Advanced Metallurgical Thermodynamics

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Module #01

Lecture #29

Phase diagram calculations

So looking at this quiz questions, the first question derives an expression for order disorder transition temperature. Many of you did it excepting that; some of you forgot the next statement which says, which follows a regular solution model. So that part you people did not bother, you simply equated delta H mixing to T delta s mixing, without bothering that it is following a regular solution model, so that means, I need to bring in omega X A X B and then try to get an expression in terms of omega. So that is the only mistake some of you have done; I think it is not a major problem.

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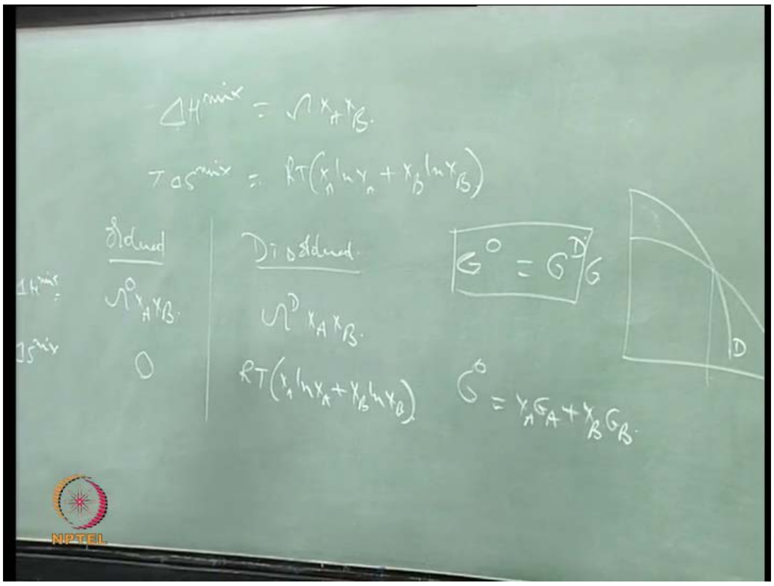

Simply only thing is, you need to find out; the moment you say regular solution model you know delta H mixing is omega X A X B, and T delta s mixing is, what we know is X R T into X A l n X A plus X B l n X B. But, if you want to consider ordered and disordered now carefully, so for the case of ordered and disordered you are basically, what you are going to do is you are going to equate G of the ordered phase and the G of the disordered phase. That is what you are basically going to do, the temperature at which the both the free energies are going to be equal is what is of importance to us. That is the temperature at which, we will see one of the phase starts becoming more stable with respect to the other phase for example, if I simply plot G of the ordered and disordered, so the ordered phase will be something like this, the disordered phase will be something like this; this will be the disordered, this will be the ordered and we are looking at this temperature. So, at that temperature this is the equation, so if you want to get G, basically G is nothing but H minus T S.

So, when we are considering the H; delta H part of it you would see the delta H mixing for the ordered will be more negative, so it will be omega X A X B, so omega of the ordered. So, this will be omega of the disordered X A X B that is, for the disordered, and this omega ordered will be more negative than the omega disordered; that has to be remembered. And when I am talking of delta s mixing term, delta s mixing term for the ordered, if it is perfectly ordered this is 0, and this is R T X A l n X A plus X A l n X B. This part if you take it then you can easily equate it; I think this part some of you have not considered, so you have to consider when it comes to ordered case, only the delta H mixing term will be there, in the ordered case in the G, in the disordered case you will have both. And you may say where thermal entropy is coming in to picture; the thermal entropy comes into picture when you are considering the individual elements.

Because whenever I am writing G naught I say X A G A plus X B G B. It starts from here, and thermal entropy would come into these two, so that has to be remembered. So, you will have thermal entropy coming in case of the disordered, and along with the thermal entropy you will also have a configurationally entropy in the disordered whereas, in ordered case you will not have configurationally entropy, you will only have the thermal entropy. So, once you consider that then the expression becomes easier and expression becomes more correct; some of you have not considered it I want you to remember this in future. Next we said a pressure effects; I think all of you have done this is very easy, so no point in going in detail. But when you say pressure affects, so some of you have ignored that that there is also a deformation which can induce pressure in to the sample which would give you a more of a shear kind of stresses inside the material and that aspect we are not considering here, you have considered only the isostatic pressure; all of you have done that I think that is fine then. Then the thing is what is the need for the coherent precipitates at high under cooling. Frankly speaking I am not really satisfied with any of the answers. When you say what is the need you have to think about why coherent precipitates should come at high under cooling, why they are not able to come, why they are coming there at high temperature, why there is a necessity for the coherent precipitates to come at a low temperature.

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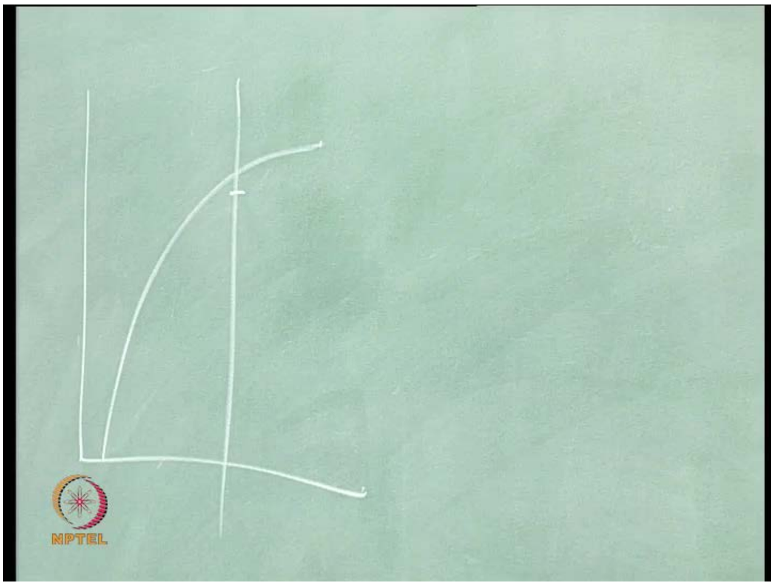

If you consider that, if you look at the alloy; any alloy, if I am, if the precipitation is taking place at that temperature, we already said that at the temperature if you are just below the solvus line you can easily have the nucleation of the second phase happening at the grain boundaries, right.

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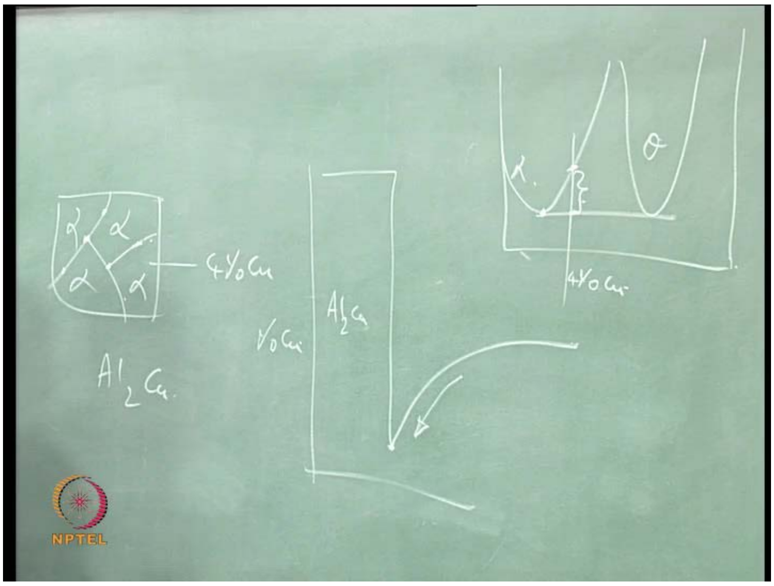

So grain boundary; if you consider an alloy at that particular condition, so the alloy would be something like this, let us say alpha phase. This alpha the moment I bring it below it wants to precipitate out the second phase, and the second phase can actually nucleate at these points, and also at these points and then grow. And for the growth of that and for the nucleation of that what you need is a diffusion of copper atoms, because the second phase is A l 2 C u phase which has a higher copper content when compared to the matrix; am I right.

So, A l 2 C u is almost one third copper whereas the matrix has only four percent copper if I am considering aluminum for copper alloy which is a traditional alloy. So, if I am considering such an alloy then if this has to nucleate and grow you need copper atoms to come from the matrix to this precipitate, and you have seen this happening when we talked about this, if this is the beta phase A l 2 C u. If we plot percentage copper what it called concentration profile; concentration profile looks like this we said, because if you remember the free energy composition diagram we drew a free energy composition diagram where you have the A l 2 c u phase here, the alpha phase here, and if you join a common tangent this is the theta phase and this is the alpha phase, and this is our alloy composition for percent copper and this composition is where the composition of alpha in equilibrium with the theta phase A l 2 c u phase. And the composition of alpha far away from the theta phase will be the starting for percent copper, and there you say, you see that there is a driving force, there is a gradient for the copper to move towards it and that will drive the theta phase to grow. These are possible at high temperature because there is a temperature thermal driven diffusion that can happen, because you can easily have atomic diffusion taking place at high temperatures at this temperature. The moment I cool these two temperatures like this, then the problem is more of a thermal diffusion; thermal diffusion is more difficult. And when the thermal diffusion is more difficult, for the alpha to nucleate there is more difficult and nucleation and growth of not alpha, of a theta phase or any phase for that matter precipitate phase to nucleate there, any phase when I say in this particular system it is theta, in some other system some other phase may be. In this system the equilibrium phase is the theta phase, so that theta phase to nucleate at the grain boundaries is more difficult, so the system starts searching for ways of the second phase formation in a way which does not involve nucleation and the growth at the grain boundary.

That is when the system starts looking for what are the other ways where I can have the super saturation being reduced because the alpha is super saturated. So, the super saturated alpha is not stable because it has a free energy of this, so this is a much higher free energy than this which is a two phase mixture, so it wants to precipitate out. Then it sees that such a precipitation at the grain boundary is difficult, and then it starts looking for what are the other ways of nucleation, then you see that the only way of nucleation is nucleating within the grain. If the grain boundary is not possible because for the atoms to diffuse from the center of the grains to the grain boundary is very difficult, so nucleation and growth has to occur within the grain. So when you say what is the need, this is the need. We should know that the nucleation at the grain boundary and the growth is difficult because of the diffusivities being low, then the system has to look for ways of nucleating within the grain, and if it is within the grain there is no possibility of theta nucleating within the grain. Theta cannot nucleate within the grain because theta has a structure which is entirely different from that of the matrix structure which is a tetragonal structure where as the matrix is f c c structure.

So, because the theta now cannot nucleate, now the system starts looking for what are the other things which can be a transient phases which can nucleate within the grain, so that is how you see the coherent phases come in to picture. Only when the phase; second phase is coherent with the matrix it can nucleate within the grain, if it is not coherent with the matrix it cannot nucleate within the grain. So, the need for coherent nucleation comes into picture because of the difficulty in nucleation at the grain boundaries and the necessity for nucleating within the grain, and the moment there is necessity for the nucleation; where is the necessity coming from because it is super saturated it cannot remain as alpha any more. Once you bring it to that temperature this much of super saturation is not allowed, so it wants to give away copper atoms. If it wants to give away copper atoms then it has to nucleate within the grain, and if it has to nucleate within the grain the only phases that can come out are either coherent or semi coherent and that too again depends on as you people already have written some of you, depends on what temperature you have, because now we know different solvus lines.

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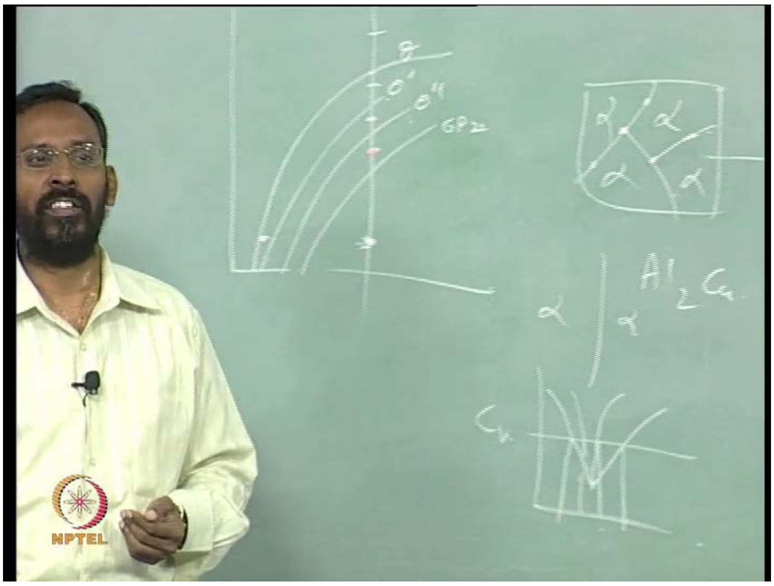

We talk this is a theta solvus, this is a theta prime solvus, theta double prime solvus and this is a G p zone solvus let us say. So, depending on where is your alloy and the temperature so that coordinate the temperature coordinate and the composition coordinate depending on where you are, you will have that particular phase. Having a sufficient driving force for, you see for a something to nucleate you also need a driving force this alloy for example, if I bring it and keep it here it cannot precipitate G p zones though they are the most coherent, because there is no driving force for the G p zones to nucleate. So, you need to have a driving force for the phase to nucleate and among the phases that have the driving force the system will choose the one, that one which has the best coherency which needs the lowest energy for it to nucleate. When I say lowest energy it involves both strain energy and the surface energy. So, something which can nucleate and grow with the lowest combination of strain and surface energy is the one that would nucleate among the phases that are possible. So, if am at this temperature for example, if am at this temperature you can see that at this temperature all these three are possible, theta is possible, theta prime is possible, theta double prime is possible.

So among this; yes, see basically if you look at a quenched in vacancies you have some of them, but to a large extent many of these vacancies; because vacancy migration is faster, they actually migrate to the grain boundaries very easily. In fact, that is a reason why you see what is called precipitate free zones. In fact, if you look at how the vacancies are and plot if you think there is a grain boundary. So, there is alpha and alpha, and if you look at the vacancy concentration, plot vacancy concentration as a function of distance you would see this kind of a thing, the vacancy concentration is very low at the grain boundary because it has already migrated to the grain boundary and within the grain you have it. And if you say that there is a critical vacancy concentration that is required for the nucleation to take place as you have mentioned also, we need a critical concentration of vacancies so that the vacancies can act as a nucleating sides and put a certain value of critical concentration. Then you see that within this domain, within this domain the vacancy concentration is lower than that critical value, so in principle within that distance there can be no nucleation.

That is the reason why we get what is called p f z and in fact, depends on whether you are quenching very fast or quenching slowly. Sometimes if you are quenching slowly then what happens is this region is going to be larger. So, you would see the same, you may see something like this, so that means there is enough time for the vacancies which are farther from the grain boundary to move, migrate towards the grain boundary and then get merged into the grain boundary or get annihilated into the grain boundary, and that is the case then you would see the p f z will be larger. That is the reason why there is a necessity to actually quench very fast if you want to avoid p f z. If you do not quench very fast that is why most of the aluminum alloys they actually quench into you know either into iced water or you know into some subcritic or I mean subzero temperature. If you simply quench into normal water, that also depends on how much time you are spending to take the sample out of the furnace. So, when you are actually doing experiments all this become important that how much time you actually you know spend on taking the sample out and then before it reach the actual quenching medium; these are all important. And if the time is longer then you see all this happening and if that is the case you get a larger p f z.

So, quenched in vacancies are also important, yes the most of the time you can have nucleation taking place there, but you should have sufficient quantity of that. There is a critical quantity that is required because if you have sufficient number of vacancies, sufficient number of copper atoms can come. See basically, A l 2 C u or G p zones has to nucleate let us say, G p zones means is mostly a pure copper. So, and a pure copper, I mean almost pure copper let us say of a critical size has to form; R star is important. So, pure copper of a critical size to form; that means you need to have sufficient vacancies where copper atoms can come and occupy there. If you do not have then you would not see any nucleation on that then the only other possibility of nucleation is it looks at certain crystallographic planes and the nucleation occurs on those crystallographic planes. If it is nucleation on the vacancies there is no crystallographic planes, it can be again random nucleation, is it clear; which one, C v is concentration of vacancies in principle, I think you all know concentration of vacancies is an exponential function of temperature.

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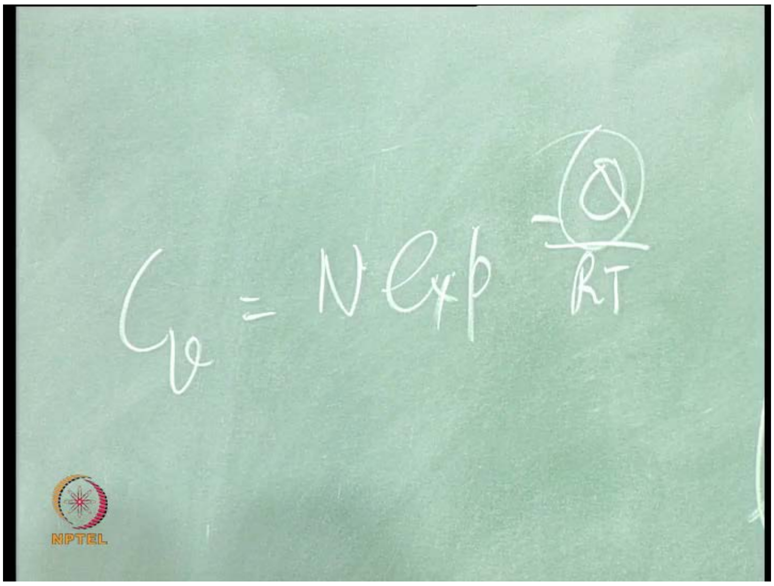

We can always write C v equal to some n which is a number of atoms into exponential minus q by R T where q is basically heat of what is heat of formation of vacancies, the amount of an enthalpy that is required for the formation of vacancies. So that is the reason why when I am at a higher temperature I have certain vacancies, if I am at a lower temperature I have certain lower number of vacancies, the lower the temperature the lower the vacancies, and if I am quenching from a higher temperature to a lower temperature, because I am not providing sufficient time for the difference of the vacancies to get annihilated, then they get retained that is what we call them as quenched in vacancies. Whenever you quench, there is a lack of sufficient time for this dislocations which are excess dislocations that are available at high temperature which cannot be retained at lower temperature, this difference has to basically go to the either surfaces or to the grain boundaries. These are the only two possibilities and that if it does not happen then you will have quenched in vacancies left out.

I think that is it and then what would be the positions this all of you did it well. Explain why uniform precipitates cannot grow, half of you have done this I think half of you could not do it. Basically, you all should know that the driving force for particle coarsening comes only from the size difference.

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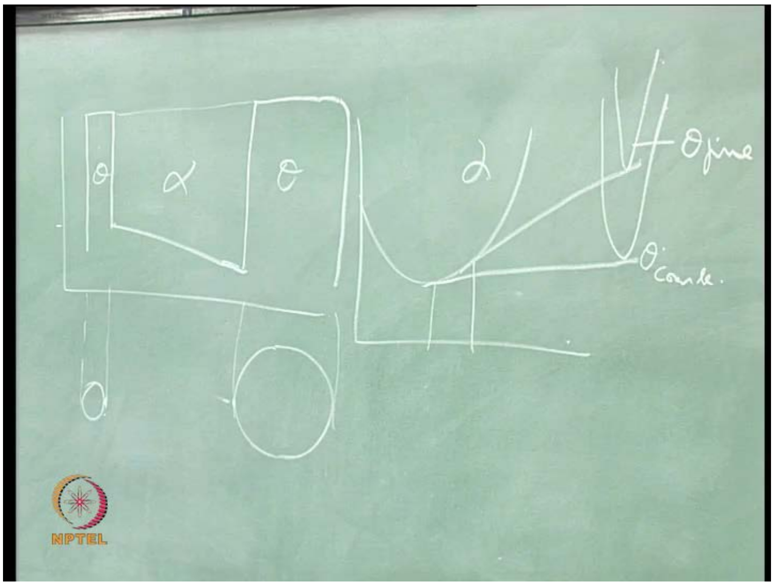

All of you know that if we draw the free energy composition diagram, if this is alpha, and if this is a course particle, and if this is a fine particle let us call it as theta phase or whatever it is, this is course, this is fine. Then if I draw a common tangent, if I draw a common tangent you see that this difference in the composition that means, if I have a fine particle, course particle, the alpha which is in front of the course particle and the alpha which is in front of the fine particle have different composition and the fine particle has a higher composition than the course particle. So that means there is, if I draw a composition gradient, I mean concentration profile you may get something like this, here you have a higher concentration, here you have lower concentration. So, and if you actually talk in terms of this, if you plot it here let us say, if you look at it you will see that this is the concentration and then you would see that there is a decrease in the concentration again. You see this is the kind of thing that you see.

The theta phase will have the same concentration that does not change and theta phase has a, so whether it is smaller theta or a larger theta it will have a fixed value of its stoichiometry. So, this a theta phase, and this is the alpha phase, and the alpha phase will have this and the moment they have equal sizes, when I say uniform precipitates that means they all have the same size, if they all have the same size; do not bother how did they come we need not have to bother about that as long as all precipitates have same size, then this difference does not exist. If this difference does not exist there is no gradient, if there is no gradient then they cannot grow, I mean dissolution of one precipitate growth of another precipitate is not possible. Only thing is we say that ideally I mean, I should say ideally if all precipitation has occurred at the same time, and if it is a homogenous precipitation not a heterogeneous precipitation if it is homogenous precipitation then in principle everywhere nucleation have taken place and this is what we call it as a site saturation case that there is no more nucleation taking place. At time T equal to zero all the nucleation has taking place and all of them are trying to grow, when they are trying to grow you get into this problem.

But if you consider a case where you have different different levels of heterogeneous nucleating sides that are available with different hierarchy and some where the nucleation takes place first, and somewhere else the nucleation takes little later. And during this process the one which has already nucleated starts growing and as a result you would see that these differences in the sizes exist, and once there are differences of sizes you would definitely see such Ostwald ripening taking place. Correct, again the same situation as that of what we see the coherent precipitates, widmanstatten precipitates are all either coherent are semi coherent. No, they might see different places not only always at the at grain boundary you will also see them nucleating and in fact, even if they have nucleated at the grain boundary they grow in a particular direction, not all grains you will see them growing. So, those grains which are favorably oriented for this planes to grow you will see them growing in for example, if you have a grain boundary you will not see widmanstatten structure growing in both the directions, you will see growing only in one direction. So, this is basically because you need to have a proper plane which can nucleate this phase and then growth can take place there. Nucleation occurs even as stalking faults, nucleation occurs, nucleation of widmanstatten can also occur at the dislocations, but what is more important is how it grows.

The growth occurs on certain planes where as a normal grain boundary alerter mass then can grow in all directions that is the difference. Now there is one aspect which we have not considered earlier which is about phase diagram calculations, we talked about it, but not really gone further so I thought today we will take it up.

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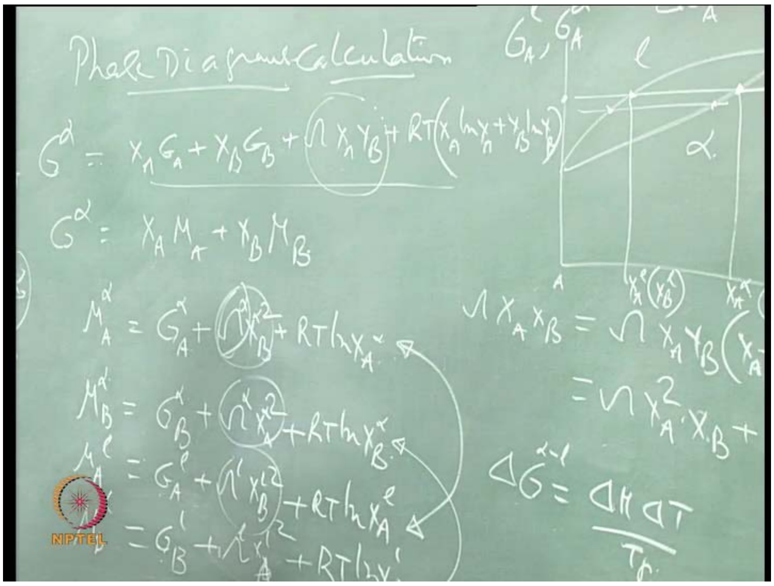

If you want to talk about phase diagram calculation let us take a simple phase diagram such as an isomorphous and then later go into the other type of phase diagram. If you look at this we said that this is a liquid, this is a solid and at each temperature you have equilibrium between liquid and solid, am I right. So, if there is equilibrium between liquid and solid you can write an expression of free energy for the liquid, and an expression of free energy for the solid which can be written something like X A G A plus X B G B plus, let us say if it is regular solution you can write X A X B plus R T X A l n X A plus X B l n X B.

This if I write it lets say for G alpha, I can also express G alpha in another way in terms of chemical potential. Why I have to bring in chemical potential here is because our equilibrium definition is from the chemical potential, all of you now that in a multi component system more than a single component system whether it is binary or turnery or quaternary the equilibrium is always defined by what is called chemical potential. When I say the chemical potential of a particular element G bar or mu oh! sorry sorry or mu, some people call it as G bar, some people call it as mu of a particular element in a particular phase is equal liquid let us say and you call it again as beta or whatever it is. Whatever number of phases that are present, if the chemical potential of a particular element in different different phases is equal then we say they are in equilibrium, the reason is once the chemical potential is equal then there is no driving force for the atomic atom atom movement. This we have seen that whenever delta mu is zero then there cannot be movement of atoms from one side of the phase to the other side of the phase, and if there is no movement of atoms we say they are in equilibrium, so that is the reason why the chemical potential has to be equal. So, we can write any free energy expression as X A mu A plus X B mu B, you can also call it as G bar or mu whatever it is. So, a free energy of any phase can be written as because what is mu is nothing but rate of change of free energy with composition, so as a result we can easily write this as this. If that is the case then basically we can find out what is mu A and what is mu B from this expression.

What you have to do is you have to basically look at all the terms which have X A as the coefficient and all those terms which have X B as the coefficient and then take them out and then equate it to mu A and mu B. So, to get that what we can do is this particular term you have both X A and X B into it here for example, X A is there so I can say mu A equal to G A because this is X A, but in this how do I do it. So, what you can do is there is a easy way to do it, what you can do is you multiple this with X A plus X B. If you multiple with this with X A plus X B, X A plus X B equal to one, am I right, so if you are multiplying with X A plus X B you can write it as omega X A X B equal to omega X A X B into X A plus X B. So, you can write it as omega X A square X B plus omega X A X B square; am I right. Simply you multiple this term with this, so that you have now, sorry this is X B, so omega X A square X B and X A X B square. So, you can easily write that this is omega X B square plus R T l n X A, so the chemical potential is actually equal to this.

Similarly, I can write chemical potential of B is G B plus omega X A square plus R T l n X B. This is for a particular phase alpha, this is G A alpha, G B alpha, omega alpha, omega alpha here and R T X l A alpha. Why I have to say alpha here also because when you say X A and X B it is nothing but the composition of a phase so that means, for example, if I am talking of this particular point, this point is the composition of alpha. The composition of the alpha can be expressed either as X A or as X B and we know that X A alpha plus X B alpha equal to one, so once I know that I can write this as like that. Similarly, I can also write omega A and omega B for the liquid. Once I write the omega A for the liquid and omega B for the liquid, where nothing but here you will see it will be G A liquid plus omega liquid into X B square of liquid, this will be alpha, and similarly R T l n X A liquid will come.

Once you get this you can simply equate these two and equate omega B alpha to omega B liquid. Once you equate this you will see how many unknowns are there, how many things that we need to find out for example, if I simply say omega A liquid is equal to G A liquid plus omega liquid into X B square liquid plus R T l n X A liquid. Once we equate this to this what are the things that I need to know, what is that that I want to actually find out, whenever you want to find out a phase diagram when I say I am talking about calculation of phase diagram what is our interest, equilibrium compositions at different temperatures that means, at this temperature T I want to find out what is this in terms of X A alpha or X B alpha one of the two, similarly here X A liquid or X B liquid. Once I know one of them the second one is known to me so that means, these two compositions are to be found out at each temperature; that is the interest of us when you say I want to calculate the phase diagram.

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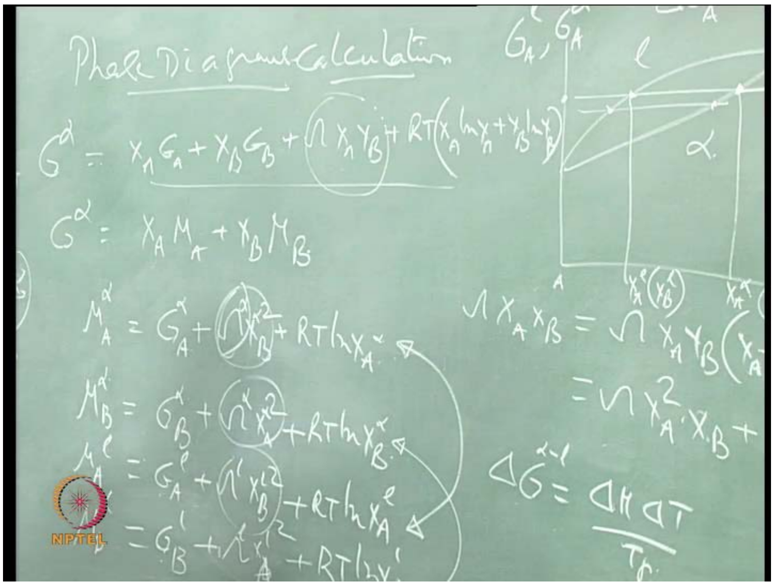

So, that means that at these temperature I have two unknowns, one is the composition of the liquid another is the composition of the alpha. So, if that is the case in this particular equation wherever there is X B I can write it in terms of X A. So, basically there is only one compositional variable for the alpha, and one composition variable for the beta. For the liquid there are no two compositional variables for a particular phase because X A alpha and X B alpha are connected with each other, am I right. So, once I know that they are connected with each other I can replace X A alpha with one minus X B alpha or I can replace X B alpha with one minus X A alpha, I can do it any everywhere. So, what I need to find out is if I want to equate this with this, if I equate these two I get an equation, in that equation I have basically two unknowns X A alpha and X A liquid; these are the two unknowns. And what should be then the known things for us, we should know what is the temperature at which we are doing it, we should also know omega liquid and omega alpha. If I know omega liquid and omega alpha that is nothing but the interaction parameter of the liquid interactions of the alpha, then only I can do this calculation. If I assume that the system is let us say ideal, then this term will not exist; these terms will not exist. Then simply it will be G A alpha plus R T l n X A G B alpha, I mean G A liquid plus R T l n X A liquid that is it. So, I will say that this whole term will not be there, and what I need to know is only temperature and the pure metal free energies at the temperature, that means what is G A alpha at temperature T, what is G A liquid at temperature T. How do I find out pure metal values, how will I get G A alpha at temperature T; H minus T s simply, and H minus T s also can be written has H at two hundred and ninety eight plus integral C p D T two hundred and ninety eight to T.

So, what I need to know is simply c p, if I know the c p I can find out the G A, similarly the T S. So, I can actually calculate the G A, but there again the problem that comes into picture now for example, if I want to calculate G A liquid and G B G A alpha at this temperature, if I want to calculate so, G A liquid; this is A for me, so at this temperature I want to calculate G A of the liquid, G A of the alpha. At that temperature what is stable, only liquid is stable, alpha is not stable, and because alpha is not stable you will not know what is the c p of the alpha at that temperature, so that problem still exists for us. What will be the heat capacity of the alpha at that temperature is still not known, that is where you need to use what are called various thermodynamic models that are available, which we talked about it one of the class, where we talk about what is the changing free energy between alpha and liquid.

If I know what is delta G alpha to liquid as a function of temperature for a given metal A by some model; there are various models once such model is what is called thermals model, we have seen that where we know the delta G is equal to delta H into delta T by T F, am I right, this we know. And if I know this which is nothing but alpha to liquid, and what I need to know is, only if I want to find out the alpha free energy at this temperature I simply have to calculate what is a liquid free energy at that temperature, and to that I add these value then I will find out what is the alpha free energy at that temperature; it will be higher than that of the liquid. Similarly, if I am at this temperature, if I want to find out what the G B alpha and G B liquid at this temperature, again at this temperature what is stable it is only solid alpha, liquid is not stable. Again I use this, so I calculate the free energy of the pure metal B in the alpha form by using this, this is not a problem for me because c p of the solid at that temperature is available, and from that I calculate G B alpha, and for finding out G B liquid I use a model like this. And once I know this model I find out the delta G, add the delta to this. So, I can always write for example, delta G is always delta G of alpha to liquid is G of liquid minus G of alpha, am I right. So, if I know G of alpha I can find out the G of liquid by simply writing that G of liquid is equal to delta G plus G of alpha; take this that side, I know G alpha so I can find out G liquid. If I know G liquid and I do not know G alpha I simply do that G alpha is equal to G l minus delta G, rearrange. So, one of them if you know and the delta G if you know then second one you can always find out at that temperature. So, what we need for any such phase diagram calculation is pure metal free energies I need to know at that temperature, and if at all the system is following not an ideal solution but if it is a following a regular solution model I need to know the interaction parameters. And once I know the interaction parameters I can happily plug those numbers, and then equate this to this and equate that to another which is nothing but mu B liquid is equal to G B liquid plus omega into X B liquid square X A liquid square plus R T l n X B liquid. So, this you equate and these two you equate, so you will get two equations and how many unknowns; two unknowns.

Two equations, two unknowns can be solved provided rest of the things is known. What are the rest of the things I need know, I need to know this value, I need to know pure metal values. Once I know all the pure metal values, once I know the omega alpha and omega liquid; this is omega liquid, then I can plug in those things and easily calculate and write a program that at each temperature keep calculating these two and equate those two. And when you equate those two and solve the two equations and then find out this, so that means at that temperature I am able to find out this and this. And now I change the temperature, ask it to again calculate because one more important thing is when I change the temperature what changes, C p changes; that means these values will change. But one thing that we always assume in all these calculations is that this is not changing; again there is an assumption. In fact, if you go to basic alpha calculations people have actually done it, but I mean by problem here is what is omega, omega is nothing but the interaction between A and B let us say, am I right.

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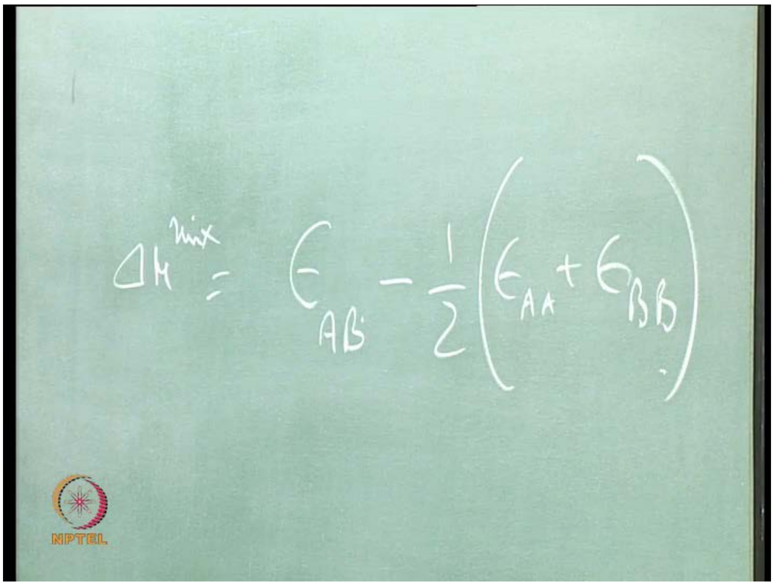

$$\Delta H^{mix} = \epsilon_{AB} - \frac{1}{2}\left(\epsilon_{AA} + \epsilon_{BB}\right)$$

In fact, omega comes from quasi chemical theory where we actually calculate delta H mixing is taken as, if you know the energy of the A B bonds minus half of the energy of the A A bonds plus B B bonds. If you have A and B elements, what are all the types of bonds that are possible, there are three types of bonds possible A A bonds, B B bonds, and A B bonds. If the A B bond energy is lower than A bond energy and B bond energy; this is am considering half, so basically you are normalizing. So if you consider these two, if this value is smaller than these two, then the delta H mixing will be negative. Smaller means what, they are strongly bonded, if this value is larger than these two then you see delta H mixing will be positive.

((no audio 41:36 to 42:09)) any I would say you know, I would say controversies in this whole thing. If you look at this equation; this equation is a very interesting equation, the moment you say that it is a regular solution model what are you saying, a regular solution model is that where the A and B have some interaction; it could be a positive interaction, it could be a negative interaction, but it is never zero. If it is zero there is no regular solution model, its only ideal solution. But when you consider the entropy of mixing, entropy of mixing is calculated based on a random; everything is random, there is no specific interaction between A and B, so that problem always exists in any free energy calculations. There are models which are available, which try to consider what is excess entropy that you get when there is an interaction between A and B. For example, what is called short range order, when there is a short range order how does the entropy change, so there are a detailed models available, but for our class I think it is a little too much. So, now what we can also do is we can also find out; after finding out this kind of phase diagrams, you can also find out how the solvability changes with temperature.

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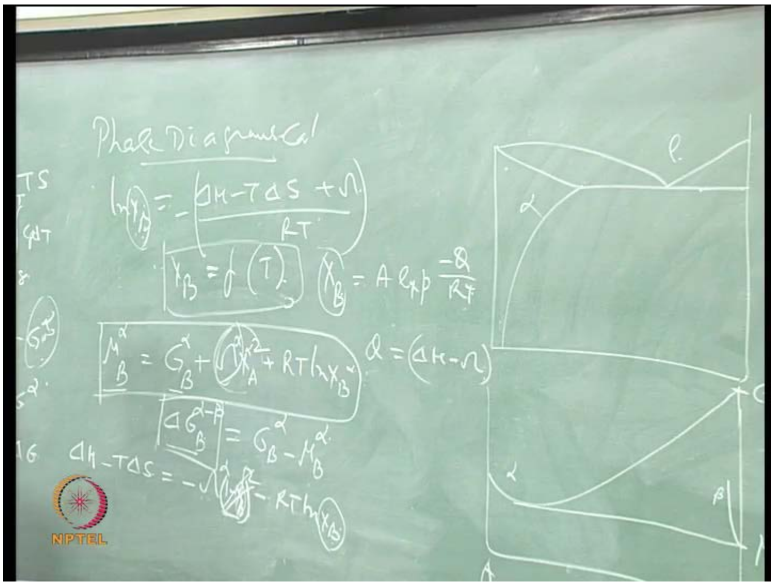

For example, if you look at let say take a phase diagram like this where liquid is giving alpha plus B instead of beta, you can also put beta if you want. And now this alpha composition changes with temperature, the solvability is changing with temperature. How do I consider this solvability change, again do the same equation. For example, take this equation where omega A is G A plus alpha omega, I mean mu A chemical potential is G A plus omega alpha into X B square plus R T X A l n X A, and try to draw a free energy composition diagram here. If I draw a free energy composition diagram how does the free energy composition diagram go, so this is for alpha, and you have a beta. Beta actually is a B; pure B, I can simply write it as beta here, but which is almost like a pure B and draw a common tangent between both of them, am I right. Now what is a this value, this is if I write this in terms of B I put B, simply I did it in terms of B because we are on the B side. So, if you look at this what is this value, this is nothing but G B alpha, am I right, what is this value, this is G B alpha; pure metal B in the alpha form. And what is this value, this is mu B alpha, am I right, because this is a common tangent and this is alpha, so mu B alpha is here. So, the difference between these two also can be written as what is the free energy difference between alpha and beta in the in the a for the for the pure metal B.

So, if I say delta G for B which is alpha to beta; beta has a different structure, and alpha has a different structure, this can be written as G B alpha minus mu B alpha. If you write that then basically you can write this whole thing as this minus this will be this, and this value can always be found out as delta H minus T into delta s for the alpha and beta. And if I put that this would be equal to, if you take this as G B minus mu alpha G B minus this, this becomes as minus of omega alpha X A square plus R T l n; not plus this is also will be minus R T l n X B, am I right. So this delta G is this minus this so you take this whole thing on this side, so this minus this is equal to this value, so you can show that. And once you show this, then what we can actually write is find out how X B changes with temperature.

You can easily write for example, l n X B is nothing but delta H minus T into delta S. So, you have to basically write this as in terms of one minus X B whole square. So, one minus X B whole square, if you write this you will have the X B term coming here, and then that can be written in terms of omega, and once you write it in terms of omega you can calculate how X B changes as a function of the temperature. So, here one minus X B square in place of one minus X B square, you find out what is the X B and then see how this and this can be connected, and you can show that how X B changes as a function of temperature. If you want we can derive this at some stage, but you can go back and see how it can be derived, and basically what you can see is how X B changes as a function of temperature because temperature comes in the denominator, and in fact you will get a term which will be an exponential term. I can write the final expression for you, X B is equal to for example, assume that X B is very very small. If you assume X B is very very small this value will be taken as very small, that means the solvability is very small if you consider, then this will go off and then you can easily write and then this term will be vanished and you can take it this way. So it will be plus omega divided by R T and minus of everything. So, see you can write X B is basically exponential; you will get a free exponential term and A exponential minus Q by R T.

You will see that Q value can be in terms of the delta H and omega. So, you can see that this Q will be nothing but that and A will be nothing but delta S by R; exponential delta S by R. So, there will be two exponential terms, one will be delta S by R, another exponential term will be having delta H. This Q will be nothing but delta H minus R plus R; you have to check whether it is signs whether it is negative or positive; you will get a term like this, so you will see that the X B is a function of the temperature. The higher the temperature the smaller this value, so that means the solubility increases. So, how solubility changes as a function of temperature can be easily seen from this kind of expression. So, we can do all these calculations just by knowing what is the chemical potential at a given temperature, and writing a chemical potential equation and finding out how the composition changes as a function of temperature. So, all calculations of phase diagrams are easier simply knowing one equation. This equation if you remember everything else can be done, and this equation also comes basically by equating one basic free energy equation with what is X A mu A plus X A mu B if you do that you will get that.

We will stop now.