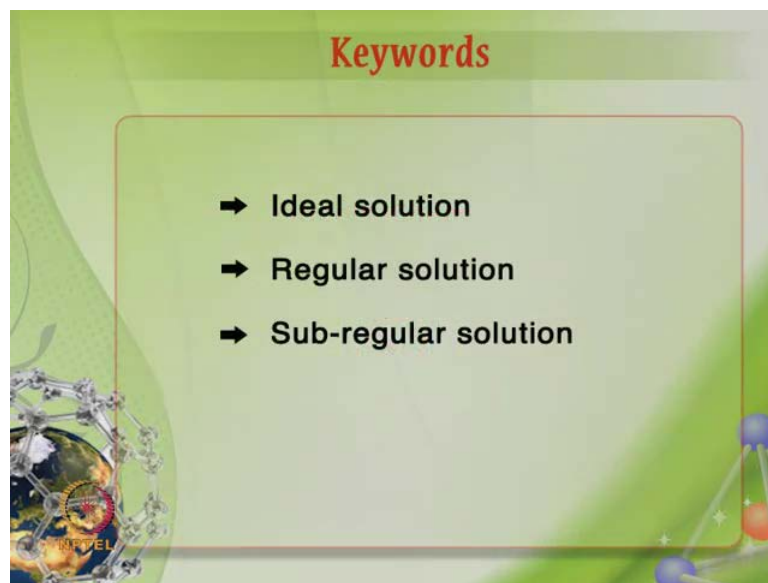


**Advanced Metallurgical Thermodynamics**  
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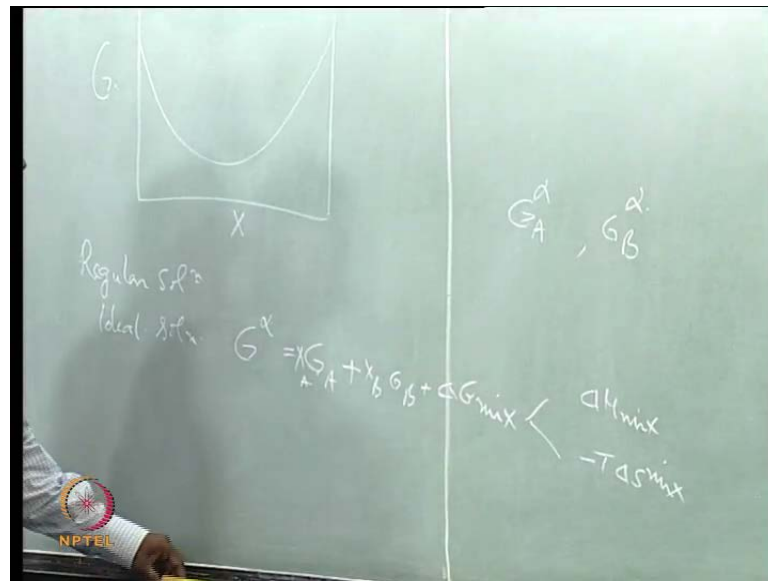
**Lecture #05**  
**Solution Models, Chemical Potential**

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If a material has a TG, in fact, my PhD thesis, one of my chapters was to do thermodynamics of glasses. So, I tried to calculate what should be the glass transition temperature for pure metals and when I calculated some of them, it turns out to be negative in terms of absolute temperature, something like minus 200 Kelvin. If that is the case, then in principle, that particular metal, by some way if I can bring it absolute 0, before it actually crystallizes, see all this is assuming, that the liquid is not crystallizing, if liquid crystallizes during this cooling, then it is not glass we are talking of. If you can retain it as a super cool liquid at absolute 0, then it would have that. The question then is how do I measure that? So, that is why, enthalpy also, we say, enthalpy is 0 at 298 where simply, because we do not know what is the base I should start with, so I assume something. So, that is why, all these standard states are come into picture. O.k., we start.

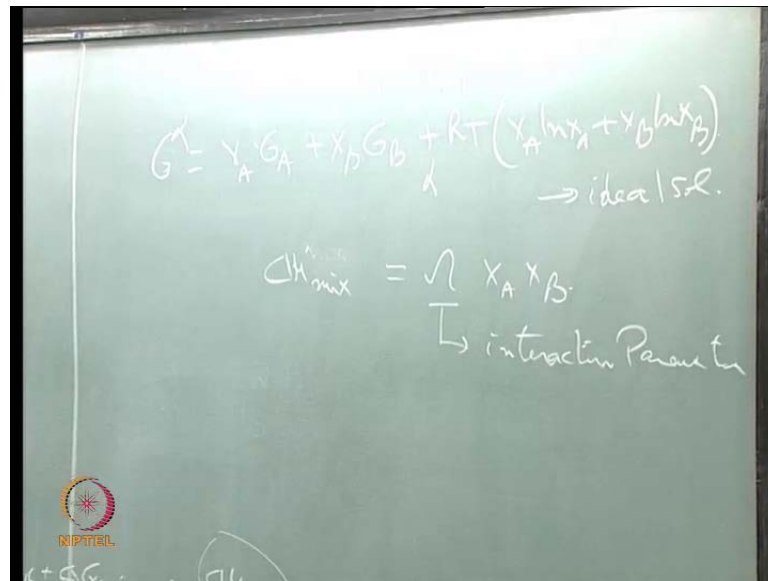
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Yeah, in the last class we have started talking about two component systems and we started plotting, what are called, G-X diagrams. And we talked about a simple model called regular solution model and also much simpler model, called ideal solution model in which the delta G of any phase, let us call it as an alpha,  $G^\alpha$ , where you put this alpha as a subscript or a superscript, depends on, you stick to something, many people, we usually use here because this is the, subscript is used for the component. For example,  $G_A$ ,  $G_B$  when I say for example, as you go along you will know, maybe today's class itself, when I, many times I have to write  $G_A^\alpha$  and  $G_B^\alpha$ , we will see what does it mean as we go along.

So, here for example, we know, that this is  $G_A X_A + G_B X_B$  plus delta G mixing, this is what we have written yesterday and we said, this delta G mixing is actually composed of delta H mixing and minus T delta S mixing.

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And as a result, for an ideal solution we have written this expression,  $G$  is equal to  $x_A G_A$  plus  $x_B G_B$  plus  $RT(x_A \ln x_A + x_B \ln x_B)$ , this is what is for an ideal solution.

And we said, the moment it is not ideal, non-ideal solution, the one of the simplistic model because all this, whenever I am talking about of a free energy of solid solution, I need to start thinking about how the A and B atoms are interacting and then give a model to it and then do some measurements. How do I measure, do measurements in terms of, if I want to measure for this, how do I measure it? Is there any way? Yes.

If you do, let us say, you take A and B metals, you mix them and then do a DSC. If there is a positive interaction or a negative interaction, you would see it in terms of what is called heat of formation. This heat of formation, we use calorimetric and more sophisticated thing is a DSC, differential scanning calorimetric, and if you use DSC in principle, one can do. So, large number of people who have been measuring this  $\Delta H_{\text{mix}}$  and from that we come to know, whether they are inter-metallic compound forming, whether there is a repulsion between them because of which there is a  $\Delta H_{\text{mix}}$  being positive and from that, you try to fit from the measurements to the model and say, yes, my model of regular solution or sub-regular solution, things like that, are working.

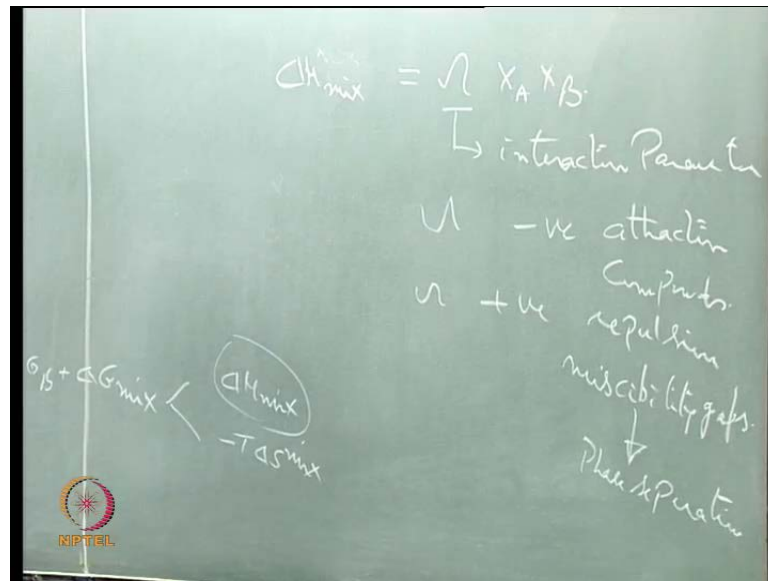
So, in a regular solution model we assume  $\Delta H_{\text{mix}}$  as  $\Omega x_A x_B$ , where  $\Omega$  is, what is called, interaction parameter. So, I can now basically put this in this

and then, simply I will not rewrite this whole thing, I will simply say, plus  $\omega$  X A X B, this whole term plus  $\omega$  X A X B, that would become the free energy of a solid solution, if at all is following a regular solution model and this boils down to this equation, when  $\omega$  is 0. When  $\omega$  is 0, that means interaction between A and B is 0 and that is what causes, what is called an isomorphous solid solution. You will see, as we go along, when we go to the phase diagrams.

And whenever you see the  $\omega$  being positive, we say there is a repulsion, A and B do not want to mix into each other and that is what causes, what is called miscibility gaps in phase diagrams and these miscibility gaps slowly lead to, what are called, the **eutectics**, **peritectics**, even to the extent of **monotectics**. We will see in possibly the next class, what is called evolution of phase diagrams, how do phase diagrams evolve just based on thermodynamics? We will see that, till then have some patience.

So, if this is negative, if  $\omega$  is negative, that means, there is an attraction between A and B, any attraction always causes the formation of compounds. And here also, depending on how strong is attraction, you have compounds with different melting points. Some of the compounds may have very low melting point and some of the compound may have very high melting points. If you look at some phase diagrams, you see, the two pure metals have very low melting points, but the compound has extremely high melting point, that is because the two elements have such a strong attraction, that this compound, the bonds in the compound cannot be broken easily. Melting point is basically an indication of bond breakage and that is why, you can easily correlate the melting point of a metal to the bond strength of that, within that particular metal.

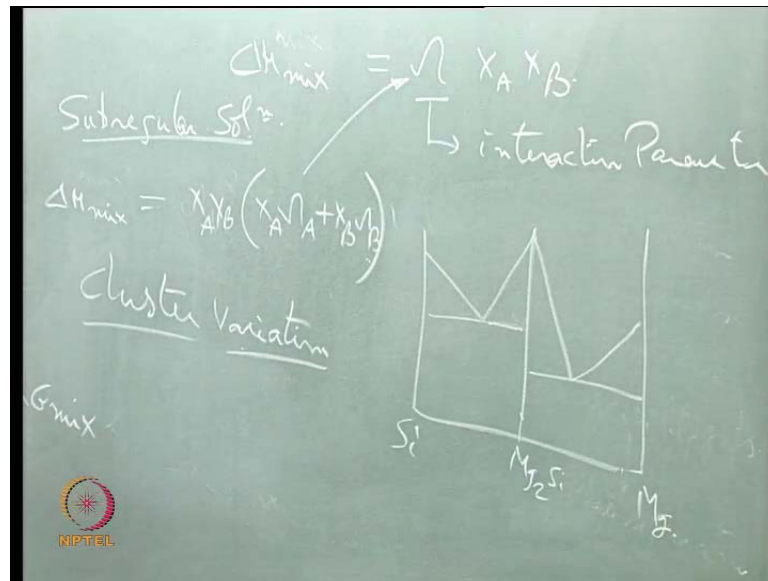
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So, you can see, so omega negative means attraction that means formation of compounds. Omega positive means repulsion, repulsion means, what is called immiscibility or I can call it as miscibility gaps, which finally, ends up into phase separation.

Now, people have seen as, possibly we have touched upon in the last class, that this cannot be always true. What I have done in this is, I have assumed, that the interaction parameter is the same throughout the phase diagram, from one end of the phase diagram to the other end of the phase diagram, I assumed it to be same, which is actually not always true. When I simply look at a number of phase diagram, I see, the solubility of one element in other is different from two ends. We took the example, possibly in the last class on copper.

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Zinc dissolves in copper very much, whereas copper does not dissolve in zinc and we try to give a logic for it based on the valency, and if that is the true, then the interaction between A and B atoms is different on one end of the phase diagram and it is different on the other end of the phase diagram and this has brought in, what is called, sub-regular solution model, where people say, that the delta H mixing, I mix up once in a while, delta H mixing is,  $\omega$ ,  $X_A X_B$  into  $X_A \omega_A + X_B \omega_B$ . That means, now we are talking of two interaction parameters, one on the A side, one on the B side, that means, the interaction between A and B atoms on the A side and the interaction between A and B atoms on the B side and which could be different.

The moment both of them become equal, then what should happen to this equation? It will become same as regular solution because assume, that  $\omega_A = \omega_B$ . If  $\omega_A = \omega_B$ , this comes out of the equation and then what you will end up is  $X_A + X_B$  and  $X_A + X_B = 1$ . So, this equation will become same as this equation. So, that is how we can visualize this and this is a kind of a next level of non-ideality.

And then people observed that this is also not really fitting in very well, why? For example, if you look at phase diagram such as magnesium-silicon phase diagram, how many of you have seen magnesium silicon phase diagram? Anybody who knows how does it look like?  $Mg_2Si$  is a very important compound in aluminum alloys, no, if you

remember, if you have not seen it, I will not bother about the actual temperatures much, but give you a schematic. Obviously, this should be silicon side, this should be magnesium side and do not bother about it, this is at the center of the phase diagram, but this is actually Mg<sub>2</sub>-Si, so that means, this on the magnesium side. So, you see a phase diagram like this, it has two eutectics and one compound.

So, that means, suddenly at the composition of Mg<sub>2</sub> Si, when 2 atoms of magnesium come together with 1 atom of silicon, suddenly there is a strong attractive interaction between the two and everywhere else. Now, for example, on the, on the silicon side, magnesium does not dissolve in silicon, that means,  $\Delta H$  is positive, if it is negative, it would have dissolved, there should have been solubility.

And similarly, on magnesium side also, silicon does not dissolve into magnesium. There are, there is almost negligible solubility on the both sides if you carefully observe the phase diagram. But suddenly, at this position, there is an attraction and its melting point is higher than that of both the pure metals, this means that the interaction at certain compositions suddenly becomes attractive. For example, there are many, many inter-metallic compounds; a famous one that we know in steels is Fe<sub>3</sub> C. So, that means, we bring 3 atoms of iron and 1 atom of carbon together and there is a strong attraction, but if you have 2 atoms of iron and 1 atom of carbon there may not be. So, this is based on variety of factors.

People have, you know, classified them into types of compounds, electrons compound, size factors compounds, let us not go into details of them, but there is a possibility, that the interactions can be specific to certain specific compositions and if I come to either this side or this side of Mg<sub>2</sub> Si composition, that interaction vanishes. That means, the free energy of that is strongly negative at these compositions and this is the reason why, people have to use some other models beyond the sub-regular because sub-regular cannot account for this simply. If you assume, that there is some interaction on the A side, some interaction on the B side and then, simply try to find out the  $\Delta H$  mixing as a function of that, you cannot actually predict, that there is a compound in the center.

So, people have brought in what are called cluster models, cluster variation models. We will not go deeper into this, just to give you a flavor, if you are interested come to me, we will talk more. Lot of people, all this, so they assume, that there are lot of clusters

inside a material and these clusters have, depending on what is the stoichiometry of the cluster, you have certain free energy or certain, certain interaction, certain interaction parameter and based on those clusters try to find out, which cluster has a lowest and then find out based on that, whether there is a possibility of a compound. If all cluster have the same enthalpy, then you assume, that there is no possibility of a compound formation in this particular system.

So, find out various possibility of clusters and compute what would be the, based on the electronic configuration and based on the atomic sizes, you see one can calculate that kind of a thing and then find out, which cluster has a lowest and from that one can find out what are the possible compounds. And in some systems, there is in fact, more number of compounds. If you take for example, aluminum nickel phase diagram, you have  $\text{Al}_3\text{Ni}$ , you have  $\text{AlNi}$ , you have  $\text{Ni}_3\text{Al}$  and a number of other compounds too.

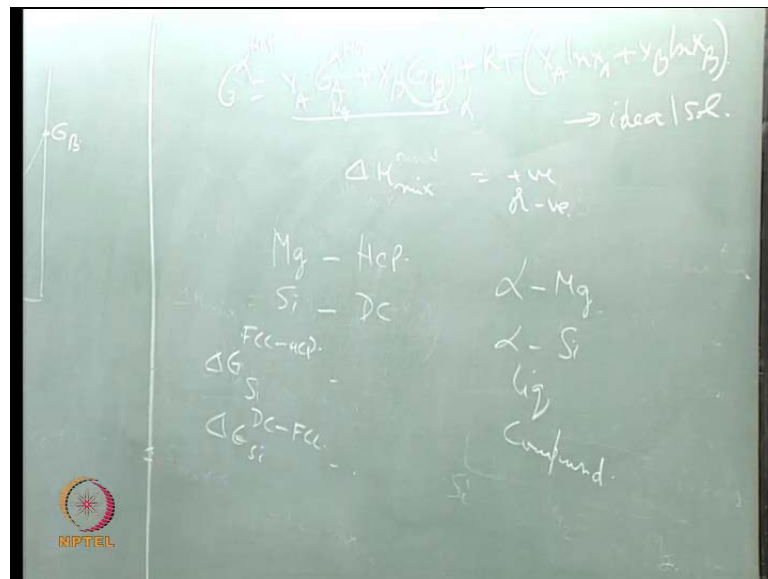
So, that means at specific positions, you suddenly start getting inter-metallic compounds. That means, those clusters at that particular composition has a lowest free energy or the lowest, highest bond energy and as a result, that cluster becomes stable there and at that composition, if for example, if I take an isomorphism system and if I choose all these possible combinations of 3 is to 1, 1 is to 1, 1 is to 2, you know, 1 is to 3 and things like that, and try to calculate for each composition what is the value of this interaction. You would find, that in an isomorphous system, they are all equal at all compositions; that means, such compounds cannot form in such a phase diagram. So, people do all these calculations and from that find out what is the possibility and once you know, that that is possible, you treat it as a phase and then start calculating the free energy for that phase too and then incorporate it into phase diagram and then check it experimentally, whether you are able to see such a compound or not in the experimental verification.

So, that is how people have been, all the caldied calculations are based on this. In addition, caldied people are also have gone a little further because these are also, you know, to some extent simpler, some cases, none of them fit, so that is why, sometimes caldied calculations are more kind of fitting parameters. So, instead of just one parameter, which is in regular two parameters, are in sub-regular, people are nowadays using in a four, five parameters.



Basically, take some experimental data that is already available, sit it with a certain model, whatever number of parameters is like curve fitting for you and once you fit it, try to extrapolate that into the other parts of the phase diagram, where you do not have experimental data available or it is difficult for you to do experiments. I gave you an example of copper tungsten, for example, I said, you simply do experiments on copper side and tungsten side, you extrapolate it and so whatever, you know, free energy function, that fits that particular experimental region, you try to find out that function and try to see again, bit of an assumption here, that I can linearly extrapolate or some other extrapolation method I can use to see, that on the other side also. So, the same thing can be used, otherwise there is no clue for us to be able to calculate the phase diagram because you have to start with some assumption and people have done that kind of the things as people went on calculating phase diagrams.

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We will have a special lecture on how to calculate phase diagrams as we go along. Now, this is all various models for finding out the free energy. After finding out the free energy you would see, depending on the value of the delta H mixing, whether it is positive or negative, the free energy curve is going to look different. For example, this is one something that we have drawn for an ideal solution, where the omega is 0 and if that is the case, these two parameters are G of A and G of B.

I need to here tell you what would happen if I am talking about a material or a system, where both A and B have, do not have the same structure. For example, take an example of magnesium silicon itself. If I am talking of magnesium silicon system, magnesium, anybody knows what is the crystals structure? It is HCP; silicon, yes, it is diamond cubic, DC. Now, because these two are different, when I am talking of solid solutions for example, I want to do thermodynamics of this system. So, I am trying drawing a free energy curve. Now, what is this free energy curve, for it should be if in this particular phase diagram? What are all the possible phases? One, there is a possibility of magnesium base solid solutions, where silicon dissolves into magnesium. Second, there is a possibility of silicon base solid solution, where magnesium dissolves into silicon. So, I can call it as alpha magnesium or alpha silicon, whatever it is, solid solutions, two solid solutions and there is a possibility of liquid, there is a possibility of compound; so, four phases possible in that system at various temperatures.

Now, if I want to calculate the free energy of alpha magnesium and say, that this curve belongs to that, the problem that I have is because of this parameter  $X_A G_A$  plus  $X_B G_B$ . This  $G_A$  is that of magnesium,  $G_B$  is that of silicon, but magnesium is HCP, silicon is diamond cubic, how do I put the free energy of both, two different crystal structures into one equation and talk about free energy of alpha magnesium?

So, whenever I am talking of free energy of alpha magnesium, that is, free energy of a particular structure, whenever we talk of any phase, we are talking of free energy of that structure as a function of composition and temperature. If that is the case, I need to have both these in the same structure. If  $G_A$  and  $G_B$  are two different crystal structures, then I cannot put it into that equation. That means, what I need to do is, I need to find out what is a stable state in this particular system. For example, magnesium stable state is HCP, so I call this as  $G_A$  alpha, that means, this is I am calculating for HCP and this is HCP now. But I know  $G_B$ , which is silicon, this is magnesium, silicon is not HCP structure, but for the equation for the free energy, in order to get the free energy of alpha magnesium, I need to have silicon also; free energy of pure silicon in the HCP form.

That is where told you, if you go calfied book by **Cauffman**, the first chapter is dedicated for this on what is called lattice stability. So, people try to calculate what would be the free energy of silicon if at all it exists as HCP; what would be the free energy of silicon if at all it exists as FCC and that delta G. So, there, it gives actually delta G of per different

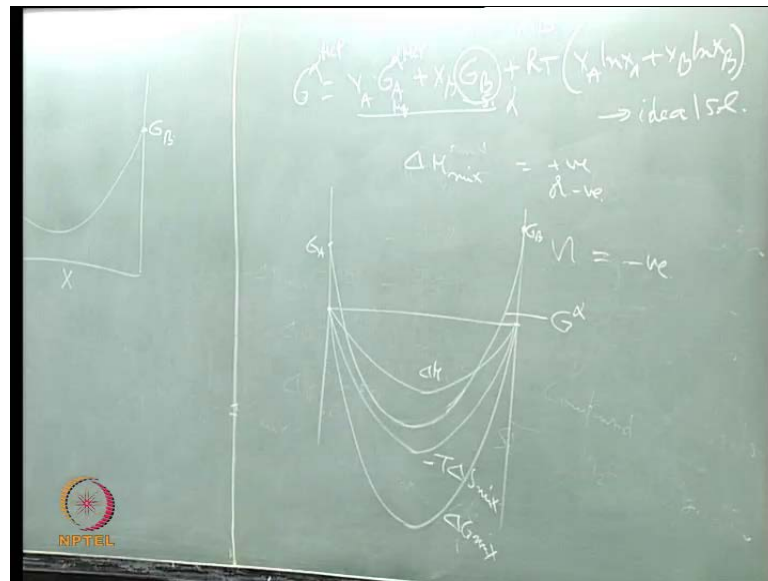
metals FCC to HCP, similarly  $\Delta G$  of silicon from diamond cubic to FCC and so on and so forth. Once these values are calculated from 1st principles, I simply add this value to the actual free energy of the diamond cubic silicon.

What I can calculate from the CP is the free energy of diamond cubic silicon only; I cannot calculate free energy of anything else from the CP because CP is that of diamond cubic silicon. What I am doing, calorimetry and finding out the heat capacity is for a stable state. I cannot find out the heat capacity for something, which is meta-stable, which does not exist. If I put this sample into a calorimeter and measure the CP of it, I would get the CP of that particular structure, what it is stable at those temperatures. If I put silicon into the DSC and measure the heat capacity, I would get the heat capacity; I would get the heat capacity of only the diamond cubic.

So, from that if I calculate H and S and get G and that G would only be that of diamond cubic, I would not get free energy of anything else there. So, that is where I need to use these things and add them to the actual free energy of silicon, that I have calculated and get the free energy of HCP silicon and put that into this equation, then only I can go forward.

So, you can see, free energy calculations are not, they look very simple when you can draw them this curve, but to get this curve it is not easy. So, so, this is how we go ahead and that is the reason why you need know these lattice stability criterions. And for various metals, people have done to this kind of calculation and some methods are available to be able to do that. So, now, if that is the case and try to draw that particular free energy and if, then after taking care of 1st part, then I have to go to the 2nd part. In the 2nd part, if it is a non-ideal solution, then I have to add this term and then, if this term is negative, what should happen to the free energy curve?

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So, if you look at this, if you look at  $T \Delta S_{mix}$  term, this is how  $T \Delta S_{mix}$  term minus  $T \Delta H_{mix}$  term and now, you have the free, the pure metal free energy, some value, whatever it is and then in such a case, if I know this is 0, then my free energy curve exactly becomes that of this, but if it is non-zero and if it is negative, let us assume that. This, interestingly, regular solution model, the  $\Delta H_{mix}$  is again symmetric, similar to that of  $\Delta S_{mix}$ , you can see it is  $\omega X_A X_B$  and that function, by looking at that function, we can say it is symmetry.

It reaches either a maximum or a minimum depending on whether  $\omega$  is positive or negative at 50. If I take  $X_A$  as 0.1 and  $X_B$  of gas 0.9, 0.1 into 0.9 is how much? 0.09 and if I take it as 0.5, 0.5, then it is 0.25. So, 25 is the highest.

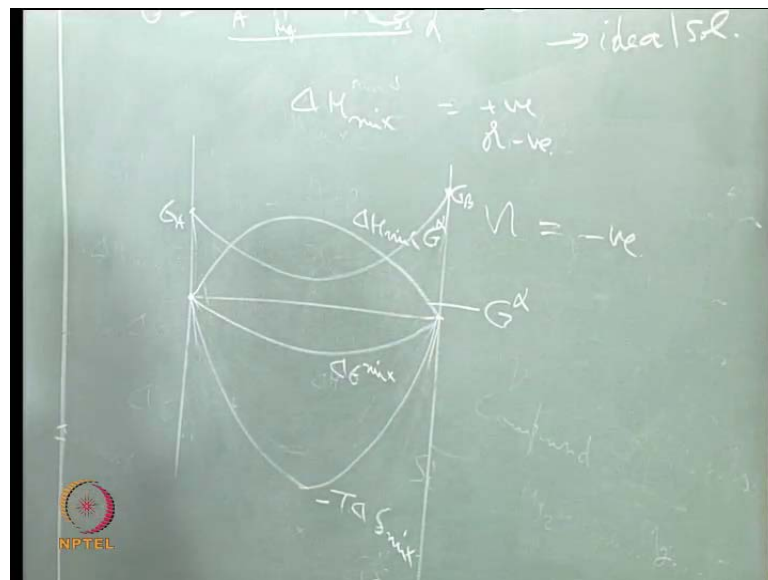
So, wherever composition I take, I will see, that maximum of  $X_A X_B$  is at fifty-fifty. So, as a result, if the  $\omega$  is negative, then this will have a symmetric curve and if this is symmetric curve, my free energy function would be, this is  $\Delta H$  and this is  $G$  of  $\alpha$ ;  $G$  of  $\alpha$ . I add these two, only one some small thing, that I have done is, I have drawn it from here. In principle I should call this as  $\Delta G_{mix}$ , this is actually  $\Delta G_{mix}$ , addition on these two gives me  $\Delta G_{mix}$  because this is 0, this is 0. And this  $\Delta G_{mix}$ , if I add it to my pure metal components, if my pure metal components have free energy values of these two, this is  $G_A$ , this is  $G_B$ , then I would know, that my value would be something like this, something like this. This is the actual

G of alpha because this delta G mixing has to be added to the pure metal components, which is the first part of the equation, then I will get the G.

Now, when I am talking of this G, depending on whether the omega is positive or negative, as long as omega is negative, your free energy curve will always be plunging downwards. The moment omega is positive, then you would see, there is the possibility of situation. Let us say take a particular case again; I will reuse this itself. So, I say, that entropy of mixing is not changing. Obviously, it will not change, is not it? Any system, that I choose, entropy of mixing is the same. We said before, that this part is unbiased by what element it is because there is no element coming in there, simply composition.

So, that is why, whether I take nickel aluminum system or magnesium silicon system, it will have the same configurational entropy. Whenever I take a fifty-fifty composition, it does not depend on whether it is nickel aluminum or magnesium silicon, what comes in terms of, what is a system? It is, here the system is represented only in omega and of course, here the actual pure metal values.

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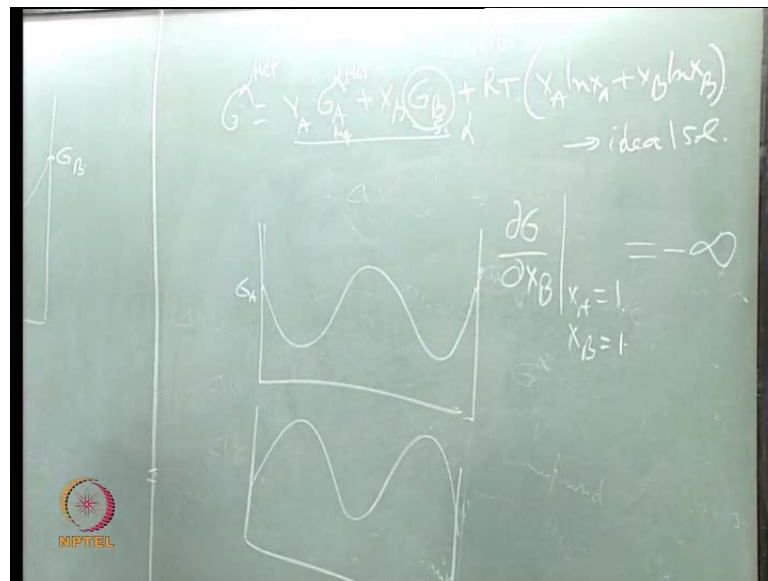


So, the interaction between two elements comes only in this. If that is positive, if it is following a regular solution model and if it is positive, then what should happen to the free energy curve? This is delta H mixing now and this is T into delta S mixing minus T into delta S mixing, combination of these two would give me delta G mixing. Now, depending on how much is this with respect to this, you are going to see the effect. If T

into delta S mixing is larger than delta H mixing, this delta G mixing will be still negative.

And accordingly, you would see that this value would curve something like this. The actual G, actual G would turn out to be something like this. This is the delta G mixing and if you add the delta G mixing to two pure metals, you would get actual free energy curve G alpha, will be like this.

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But now, if you see, that this is going to be larger than this value, then you, we would be end up in situations where the actual free energy curve, actual free energy curve may be something like this. And you may ask me, why it should go down and then come up, why cannot we have a free energy curve which goes like this? That is where the question that Aneesha has asked in one of the last classes, is comes into picture.

Now, if you take this particular equation, which is  $X_A G_A + X_B G_B + RT (X_A \ln X_A + X_B \ln X_B)$  and try to find out the slope of it, that means, differentiate this equation with respect to  $X_B$  knowing pretty well, that  $X_A + X_B = 1$  and try to differentiate this and find out, that value of  $dG/dX_B$  at  $X_A = 1$  or  $X_B = 1$ . I want you give this as an exercise to you, please do it in your room and come back to me in the next class. You would see, that if you do this, you would find this value is minus infinity; please do it for yourself.

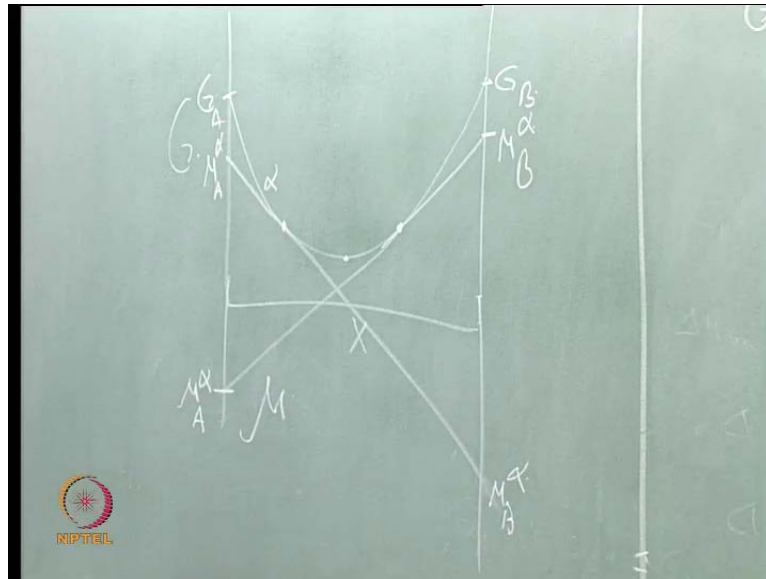
So, the slope of free energy versus composition G-X diagram, the slope of the free energy curve has the  $X_A$  tends to 1 or  $X_B$  tends to 1 is minus infinity. That means, free energy always, curve always has to go down. That means, free energy has to, that means, when I add a small amount of B to A, free energy decreases because this is a function and for this function, this is what you get and if you get that, then you see, when you add a small amount of B to A or small amount of A to B, you would see the free energy can never increase.

Later, as you add more and more B to A, it may start increasing because of this being positive, but towards the two pure metal ends, this, however positive  $\omega$  is, however positive  $\omega$  is because of the nature of this  $\ln X_A$  and differential of  $\ln X_A$  brings you, that you would see as you go along. If you calculate that, if you do this differentiating, you would see, you would tend to see, that whatever may be value of  $\omega$ , however repulsive the interaction between the two metals is, that on the pure metal ends the free energy has to decrease when you add the two. And that is the reason, why you see it is very, very difficult to purify a metal.

You can talk about the four 9s, five 9s, six 9s, but you can never talk about 100 percent of A or a 100 percent of B. And the more nines you want, the more difficult it is because we are somehow pulling the system away from its nature. It wants to have the elements inside it and such metals are not really stable. Also, any possibility, they would try to grab up a little bit of oxygen from the atmosphere something like that. So, that is why, you would see, one can calculate this and then see.

This is one aspect, now the second aspect that is important for us to know and we will come back to this when we talking about to this phase diagrams.

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Second aspect is, whenever I have a free energy curve like this, there is one parameter, which we define called chemical potential. All of you must have come across this how do you define a chemical potential?

(C)

Correct; change in free energy as a function of composition. Basically, if you want to relate this, if I draw, if you take this particular curve and draw at any particular composition a tangent to the free energy curve, wherever this intersects, these two values give me on one side chemical potential of A in alpha. If this is alpha phase, this is chemical potential of B in alpha.

Chemical potential indicates, indicates what is called the activity because there is a relation between chemical potential and activity. You must have seen  $R T X \ln A$ , that equation you must have seen, chemical potential is always proportional to the activity or activity is proportional to the chemical. So, whenever you see a chemical potential of, for a particular element in phase is higher, we say, that particular element is more active in that particular phase here. For example, if I draw this and show you, that  $\mu_B$  in alpha is higher than  $\mu_A$  in alpha, I can say, that for that composition at that temperature, B atoms are more active in alpha than A atoms.

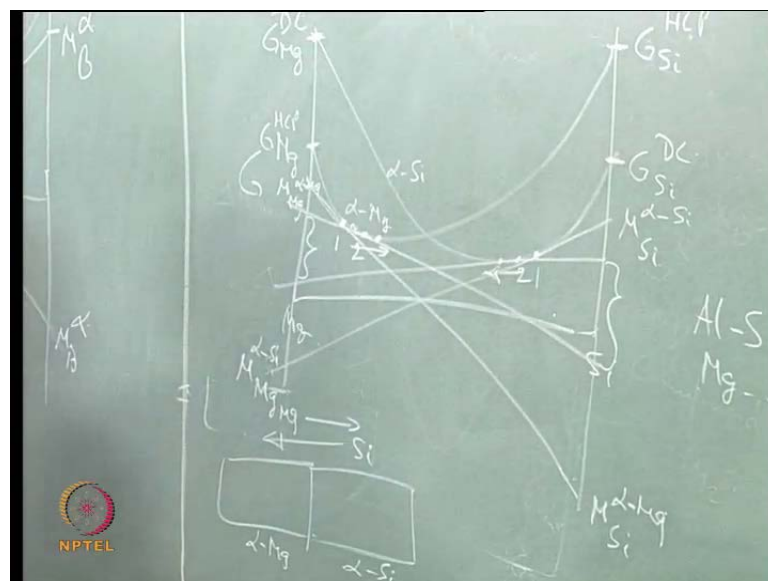


So, activity and chemical potential are directly related and this is what we are going to use it to understand, what is called, the equilibrium between the two phases. When you bring two phases together and keep them together what would happen?

So, at any composition and these chemical potential are not fixed for a given temperature, they depend on the composition. For example, the same phase I come to, here on this side of the free energy diagram and again draw a tangent, you would see, that this is  $\mu_B$  in alpha, this is  $\mu_A$  in alpha. That means, these two compositions, if I take alpha of, let us say, 30 percent B and alpha of 70 percent B and take two of those pieces of these two alpha, you would see, the alpha on this side would have higher activity for pure A when compared to B and on this side higher activity of  $\mu$  would be B.

So, in principle, if I bring these two pieces of, let us say, two alphas, let us say, one has 30 percent of zinc, whatever it is B element, and one has 70 percent of B element, bring them, weld them together, hold at that particular temperature as a function of time. You would see, because one has B atoms being more active, another has A atoms being more active, you would see from this side, B atoms will diffuse towards this side, A atoms will diffuse from this to this and both of them will come to an equilibrium at some stage, so that the composition of both the mixtures will become same, of some equilibrium composition, if I take the same phase.

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If I now take two phases with two different compositions, what would happen, you would see that in a minute. For example, if I take two phases, I can always represent two phases with two free energy curves. The only, deliberately I am drawing these points different because I do not know, and carefully if you can observe, now let us take a system of, let us say aluminum-silicon or magnesium-silicon again.

If you draw these two free energy curves, one is for that of alpha-magnesium; let us say, another is for alpha-silicon. You will see, on the pure magnesium side and pure silicon side, you would see two points here and two points here what does those two points mean? On the two pure metal ends you have two free energy points, what are those two free energy points?

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This, these two points, can you tell me what are these two points? And what is the second one?

(( ))

I am talking of this side, do not again bring...

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Yes, this is the free energy of magnesium in the alpha form; this is the free energy of magnesium in the diamond cubic form or HCP. When I say alpha, this is magnesium G of magnesium in the HCP form and this is G of magnesium in the diamond cubic form. And obviously, the free energy of magnesium in the diamond cubic form has to be higher. And similarly, on this side, if I see this is free energy of silicon in the diamond cubic form and this is free energy of silicon in the HCP form, and if I carefully observe for one particular curve, I am using free energy of the same structures, pure metals for calculating that free energy. If I take this particular curve, I am using HCP, HCP; if I am using this curve, I am using diamond cubic, diamond cubic, otherwise you cannot, not draw the free energy curve. So, this is how free energy of two different phases.

If I assume these are the two at, at room temperature in principal, let us say, I am forgetting the existence of an inter-metallic, now if you want even to bring to in inter-

metallic into the picture, you can also draw that, but for today's class we do not need it; in next class we will bring that.

Now, if I look at two compositions of magnesium, you know, magnesium-silicon alloys, one, let us say, containing about 20 percent silicon, one piece containing 20 of silicon in magnesium, another piece containing, let us say, 80 percent of silicon-magnesium and then put them. Let us say, this is one composition, this is one another composition somewhere here, if I draw the free energy curves and draw the tangents.

So, that means, basically, what I am doing is, I am taking two pieces of alloys, welding them together, one containing 20 percent silicon, another containing 80 percent silicon, weld them together, hold them at that temperature and see, what happens?

You would see actually, that whenever I do this, there is, because the activities are different and which is represented by these free energy curves and the tangents to them, for example, if I draw a tangent at this particular composition, I will see, that this tangent go like this. And similarly, if I draw a tangent, this tangent goes like this. And now, if I look at it, what is what are these values? This is  $\mu$  of magnesium in alpha, alpha magnesium; this is  $\mu$ , I am sorry, I am, this is  $\mu$  of,  $\mu$  of magnesium in alpha silicon; this is the alpha silicon solid solution. So, that where it is intersecting. Similarly, this intersection is  $\mu$  of silicon in alpha magnesium; this is  $\mu$  of silicon in alpha silicon. This side is pure silicon side; this side is pure magnesium side. So, the two chemical potential, always remember, we cannot say this is the chemical potential of a particular phase, we always say this is the chemical potential of a particular element.

Chemical potential is always for a given element activity, is always for given element activity, is never for a phase activity of elements we talk about. Similarly, chemical potential of elements, element in which phase, that is what we look at. So, if you look at it, this is chemical potential of magnesium in the alpha silicon, this is the chemical potential magnesium in alpha magnesium, what does this tell you? This tells me, that the chemical potential of magnesium in alpha magnesium is higher than the chemical potential of magnesium in alpha silicon.

So, in my mixture, in my piece, that I have taken, two pieces that I have taken, one is that this is alpha magnesium side, this is alpha silicon side, 20 percent magnesium, 80 percent silicon; I said, one is the alpha silicon side, another is alpha magnesium side. On the

alpha magnesium side, if I look at it, the activity of magnesium is high and if you look at it, alpha magnesium side, alpha activity of silicon is lower. So, this, here you have higher activity of magnesium, lower activity of silicon; here, you have higher activity of silicon, lower activity of magnesium. As a result, you see that the silicon atoms will diffuse in this direction, magnesium atoms will diffuse in this direction because you have a higher activity there.

So, if I look at for a given element, because an activity in the alpha magnesium is higher, so this element moves from alpha magnesium side to alpha silicon side. Similarly, silicon moves from alpha silicon side to alpha magnesium side and in the process, what happens in the process, the composition of two starts changing; alpha magnesium would keep on getting more and more silicon and alpha silicon would start getting more and more magnesium. So, these two compositions will start moving towards each other, when more magnesium is added to alpha silicon, the composition will move in this direction; when more silicon is added, alpha magnesium, the composition will move towards this direction. So, the alloy composition of the two phases starts moving from here to here and from here to here something like that.

And now, at these two different new compositions, if I again draw common tangents, I mean, if I draw the tangents I will see, that this tangent now will start moving. In fact, if you take straightly of, I, I will show you, that this tangent would start moving like this. If the composition changes from here to here, I mean here to here, this is the 1st case, this is the 1st case, from there you have case number 2. From 1 to 2 if you have moved, you see what has happened is this difference has come down. What does it mean?

That means, the activities of two pure metals in the two phases are coming closer and as this keeps on happening, at some stage you would see, that you reach a particular composition of alpha magnesium and a particular composition of alpha silicon, such that when I draw a tangent for one, that tangent becomes this tangent also for the other phase, this is what we call it as common tangent. So, that means, you would reach a situation where the tangents are the same.

When the tangents are the same, what does it mean? This particular composition is  $\mu$  magnesium,  $\mu$  of magnesium in alpha magnesium, it is also  $\mu$  of magnesium in alpha silicon, activity of magnesium in alpha magnesium and activity of magnesium in alpha

silicon becomes the same, and the, once the activity on both the side is the same, then atoms cannot moves and that is the definition of equilibrium.

In any multi-component system, equilibrium is defined not simply by which has the lower free energy, it is defined by equality of chemical potentials and when the chemical potentials become equal, then one element cannot move from the other side. From one side, other than you see where the element are there, remain there and that is an equilibrium thermal equilibrium at that temperature. And within that material, there may be thermal vibrations because the temperature is not absolute 0. Thermal vibrations are there in alpha magnesium; also, thermal vibrations are there in alpha silicon. Also, atoms are moving in that, but they are not moving in across the inter phase and because there is no activity gradient, the gradient in the activity has became 0 and **once the...**

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### Additional Input

#### Fick's First Law:

- The standard equation that is generally used for Fick's first law is  $J = -D \frac{dC_i}{dx}$ , where "C" is concentration of an element "i".
- This equation should actually be written as  $J = -D \frac{da_i}{dx}$ , where "a" is activity of an element.
- The standard equation assumes the solution to be ideal and hence the activity is assumed to be equal to concentration.



That is the reason why, whenever, you remember a long back, if you remember Ficks first law,  $J$  equal to minus  $D \frac{dc}{dx}$ . All of you, in one voice you have said  $dc$  by  $dx$ , actually this is not  $dc$  by  $dx$ . You would see this different if you have, see taken any ternary system for example, if you take, people have done this interesting experiment, they have taken cast iron with about 3 percent carbon in it, but about 2 percent of silicon in it. This cast iron, they are weld it to another steel containing about 0.4 percent carbon, what do you expect? When these two are kept at high temperature, you expect, that the carbon should defuse from the cast iron side to the steel side, is not it? One side is 3

percent of carbon, another side 0.4, 0.4 percent carbon; you actually see the reverse carbon will go from the steel side to the cast iron side. People started calling this as uphill diffusion.

And the reason is, here is, though the concentration gradient is there, there is no chemical potential gradient. The reason, silicon, the moment it is present, it locks up the carbon and reduces the activity of carbon atoms. There are certain elements, which have this tendency, for example, compound forming elements, carbide forming elements, the moment I add to alloy steel, all this carbide forming elements will lock up the carbon. Let us say, I add chromium, vanadium, titanium to cast iron or steel, you see, all this lock up the carbon and reduce the activity of the carbon. Once the carbon forms a compound, the carbon atoms cannot move further because they are strongly bonded with some other element. So, once this activity of carbon comes down, now you have to actually see the activity gradient and not the chemical and the concentration gradient and people have actually done this.

And this problem does not arise if I am taking two binary systems. Let us say, one steel of 0.4 percent carbon, other steel of 1 percent carbon with no other alloying element present in it. If I take, definitely from, carbon will flow from 1 percent carbon side to 0.4 percent carbon side, there is no problem. So, because there, the chemical potential is given by the concentration gradient, **chemical potential is the...**

Whereas, in ternary cases, the chemical potentials are changed because of the presence of ternary interaction and that is what we have to remember and that is how we understand the chemical potential. So, we should say that it is  $\mu$  of A in alpha should equal to  $\mu$  of A in beta has the equilibrium concept.

With this we will stop.

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The slide features a light green background with a central white rectangular box. At the top, the title "Advanced Thermodynamics" is written in a bold, reddish-brown font. Inside the white box, the text "End of Lecture-5" is centered in a bold black font. Below this, the text "Next Lecture: Phase rule and phase diagrams" is also centered in a bold black font, with "Next Lecture:" in a reddish-brown color. The slide is decorated with a molecular model on the left and a ball-and-stick model on the right. A small globe is visible in the bottom left corner.

**Advanced Thermodynamics**

**End of Lecture-5**

**Next Lecture:** Phase rule and phase diagrams