Phase Transformation in Materials

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Lecture - 07

G-X curves

So, as you have seen in the last lecture that, I have shown you how to derive the free energy of a regular solution. But you know mathematics due will not say everything mathematic equations are always just for to calculate different parameters and values. The graphical representation of this equations are actually more vital that is why you come to know the signs of solid solutions how the solid solutions are stable whether they are unstable or metastable, it will be all clear from these diagrams.

So, let us move forward I discussed with you the first case for the regular solutions where for different for the value of value of omega less than equal to 0, I have told you two separate cases. One case when temperature is small other case when temperature is high. If temperature is small; obviously, the entropic contribution is small because entropy has minus T delta x delta S mix and delta S mix is nothing but R in to minus R in to log of a x A in to log of x A plus x B in to log of x B.

So, in other way temperature increase will need to increase of this term, delta h mix will not change drastically it will be having small changes. So, if the entropic term is increasing as to because of increase of temperature, solid solutions will be more preferred, but more or less preferred has no meaning it is basically solid solutions will be always preferred for any value of omega less than equal to 0.

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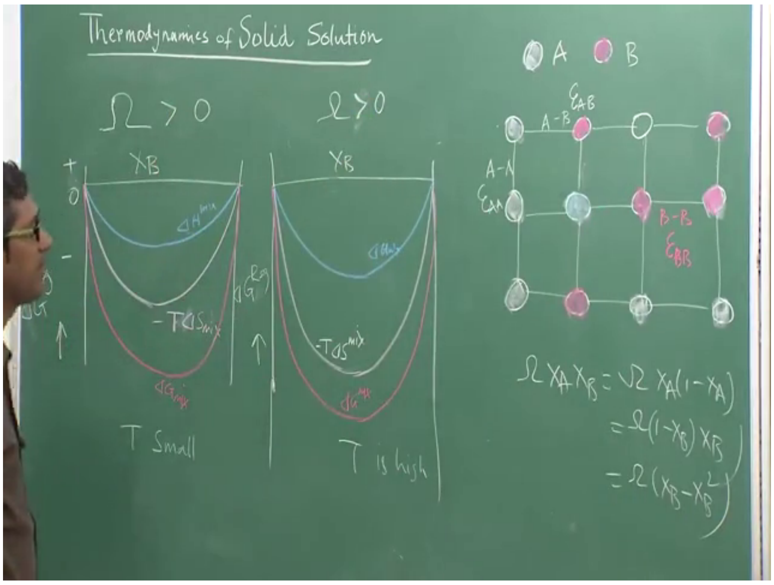

So, now, we are going to look at when omega is equal to more than 0; that means, it has a positive value see if that is the case then what is going to happen. So, we are again going to discuss two cases when temperature is high and temperature is small. So, if temperature is small what will happen and temperature is high what is going to happen.

Simply I erase this color plots on I make the same plots on these so that you can follow it up more.

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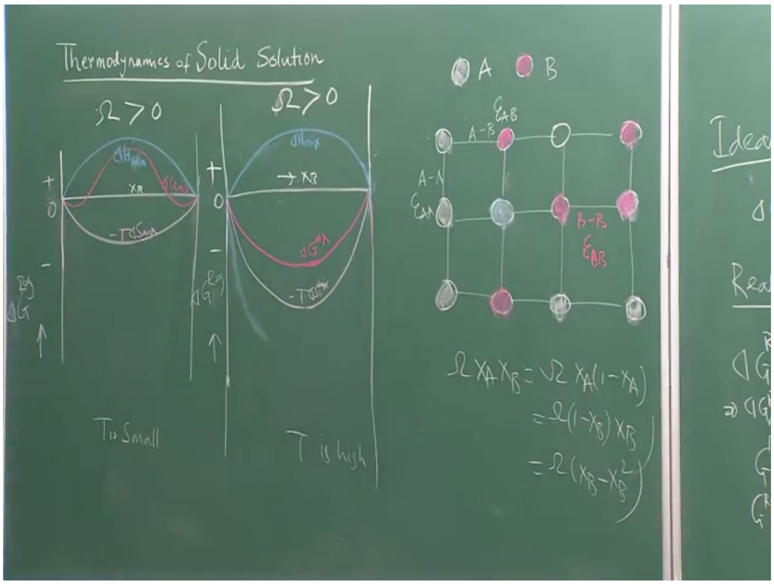

Only thing we have to do is that we have to increase the y axis, because now because it is high more than gamma is more than equal to 0 more than 0 actually or higher than 0. So, therefore, we need to plot it on the positive axis also. So, for T equal to mall small actually as you see when T equal T is small the entropic contribution is small correct because T is present in this equations because it is present in equation therefore, value of entropic contribution or delta S mix will strongly depend on temperature, T delta S mix will be higher or so it will be lower not higher. So, let us first plot what will happen to delta h mix; obviously, delta h mix because omega positive it will be positive.

So, this is what is your delta h mix now, entropic term will be always negative because of the nature of the logarithmic terms x A and x B are fractions. So, log of any fraction is always minus so, but it will be low because temperature term is low correct. So, what will happen in delta G mix that is what the interesting thing situation comes, because delta G mix is summation of these T, one is positive other is negative. As you see here when x B this is a function of x B right this is a function of x B when x B is small or x B is very high in this two zones range of values x B small or range of value x B high; in these two zones the value of h mix and delta what is called delta T delta S mix is almost similar.

So; that means, that this value in fact, delta this value will be little bit higher. So, therefore, negative contribution is more. So, this will go up. So, go down and up and it will be like this. So, that is my delta G mix. So, that is what is going to happen so; that means what? Delta G mix passes through a it starts with a 0 goes down then again it increases and it is a maximum value and decreases and then again becomes 0 at x B equal to 1. So that means delta G makes as an inflection point because it was a downward slope and there is a upward slope and when the these two slopes will match a certain point it will have an inflection point here inflection point there.

Please remember this plot because this plot is very important for many phase transformations, this one will help us in understanding many phase transformations. Now let me move little further and explain what will happen when sigma equal more than equal to 0, but temperature is high. What you can see here when temperature is high as I said in the last lecture also the important aspects of Important contribution, because temperature high is comes from the entropic term because T is directly visible here.

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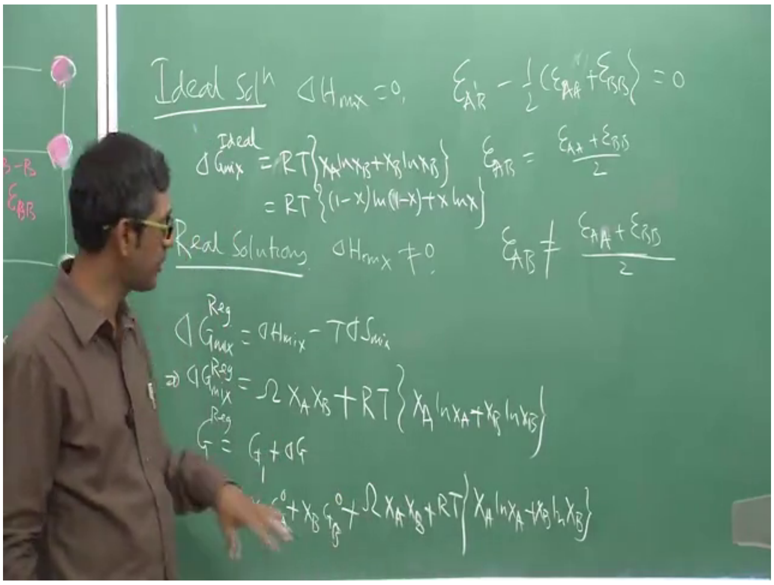

So, therefore, entropic contribution will increase substantially, but enthalpy contribution which is coming from this sigma X B will not change much because we know that bond energies do change as a function of temperature, but normally they do not change drastically. Therefore, delta h mix will remain almost similar, almost similar it may change little bit. So, that is my delta h mix. So, I write it delta H mix an entropic term as I said will increase because of temperature. So, this will go down much further and because of that the enthalpy.

So, because of the free energy will also be free energy will not be like this, there will be some line like this because the summation of these two, but whatever may be the situation, oops I am sorry I should draw it the real red cut chalk so; that means, what? Again even if you have positive value of sigma as I say omega leading to positive value of it delta h mix because the contribution of entropic term is so, high at high temperature delta G will be again negative and look it is a parabola inverted parabola again. So, what I what we found that for a three cases when sigma gamma is more than 0 temperature is high, when gamma is less than 0, but temperature is low and high solid solution is preferred. This is very important from in metallurgy and material science because thermodynamics tells you what are the possibilities exist and rather it is more logical to say it talks about impossibilities. So, thermodynamics tells you that under these three conditions solid solutions will be easily formed while prefer.

So, because of that alloying is. so versatile, alloying is can be done very easily that is the reason because thermodynamics promotes alloying thermodynamics helps us to form alloys. It tells you that it is possible to form alloys there is the first conclusion which you can draw from these plots and using simple regular solution theory I can tell that if I move on further I can even conclude most important things second important aspects it tells you that it is rather impossible, I would say impossible to prepare a 100 percent pure metal because of increase of free energies.

See as you see if I make a metal more and more pure suppose if I try to reduce the solid if I try to reduce the x B concentration this is x B say x B is one here x B is 0 here. So, by making pure a I have reducing the X B concentrations. So, by making X B concentration as small as possible or rather vanishingly small what I am doing I am making delta G mix very low or I am actually making delta G or G of the solid solutions or G of the things higher.

So; that means, that this higher G radius with having higher G with not stable which we know that from the or discussion that G relative values of G of different phases tells you whether they are stable or not stable. So, that is why it is impossible to make h100 percent pure metal except few may be gold or silver it is very very partitioned that thermodynamics makes you tells you a upper bound of purity, you can get maximum 5 9 or 9 point, 99.999 or 99.999 or 69 purity, but you can never achieve a purity of 100 percent because thermodynamics will be violated then this is the main reason of not having purity.

So, alloying is in a nutshell alloying is more alloy or more easily possible in systems like metals or ceramics, because alloying will reduce the free energy of the system and by reducing the free energy of the systems we can simply make these solid solutions formed easily and this has change the civilization because without alloys civilization would not have seen the you know application materials which we now see like steels or aluminum alloys or titanium alloys, copper alloys it is only possible because of alloying. So, a whole theory of alloying is based on these quasi chemical or I would say not fully based on, but I would say that primarily based on these concepts of these thermodynamic concept of solid solutions and the quasi chemical theory. So that means, in a in a very simple fashion I would say that it is possible actually to get you know explain all the phase transformations behavior if then using these four different you know plots which will see later.

So, in the next 5-6 minutes or may be 7-8 minutes whatever we have we are going to discuss with you some other things like I can more about chemical potentials. So, as you know that chemical potentials I actually tells you in an alloy or in a solution the stability conditions and I told you the (Refer Time: 12:23) stability conditions in the last class, the stability conditions tells you the chemical potential of a phase of a component in book the both the phase is must be equal. So that means, what graphically we have seen how to determine chemical potential in the last lecture even last to last lecture also, but mathematically we should also know how to calculate chemical potential.

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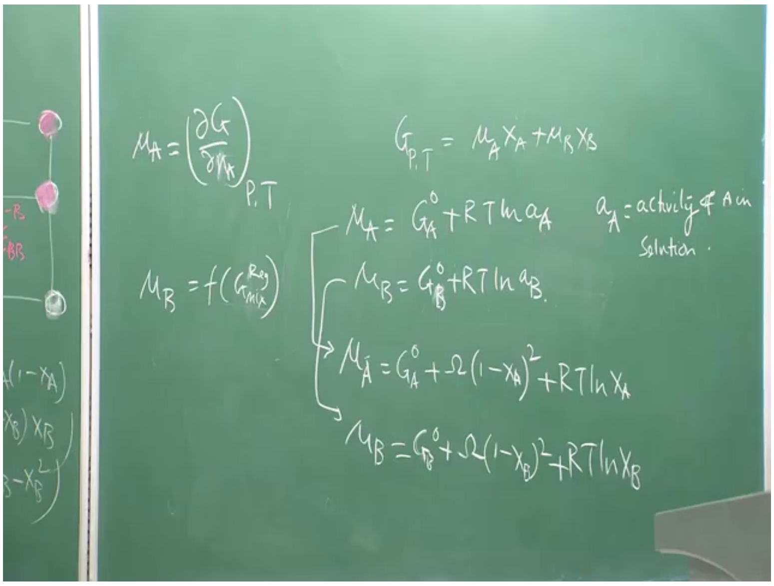

So, chemical potential as I told you is comes basically because of the free energies is depends on the compositions, and we know that chemical potential is given by this function. At a constant temperature pressure is nothing but derivative taken for G as derivative as a function of n A or n A is the number of moles of P and this can be again converted to the mole fractions and I told you in the beginning in the last class that G as a constant temperature and pressure is nothing but mu A x A plus mu B, x B correct. So, what is the actual expression of mu a mu A is related to G A 0 plus R T log of a (Refer Time: 13:50). Where a is activity of a in solution it may be liquid or solid similarly and G a 0 is the free energy of pure component T is the temperature.

Similarly mu B can be written like this, now I will not do the digital calculation is simply part appear question or assignments whatever we will be providing to you, you need to do the homework and you will find that this mu A can be written in terms of mole fraction. Because see ultimately activity is what activities tells you whether what is the propensity of a component to form solution from the solutions or propensity component to react that is what is activity.

We know that for I know calculate activities you know from thermodynamics that we need to demarcate within solid liquid and gas, but it is always better to convert activity in terms of mole fractions and we know for Raoults the Raoult’s law tells you that in a liquid solutions activity is equal to mole fractions when it is dilute or very concentrated that is a region and b region I can always apply Raoult’s law, but only when I you know you prepare solid solutions or liquid solutions which are having concentration in the middle of the x B or x A values like 0.4 0.5 0.6 0.7 or even 0.8 or 0.3 of x B the deviations from the Raoult’s law is observed.

So, that is why you need to know what is the actual expression of the chemical potentials as a function of mole fractions, and it is seems these are related to the gamma. So, this is G A 0 plus gamma multiplied by 1 minus X A square this is what I am asking you to derive X A square plus R T log of X A. So, what I convert; I convert from here to this what I added is two terms basically one term sigma draw this this is multiplied by 1 minus X A square gamma multiplied by 1 minus a square plus R T l n X A similarly I can write down if the chemical potential of B is equal to G A G B 0 plus gamma 1 minus X B whole square plus R T log of X B. It is very easy this actually comes down directly from the expression of G are given. So, G is basically equal to G A 0 plus sigma f x A minus X B plus the entropy terms from there it comes, but you must know that relationship between this and how it is live is to a function of G, G mix regular that you should derive yourself and then you can get down this two equations.

Both chemical potential of A chemical potential of B as a function of X A and X B. This is important because you will like to plot this chemical potentials at a fixed temperature for different values of mole fractions of a or b and then because the chemical potential actually determines this relative stability or the phases stability of the phases depends on the equal chemical potentials are equal or not at the interface on or it is not true.

Finally, it boils downs that this whole theory of quasi chemical theory allows you to not only get the G or delta G mix of regular solutions, but also calculate the chemical potentials and by plotting with the next class I am going to discuss that by plotting the chemical potentials as well as the tilde G mix as a function of x B at different temperatures, will be able to tell whether a particular phase is stable under temperature at a particular temperature or not very easily.

So, before I wind up this today's lecture, I would like to tell you that thermodynamics from the basis of both phase diagrams and phase transformations. In fact, we are going to further discuss about the effect of what kind of solid solutions are there whether it is a order or disorder. If it is a order what will happen to the free energy expression because this here we are not talking about any ordering or clustering we are simply considering it is a random solid solution. That means, atoms of A and B are randomly arranged inside the solid solution, they are not they are not sitting they are no sitting references like many students have right.

So, they can sit anywhere in the lattice A and B atoms and that is a random solid solutions, but that is may not be true always. So, in many cases we will find order solid solutions many cases will find you know partially order solid solutions, what will happen to the free energy when these situation arises. Again you have to modify that regular solution, the free energies expression from the available from the regular solution model.

We like will modify it and will plot it, I am show you what will happen in the next lectures.