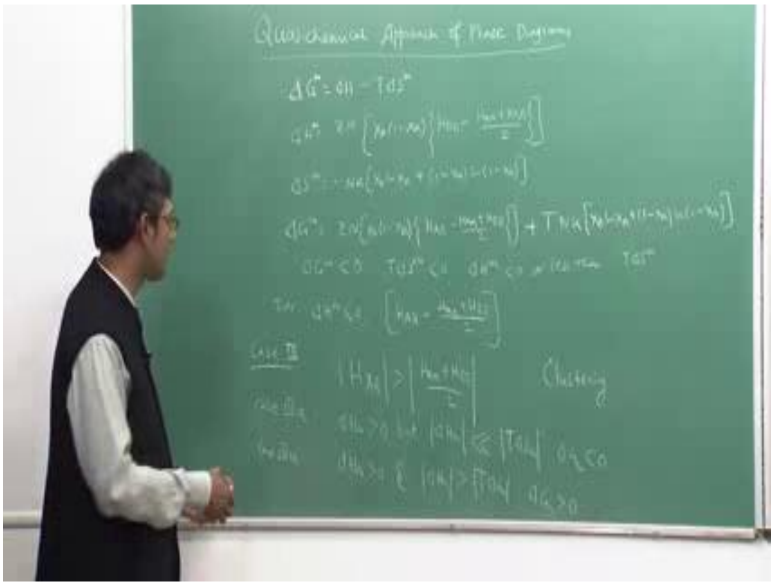

Now, the case 3 is the most interesting case. Let us discuss that. Case 3 is the most interesting case in the sense that in case 3, we get a situation like this where the absolute value of h a b is higher than the average value of h a a and b b in absolute that is in mod. What does it mean? This value is greater than these two values. Then, this term will be positive and if this is positive, then delta g m value will depend on whether the enthalpy contribution is higher than entropy contribution or not. If the enthalpy contribution is higher than the entropy contribution, once situation will arise otherwise if suppose all this is positive, this enthalpy contribution is positive, but the value is lower than the entropy contribution, then it will not change much. It will be same as what we have seen earlier.

What I meant to say is that delta g m to be negative, this to be either to be negative or because the entropy contributions is negative, this can be positive, but the value of this part will be lower than the value of the absolute value of this part will be lower than the absolute value of entropy contribution. In that situation also delta g m will be negative, correct. So, this can give two cases. Case 3, a is the one in which delta h m is positive, but the contribution of delta h m is much lower than t delta s m, correct.

So, that means t delta s m term will be much higher than the delta h m and this will be playing the main role. In that case, again delta g m will be negative. Therefore, solid solutions or liquid solutions are formed, but incase 3, a3b if delta h m is positive and higher than and this value is higher than t delta s m, then delta g m will be negative positive because this is positive and this value is much higher than this, then delta g m will be positive. So, if that is the case, there will be a problem.

Now, let me tell you what is the real aspect of the situation if the bond energies of a dissimilar bonds or enthalpy corresponding to dissimilar bonds is higher than average values of enthalpy corresponding to dissimilar bonds. That means, what similar bonds are preferred a atom will like to be surrounded by a atoms and b atom like to surrounded by b atoms. This is known as typically clustering.

What is the meaning of clustering? That means we have segregate region in the solid solution in which a is surrounded by a or b is surrounded by b. It is very different from the last case in which I said a will be surrounded by b or b will be surrounded by a. It is super lattice of ordering, but here it is opposite a is surrounded by all the a, b is surrounded by all the b. That is known as clustering or segregation in the literature and although this clustering or segregation will happen that depending on the absolute magnitude of delta h m and t delta s m, these two situations will be possible.

In case 3, a should not to be discussed because this is similar to the last case. B is what we need to discuss. I will just do that. So, I will remove all this stuff in case 3, b is what I want to discuss in detail. As we know the free energy for these will be positive, so it can give different situations.

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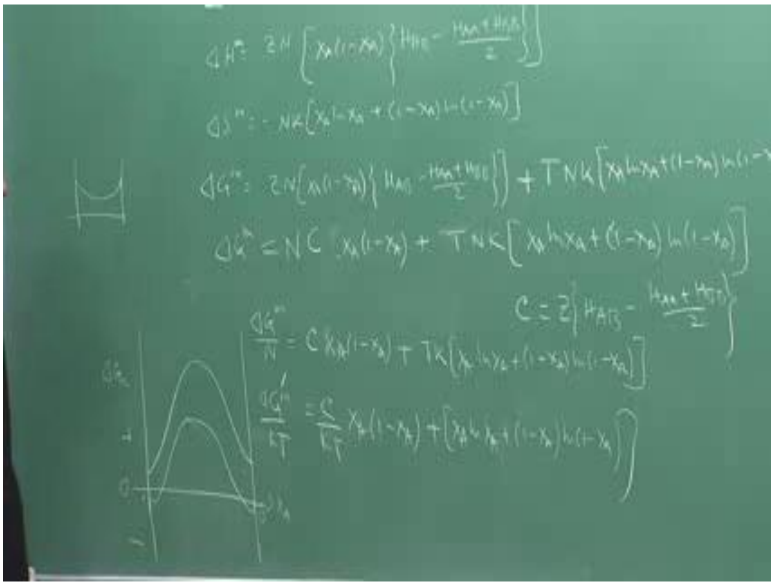

Let me just draw a figure and explain it. This is 0, this is negative, this is positive and this is x a, right. This is 1, this is 0 x a. So, it can be like this or it can be like this. If you can see a free energy is positive and free energy has a curve at a particular shape, it is opposite to this shape I discussed, correct. So, this kind of shapes arises because of clustering in the atoms.

To explain it in mathematical terms, let us write down you know this particular equation in a little nice manner, delta g m. Let us write down this particular equation in a very nice manner. Let me see how we can write down. We can write down this like this n c x a into 1 minus x a plus t t n k and multiplied by x a ln x a plus 1 minus x a log of 1 minus x a, where c is c is what c is given by this c is equal to z h a b minus h a a plus h b b by 2 this is what is the equation.

So, I can write down delta g m by n taken common. So, this is c into x a 1 minus x a plus t k x a yeah x a ln x a plus 1 minus x a ln1 minus x a. So, this is nothing, but delta g m star. This is per atom because we have divided by per atom. So, this is equal to c x a or let us do one thing c by k t and let me just keep it c by k t. This is k t x a 1 minus x a plus x a log of x a 1 minus x a log of 1 minus x a. What I have d1 is that I have taken k t also out. So, it becomes delta g m by k t equal to c by k t into these terms. So, now I can plot this data, this equation nicely. How I will do? I can plot it this data like this. I will do it here.

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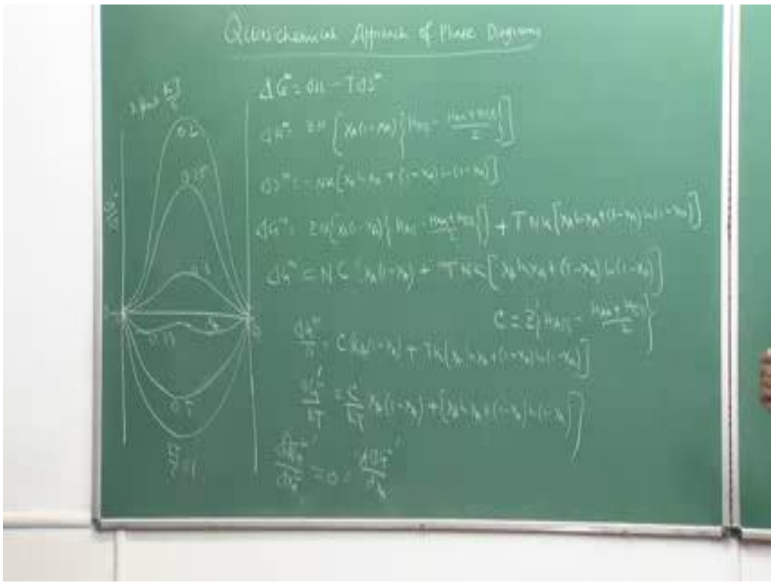

So, what I am plotting is delta g m by k t, this term as a function of x x b x a where x a is1 here x a is 0 there. So, if I plot it, let me first say whether I can do it nicely. So, I will plot it for different value of k t by c. Remember c is also energy term. C is what correlation number multiplied by this enthalpy corresponding to different bonds. So, I will plot for different values of different values k t by c. So, when k t by c is very high, that means thermal energy term is very high. Let me just see because otherwise I will make mistakes. Those values I do not remember. Let us suppose the value is 1 and this is from the text book. Actually I am drawing. This is 0 for delta g m by k t. So, given the value is 1, this will look like this. So, when k t by c is 1, this will be like this.

Similarly, when the value is 0; 5, please follow these curves. This will be like this. So, when it will become 0. 3, it will start swing very important inflation points and when it will become 0. 3, it will be like this 0. 23. It will be this and 0. 2, it will be like this. So, that is the actually the curve will change as you see here when k t by c is high means what entropic term is dominating k t by c k t corresponding to the entropy term t k. This 1 c is corresponding to enthalpic term.

So, therefore when k t by c is high, therefore entropy term is high. That normally happens when temperature is high. This will be showing us simple solid solution or liquid solution and this is what will happen. You add water or kerosene and heat it up to high temperatures at 45 to 55 degree Celsius temperature. They will be mixed nicely at high temperature because this temperature that we return will be higher than the bond energies, but as you keep on decreasing it or it becomes 0. 33, you can see here this started showing them visibility gap or started showing the difference of different change in the slope of this curve and when it is become 0. 3. 2. 5; already this as shown a hump in the curve.

This is all showing downwards and this is showing upwards. So, this is the typical feature of phase separation which is seen in case of monotectic and synthetic alloys. So, the monotectic and synthetic alloys you can explain the formation of these phases. You can explain the formation of these phases very nicely using this formalism, very clearly, correct. Very easily you can show high temperatures. It will form a simple solid solution, liquid solution and all of them are mixed nicely. As you cool it down to lower temperature below the critical temperature, it will show phase separation or two liquids will be separated and as you keep on going down, this separation will be increased and increased and finally, they will form a liquid solution. So, by this formalism case 3 can explain the liquid miscibility gap or monotectic synthetic phase diagram very nicely. That is the idea.

Now, as you clearly see here I just do not want to give you detail version of that. As you see here the curve actually undergoes tangention. There is no inflection point here. The two inflection points start forming here. They grow and then become a strong hand here. You can see here inflection points are developing here, correct and you know inflection points, what happens because curvature changes the curvature of the curve actually undergoes negative to positive or positive to negative. So, that means at the inflection point, the curvature is 0.

So, therefore if you take this one at the inflection point, if you take this to be 0, this is double derivative of delta g m with composition you will find the critical temperature t c very easily. Not only that you know when if this inflection point develops, you will also find that this will be all satisfied. Other equations also satisfy. What is that? This one will be satisfied, correct. So, by these two equations, I can calculate what is the exact composition at the temperature for these separations or critical or the critical temperature for separation or composition for separation. I can calculate.

Well, I will try to do that in next class, but the point I am trying to make is that this theory all can explain the origin of different phase diagram because different phase diagram originates due to the change in the free energies. So, if you know how the free energies are getting changed, you can explain it nicely how the different phase diagram will evolve we will do in next class. But in next class also I will start a new topic that is the solid state phase transformation, especially the steels will come into picture and we will detail discuss about these aspects.