Advanced Metallurgical Thermodynamics
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Lecture #28
Miscibility gap in phase diagrams

We just looked at first quiz answer scripts. I am generally happy because people did reasonably well accepting that two questions which I thought people could have done better. First question was about an expression to find out the Miscibility gap, the temperature at which the Miscibility gap closes. In fact, only three who have done it correctly. One is Vijayalaxmi, Prerana and Raghukiran. Very happy to see these three doing it right. Rest of them basically tried to equate.

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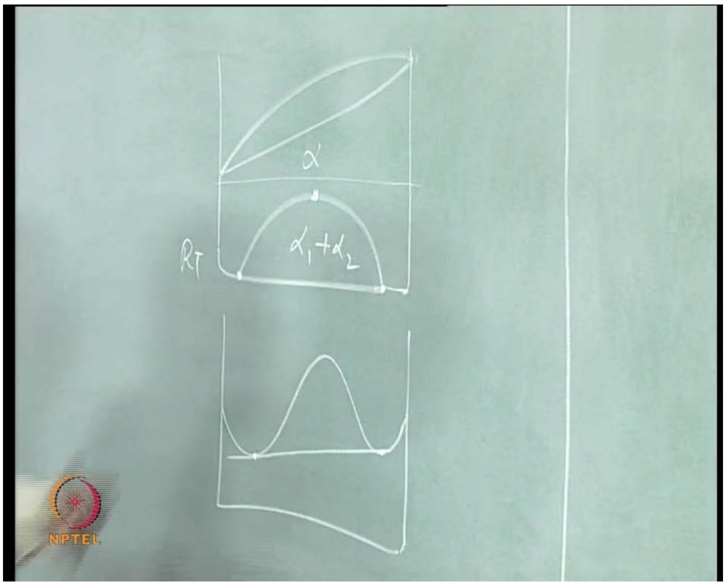

What we are talking about is Miscibility gap. I want do this today. So, we are looking at this phase diagram and we are interested to find out this, what is a temperature at which the Miscibility gap closes. That means, the temperature above which you have single phase alpha, below which you have alpha 1 plus alpha 2. If you look at what is called the free energy composition diagram, at any temperature within the Miscibility gap, we know that the free energy composition diagram looks like this, something like this and we can talk of a common tangent and these two points are what we call them as binodals.

If this is done at room temperature, these two points basically corresponds to these two points. Am I right? We said that and we said at temperature something like this, the same free energy curve would look differently.

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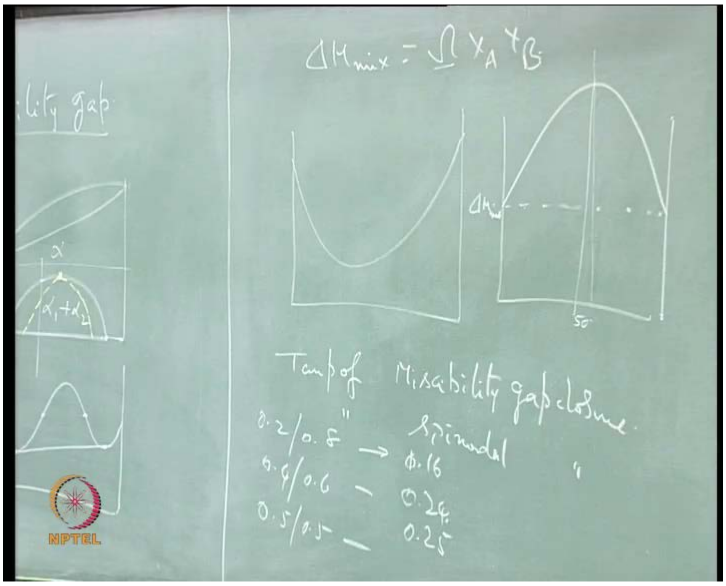

If you draw it once again, the free energy curve looks something like this. Am I right? So, that means, there a single phase is stable whereas, here a single phase is not stable. It splits into two phases and that brings us to two more additional points which we discussed, which we call them as spinodal points and in principle, whatever we are discussing here, the temperature for Miscibility gap closes is also the temperature at which the spinodal closes. Obviously because if I draw a spinodal curve with a different color, let us say chemical spinodal. Mind you, I am not talking about coherent spinodal. If I draw a chemical spinodal, chemical spinodal also closes at the same temperature.

So, in principle whatever temperature that we are talking about, the temperature at which of Miscibility gap closes, where the Miscibility gap ends is same as where the spinodal ends. What we call is a critical temperature for the spinodal decomposition at temperature at below which you have the spinodal occurring and what is the maximum temperature where the spinodal can occur? It is this temperature below which you can see. In fact, for every alloy, there can be a different spinodal temperature.

Similarly, for every alloy composition, there is a different temperature at which the Miscibility gap is no more there, but if you look at where is the maximum. The maximum usually comes at 50-50, provided we assume that the system is a regular solution model. That is what this question also clearly says assume that the system is following a regular solution model. The moment you assume that it is following a regular solution model, then we know the delta H mixing is omega X A X B and this omega X A X B is a symmetric function. If I plot the omega X A X B, if the omega is positive, then delta H mixing will look if somewhere I have, sorry if somewhere I have 0 here, the delta H mixing would look like this, perfect symmetric and it would go to maximum at 50-50, sorry at 50-50.

So, a omega is a single omega for the whole composition range, and that if you give a particular value, any value to it, then you can see that the maximum value of delta H mixing, for example, if I take a simple case like I take X A as 0.2 and X B is 0.8. Am I right? Then, X A into X B is how much? 0.16. So, if I take 0.2, 0.8, then the X A X B is the 0.16. If I take 0.4, 0.6, X A X B is 0.24. Only when I take 0.5, 0.5, you would say it is 0.25. Only then this is the highest.

So, that is why the maximum value or the minimum value of delta H mixing depending on whether omega is positive or negative is only at 50-50. At 50-50, the delta H mixing will either go to maximum or go to minimum, provided you will have omega positive or negative. When does it not go to a maximum or minimum? When omega is 0. As simple as that. When you have an ideal solution, then when omega is 0. Then, obviously, delta H is mixing is 0.

So, that is a very remote situation. We are not considering that. So, we are looking at omega being positive. First and foremost is when does, when you getting a Miscibility gap? When omega is in the solid is positive. This is very clear. All of you? I think this is very clear. Then, the next question is, what is a temperature at which you get this maximum? If you want to look at that, then obviously, we said one easy way to look at it which is what many of you, I have actually done, but at the same time, I said that correct way of doing that is another way which many of you have not done.

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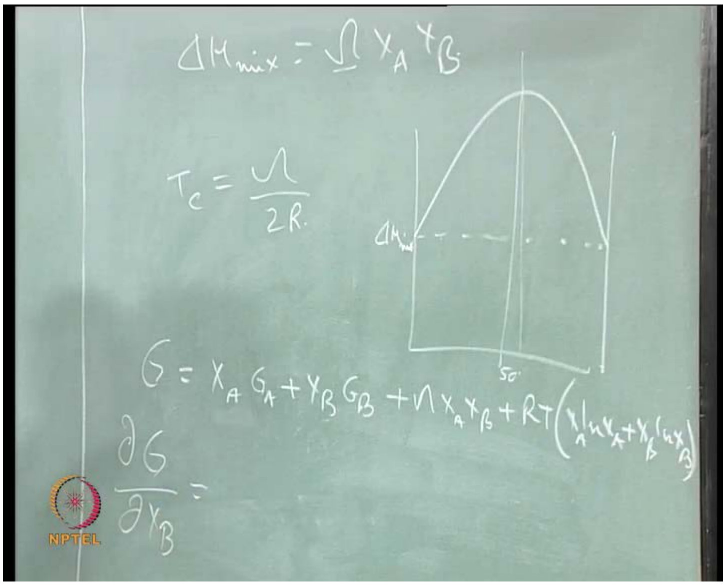

So, I said the easy way is to see what the free energy is. G is X A X B X A G A plus X B G B plus omega X A X B plus R T X A 1n X A plus X B 1n X B. This is the final formulation that we have. If that is the case, we said in principle it is a combination of delta H mixing and T delta s mixing which is going to decide this result. As a result, when T delta is mixing dominates the delta H mixing; that is when you would see that Miscibility gap closes. So, we said that if you can assume these as standard states and assume it to be 0, G A and G B. If we assume G A and G B is to be 0, basically you equate these 2 and that is one crude way of doing it. Then, equate these 2 and if you look at omega X A X B is equal to R T X A 1n X A plus X B 1n X B and then, equate these 2 and find out that T where this is equal, which is a very simple way of doing, but that is not the accurate way of doing.

The accurate way of doing is when binodals meet, when the binodals meet at a particular point and when binodals meet also the spinodals also meet. So, you should find out that particular composition and temperature, where the 2 spinodals are basically meeting. What is a definition of a spinodal? Where second derivative of the free energy is 0. So, basically take this expression, find out the second derivative and equate it to 0 and you would find that particular and again, put one boundary condition there that I am assuming X A equal to X B because I know that this would happen at 50-50. Of course, under situations where it is following a regular solution model, we are already assuming that it is a regular solution model. Once we assume that and then, put a condition that it is happening at a X A equal to X B, that equal to 0.5. Then, you would get an expression which is what actually T c equal to omega by 2 R. If you do this, you will not get T c equal to omega by 2 R. Many people have done this up to this and then, put T equal to this divided by this and then finally, said omega equal to, I mean T c equal to omega by 2 R.

How do you get from the T c equal to omega by 2 R? You will not get. Just because you put X A equal to 0.5, X B equal to 0.5, what are you going to do with this lan X 0.5? So, lan 0.5 does not give you the value that you are talking about. So, let us try to do that for your benefit today and then, see whether this really happens and you would see very easily that it happens. Let us look at the first derivative. I hope you people still remember in your marks. So, first derivative for this. Before you all do that, we should try to see there is one more boundary condition in this. What is the condition that we know in case of a binary? X A plus X B equal to 1.

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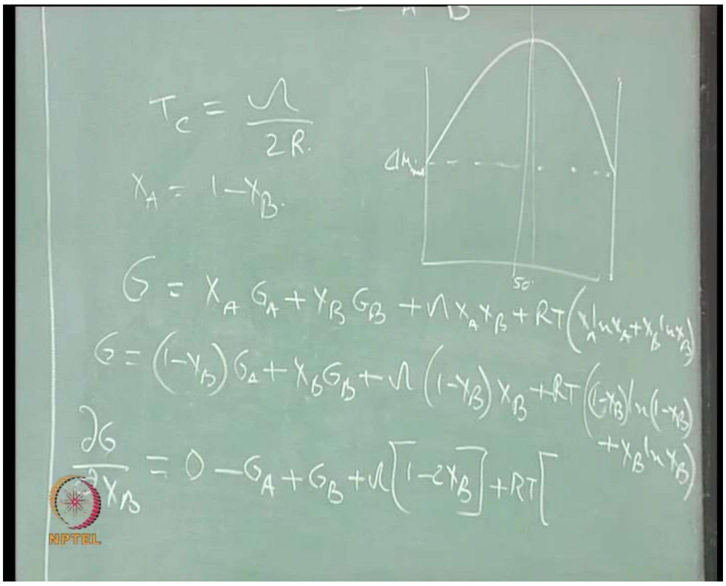

$T_c = \frac{\Omega}{2R}$

$X_A = 1 - X_B$

$G = X_A G_A + X_B G_B + \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$

$G = (1 - X_B) G_A + X_B G_B + \Omega (1 - X_B) X_B + RT((1 - X_B) \ln (1 - X_B) + X_B \ln X_B)$

$\frac{\partial G}{\partial X_B} = 0 - G_A + G_B + \Omega [1 - 2X_B] + RT[$

So, I can write X A always as 1minus X B.

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Am I right? So, simply wherever X A is there, we have put 1 minus X B and this, this, things like that. Once you do that, now you do this. First derivative we do with respect to B and you do with respect to A also and there wherever X B is there, you can put 1 minus X A. It does not matter. Usually, we consider B as a solute, as a solvent and that we are doing with respect to X B. If you do this, this is a G A minus X B G A, so G A is 0, derivative of a constant is 0. That much I hope you still remember.

So, this is minus G A, this is minus X B into G a. So, it will be minus G A derivative and this will be plus G B plus here there are 2. So, it is X B minus X B square. So, omega into X B is 1, derivative of X B is 1, X B square is minus 2 X B. Am I right? Now, you look at this is a little more complicated and l n is 1 minus X B is there. So, what we simply do is, we change the derivative here to 1 minus X B. That way we can easily do it.

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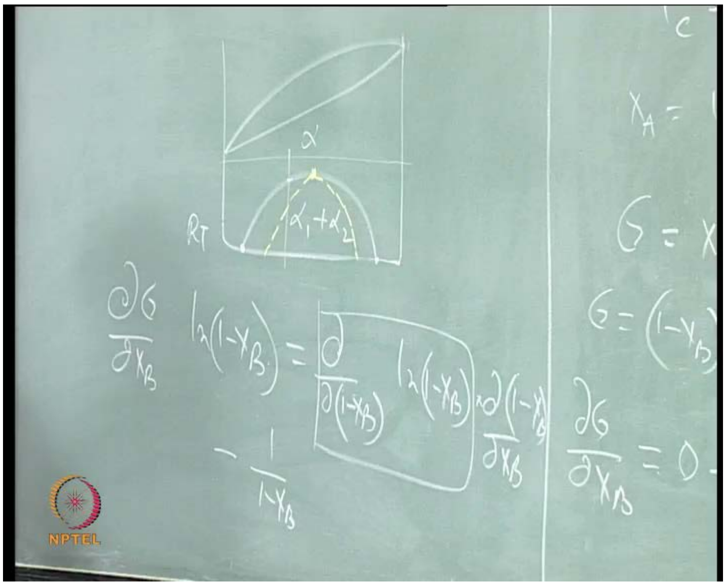

Whenever you want to do, dou by dou X B of l n X 1minus X B you want to do, you can simply write it as dou by dou 1 minus X B of l n X B l n 1 minus X B into dou by 1 minus X B by dou X B. I can always write like this. So, this I am dividing into 2 parts, so that this is easy for me and this is again easy for me. So, instead of changing dou by dou X B, I am taking, I will take dou dou by dou 1 minus X B. Once I do that, it becomes very easy and this will become, I will do it in two parts.

First, I can keep this and then, derivative of this. This will be what? Minus 1. Am I right? 1 minus X B derivative is minus 1. So, that means, this is minus l n 1 minus X B. That is one and then, I now keep this and then, take derivative of that, take derivative of this.

This is what? 1 minus X B, 1 minus 1, 1 by 1 minus X B. This is the derivative, this part and the derivative of this part is minus 1. Am I right?

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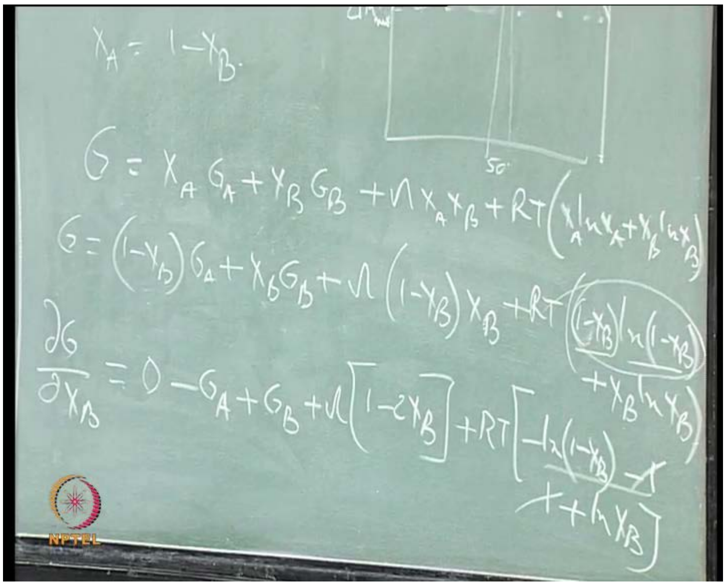

$$x_A = 1 - x_B.$$

$$G = x_A G_A + x_B G_B + \Omega x_A x_B + RT\left(x_A \ln x_A + x_B \ln x_B\right)$$

$$G = (1-x_B) G_A + x_B G_B + \Omega (1-x_B) x_B + RT\left((1-x_B)\ln(1-x_B) + x_B \ln x_B\right)$$

$$\frac{\partial G}{\partial x_B} = 0 - G_A + G_B + \Omega\left[1 - 2x_B\right] + RT\left[-\ln(1-x_B) \cancel{-1} \cancel{+1} + \ln x_B\right]$$

The derivative of this part is 1 by 1 minus X B l n of anything is 1. So, derivative of this is minus 1. So, this is minus 1 by 1 minus X B and if I do that and this, I am basically keeping this constant. So, that would become actually minus 1 because this 1 minus X B divided by, I mean multiplied by minus of 1 by 1 minus X B. So, its gets cancelled, so you get minus 1 there. So, this whole part is simply this derivative of that. Is this clear or still some doubts? Then, the rest is again X B. You keep X B and derivative of this is simply 1 by B. So, it is plus 1 and keep l n X B and do this. So, plus l n X B. This is what it is. So, plus 1 minus 1 goes off and you have l n X B minus l n of 1 minus X B. This is what would you get and that is what is going to be the final expression.

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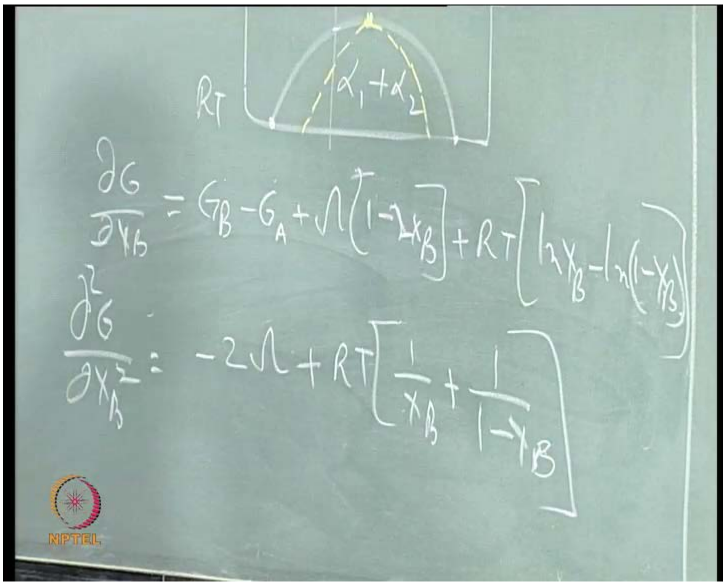

The final expression for that is if I say dou G by dou X B is equal to X G B minus G A plus R into 1 minus X 2 X B. Am I right? Plus RT into l n X B minus of l n 1 minus X B. This is the first derivative. Once I know the first derivative, I can easily do the second derivative, dou square G by dou X square. If you do that, this and this term cancel. This term will vanish because it is derivative of constant which is 0 and then, this it is omega. Again it is constant. So, minus 2 X B is minus 2. So, this is minus 2 omega.

The derivative of omega minus 2 omega X B is minus 2 omega plus RT into l n of X B again is nothing, but 1 by X B. Am I right? 1 by X B minus l n of 1. So, again 1 by 1 minus X B and because this is minus and you will get a minus there, so that will be plus. So, this is what you would get and this is what if you equate it to 0, you will see.

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I have never done these derivation for you assuming that you all can do it.

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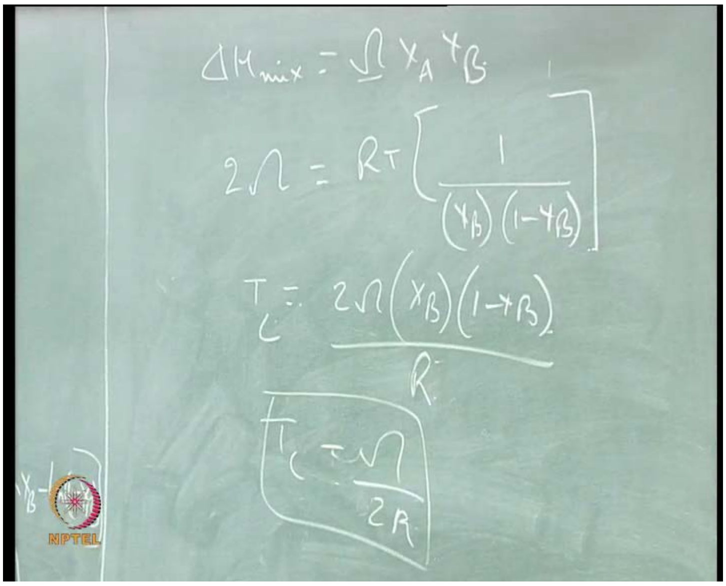

So, you can see that basically 2 R 2 omega is equal to R T into, if you take it, so it is basically 1. Am I right? If you do MCM there, you would basically get that. So, that means, T is 2 into omega into X B into 1 minus X B divided by R. That is what is T c. Solves the problem. You put X B as 0.5 and you see this is 0.5 into 0.5. So, 0.25. So, you would see that T c is omega by 2 R. What are the assumptions in this? Whole derivation, regular solution model and one more assumption.

Yes, we are assuming that the spinodal or the Miscibility gap closes at the middle of the phase diagram. It is an assumption. It need not, but in a number of cases, you see that, provided your phase diagram is a simple isomorphous and there is nothing else on the other sides. In number of cases, you have a Miscibility gap. If you go back and see some phase diagrams, you have Miscibility gaps only in a certain region. Rest of the region, you have possibly intermetallic compounds and things like that.

This is really a fascinating thing that you have an intermetallic compound in phase diagram, you still have a Miscibility gap in certain region. There are number of cases. I want to you to simply go back, if you are interested see Massalski example, 3 volumes of phase diagram. Just go through. You will see phase that basically tells that this itself is wrong assuming that you have regular solution model. Regular solution model basically assumes that the interaction parameter is the same from one end of the phase diagram to the other end of the phase diagram, which is actually not true. In fact, it is not true in all the cases where you have intermetallic compounds. Whether you have Miscibility gap at all or not, the fact that you have intermetallic compound in a phase diagram indicates that at a particular composition, there is a strong negative interaction between a and b. Otherwise, you would not get intermetallic compound.

So, that means, at some other places, other two sides for example, you take iron and carbon f e3C. At 6.67suddenly you get fe3c. You do not have any other compound in the whole of phase diagram up to 6.67. So, that means, that there is something special happening at 6.67, where you have 3 atoms of iron and 1 atom of carbon. Suddenly, such a configuration you see there is a strong attraction. This is true with other compounds also. If I take gold, copper, c u, a u, you have 3 compounds we talk about. AuCu, Au3Cu, Cu 3Au. That means, at 3 is to 1, 1 is to 1 and 1 is to 3. These 3 compositions, you have an intermetallic suddenly, at no other compositions you have.

That means, at other compositions, the interaction between A and B is not as strong as at these compositions. So, that basically tells that omega is not really constant at all compositions and in other cases also which I have told you earlier. For example, copper, zinc. If you take an example, we see that zinc dissolves in copper to a large extent; whereas copper does not dissolve in zinc less than 1 percent, whereas zinc solubility in copper is almost 40 percent, 38 percent also.

So, this basically means, the interaction between the copper and zinc, on the copper side is different and on the zinc side is again different. That is a reason why people had to go to sub-regular solution models and wherever inter-metallics are coming into picture, people do not use, neither of these regulars or sub-regular, we have what are called other models called cluster models.

So, you assume that there are clusters inside the material and try to look at what is all kinds of cluster. 1 is equal to 1, 1 is to 2, 1 is to 3, all kinds of possible clusters that I can think of and then, try to calculate free energy of each other clusters and see which clusters have a lower free energy. Those clusters will be the one’s which are stable. If all clusters have the same equal free energy, that means, we say that particular system would prefer to be an isomorphous system, but there is no special attraction for any particular cluster. In a particular system, where let us say it follows a ideal solution model let us say.

In such a case, if I calculate all the possible clusters, you can find out innumerous range stoichiometries. You can consider 1 is to 1, 1 is to 100, whatever you want to consider. So, all possible combinations if you start calculating the free energies and if you find that all of them have the same equal free energy, that means in principal, you do not have any compounds. If there is a particular compound which gives you a much lower free energy, that means that particular compound is the one that you will observe. Rest of them are all equal free energy.

So, that is how people actually calculate using cluster variation model and then, see whether you get compounds or not get compounds. So, that is how we do. So, this is a way to calculate and this is the same solution whether you are calculating the T c for the spinodal because you know T c for spinodal basically means the two spinodal points are meeting at that particular temperature. Am I right? So, that means, again it is the same. Clear? So, I want you to remember this and when you want to do it next time, you should be clear about it.

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Omega fundamentally represents what is the attraction between A and B. For example, it is more related to, you know more related to the valence mismatches. For example, sodium and chlorine, one with one electron less and another with one electronic extra. So, you have an ionic bond coming into a picture. Am I right? So, that means, because of this particular sodium wants to stabilize its configuration by taking some other electron let us say. So, it tries to combine with an element which has access element electron. It try to look for which are the one's which have and once you put the other element in combination with sodium, you suddenly form a compound. H2O is another example of that. So, all compounds basically are related to their electronic configurations.

At the same time, when you are talking about intermetallic compounds, in addition to electronic configuration, there is also a size effects are coming into picture. They may want to form a compound, but when second element sitting inside the lattice, they may be so much of a strain that, that is going to counter act the chemical affinity between A and B. So, as a result, you may see such a compound may not form, though electronically, it would like to form. So, it is a combination of both the factors. We cannot just say it is a size factors. In fact, there are number of what are called size factors compound also. They are nothing to do with the electronic configuration. Just because the size of the B element is such that it fits into the whites. For example, there are number of A to B type of components. Most of the A to B type of component are all to what we call white size factor components, where the second element fits into the lattice of the first element somewhere, so that it forms a good compound.

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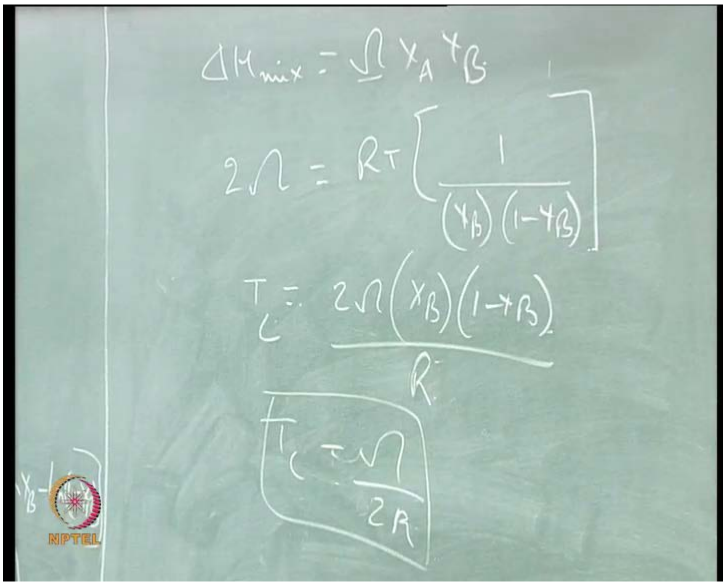

So, there are different types. So, you have to consider each element carefully and then, look at it and when you look at different elements for example, Mg2Si. One such example is a size factor compound. You do not see that in every other things. Al2Cu is also another which is to some extent a size factor type of compound. So, it looks like a aluminum and copper atomic sizes, where they are going. Of course, they are more of substitutional, but there atomic sizes are such that aluminum is much bigger when compared to copper.

So, you have to look at in fact, even the whole bulk metallic glasses also people are talking about in terms of the size factor. They say that if I can take that one element with a bigger atom, another element with a smaller atom, then this smaller atom fixed into the bigger atom lattice and makes the whole packing very dense and the moment dense packing is acting and then, the structure is more stable

So, whichever makes such a dense packing possible, you would see such a thing is stable. For example, the best zirconium base bulk metallic glasses are zirconium beryllium. The best iron based bulk metallic glasses are iron boron. One is a very small element, another is a bigger element. Zirconium beryllium is another. Palladium, nickel, phosphorous is the bulk metallic glasses with the highest what is called critical diameter, almost 70 millimeter people have found palladium, nickel, copper, phosphorous. Again, phosphorous which is very small, there it goes and sits into the palladium lattice, and then, makes that stable.

Incidentally, if we look at even the phase diagram also, palladium, phosphorous you get the best. There also there is a critical amount of the boron which when it goes into the lattice, the structure gets stabilized and that is what people call it for example, iron-boron. If you look at it, 20 of boron and 80 of iron is the one, where you actually see this is happening and that is reason why, if you look at iron boron phase diagram, you have a deep eutectic at 80-20. Same thing palladium phosphorous, you go to and see a palladium phosphorous phase diagram at 80-20. You have a deep eutectic. That means, such a configuration, the liquid will have a high density and such a liquid gets stabilized and once it is stabilized, obviously once liquid is stabilized, glass is stabilized. It need not because the question is whether it would like to form a regular configuration or it would like to have a randomly sitting and then giving you high dense random packing, we call it as dense random packing. It is dense, but it is a random packing.

So, such kind of structures are all there. There are so many liquid. That is why we say bulk metallic glass that where viscosity is very high. Why is it high? Because it has a dense random packing. So, you put those elements. That is why, not every 2 elements just because for example, I take some multi-component system 5 elements. It does not mean that everywhere 5 elements if I choose, I will get a glass. For example, we are working on what are called high entropy alloys. In higher entropy alloys, we do not get a glass. We still have 6 elements. We can even put 8 elements. It does not mean that it give a glass, so just because you have more elements.

So, that is where you have to look at whether they have strong attraction first of all because liquid gets stabilized only when the delta H mixing is negative. So, that is one you should look at whether A and B have all these elements. When you put them what is overall delta H. See for a binary, I can easily talk about 1 omega. How do I talk about a omega for a binary system or auxiliary system? So, I have to consider individual interactions, multi-component interactions. So, this is little more a involved calculation, but one can do it if he is interested. Second is look at size factors again. We know that you would get a glass whenever the size factor is greater than a certain number, so that solid solution is not preferred. We know from Ume Rothery that when the size factor is less than something, you get a solid solution.

So, all those conditions which would prepare a solid solution formation would lead you to a high entropy alloy without being amorphous and all those conditions which do not encourage, which are not conducive for a solid solution formation are the one’s which would lead you to a glass, provided you have multi-component system. So, that is why, it involves a lot of thermodynamics to understand. Why? For example, in a multi-component system, in a 5 component system, how do I know which is the best composition for me to get a glass? In a binary also for example, if I look at the phase diagram, I can say oh at this composition, I have a eutectic. Because I have a eutectic, I can say yes it would form a glass. In fact, there are many interesting cases I would show you all.

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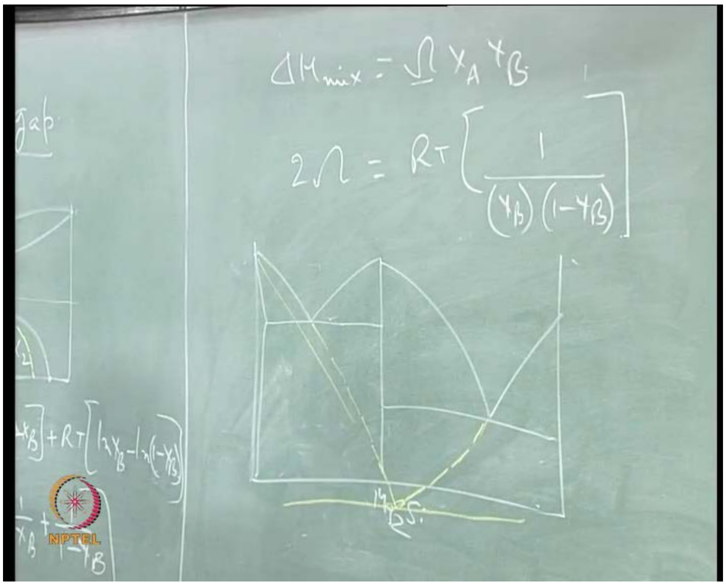

If you have a phase diagram which looks like this. Let us look at this. Take a case like this. It has 2 eutectics. Any example that you know? Mg2Si very simple. If I take this system, there is Mg2Si at the middle. Let us say if I cool this very rapidly and Mg2Si being a compound, you need atoms to sit in specific positions and that is not time is not allowed for such a thing to happen. So, what happens is Mg2Si cannot come out. Then, what should come out? The liquid would remain as liquid and it remains as a liquid until you, if you look extrapolate, this liquid occurs to a particular point, where you have another eutectic which is what we call it as metastable eutectic.

So, in a phase diagram if there is a eutectic, a normal eutectic like iron-boron, I can say yes that is a composition where you can get a glass, but if you see things like this, if you start thinking that this is not forming what is, then going to form that liquid at that particular composition is going to be under cool continuously until you reach this temperature. So, that means, in this alloy though the 2 eutectics are shallow eutectics, still this particular phase diagram can give you glass. Though I may say that, sir if I do the T naught, the T naught is not really very sharp, do not very deep, it is shallow, but in spite of that, you would see that you will get a glass because if this is removed, then you get a different metastable phase diagram. In that metastable phase diagram, the eutectic may be very deep.

So, this is how you can see the movement. You see a deep eutectic, whether it is in the stable phase diagram or in a metastable phase diagram. Then, there is a tendency for the formation of a glass, but this is easier to see in a binary. How do I see? It is turnery. How do I see it in a quaternary or a quinary or in a auxiliary? So, that is where you need to do certain calculations to find out which are the compositions, where the delta H mixing for example, is highly negative. So, I try to calculate delta H mixing for the whole multi-component system and find out where it is negative and also find out which is the composition where you have the size factor being highly positive.

Where do you have the highest size factor in a normal binary system? Where do you usually get a highest size factor? It is usually at 50-50. Whenever I put B into the highest, misfit comes into at 50-50, provided both are substitution. That is where you will have highest strain. That is a reason why you would see Miscibility gap more or less will go up. You need a higher temperature to overcome that misfit, to accommodate that misfit.

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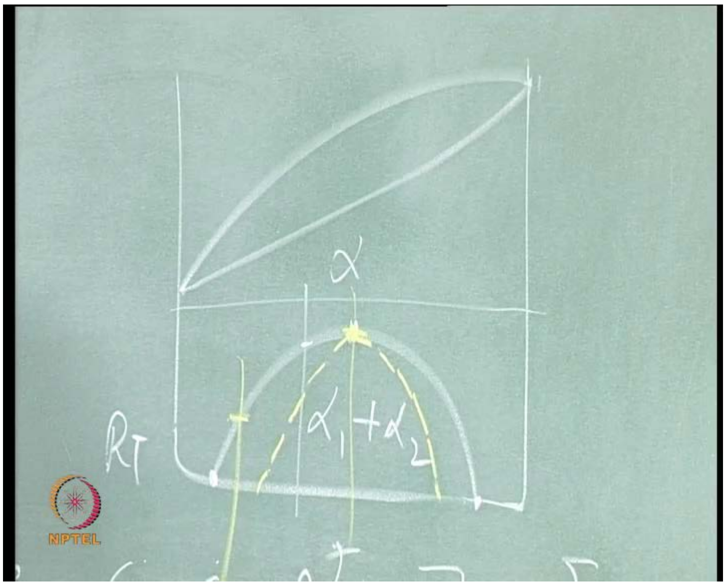

That is the reason why the T c is lower here, T c is higher here. This is T c for this alloy and that is T c for this alloy. So, at 50-50, you have most strains. So, you need higher temperature to accommodate those strains, so that you get a single phase solve solution. So, similarly you would see that in a binary, you can say it is at the highest. What about in a multi-component system? So, you try to calculate where this size factor is going to be the highest and then, look at these two combinations.

One is which is simply chemical interaction, another which is a topological interaction, which is a size factor related and see a combination of these two. People do all this calculation. We ourselves have been doing it and if you are interested, it is a very very fascinating field and then do experiments later. Identify that composition, do an experiment later and then, see whether that works out correctly or not. So, this is how people regularly do to identify that. Any other question? The other point I think which most of you, yeah the only point in the errors in the phase diagram which we discussed I think in one of the classes, where the phase diagram which looked like this.

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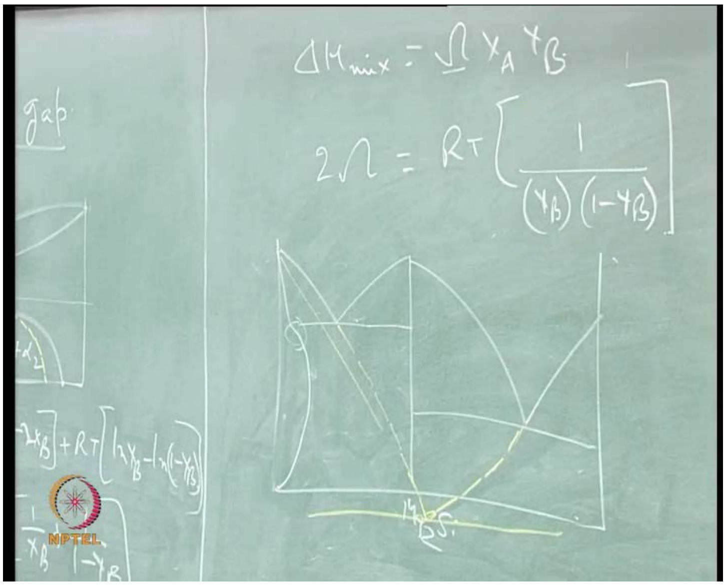

So, this error many of you could not by that time possibly you did not know, but after the class I think we discussed. So, now, I think by now you know this. That is it. I think rest of the things were easier and many of you have answered it also. I think we will leave this. If there are any further questions, please feel free.