Phase Transformation in Materials
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Lecture - 06
Thermodynamics of Solid Solutions

We have been discussing about the thermodynamics of solutions for the last 2 lectures, today we are going to continue and discuss even further. So, I started discussing about the idle solutions, as you know in ideal solutions the heat of mixing or rather change of heat of mixing or change of enthalpy rather is 0 and that is the very idle situation.

And therefore, it is cannot be applied for the real solutions and that is why we need to modify these aspect which we will discuss today in this lecture. Now before that let me just tell you that we know that I discussed with you about 3 important aspects, one which is a thermodynamic importance phase.

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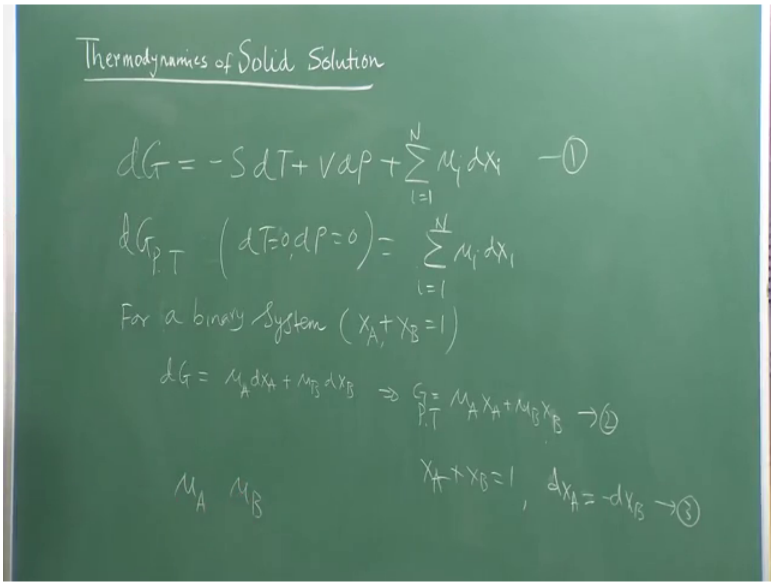

Thermodynamics of Solid Solution

$$dG = -S\,dT + V\,dP + \sum_{i=1}^{N} \mu_i\,dx_i \quad — ①$$

$$dG_{P,T} \quad (dT=0, dP=0) = \sum_{i=1}^{N} \mu_i\,dx_i$$

For a binary System $(x_A + x_B = 1)$

$$dG = \mu_A\,dx_A + \mu_B\,dx_B \Rightarrow G_{P,T} = \mu_A x_A + \mu_B x_B \rightarrow ②$$

μ_A μ_B

$$x_A + x_B = 1, \quad dx_A = -dx_B \rightarrow ③$$

The free energy change for a solution is in general is given by, d G equal to S d T plus V d P plus summation of the chemical free energies of the system, that is actually summation of the chemical potential multiplied by the mole fractions of individual elements summed over from element one to element N. So, this actually boils downs to, if I integrate these equations. Obviously, I can get at let us do the first thing at constant temperature and pressure or pressure temperature, d T equal to d P equal to 0 or d P d T equal to 0 d P equal to 0 therefore, is equal to summation of i is 1 to N mu i d X i.

So, for a binary system we can write down very simple binary system, will have 2 components let us suppose it has mole fraction of a as X A mole fraction of b as X B so therefore, this equal to one. So, the binary system we can write down this d G equal to mu i mu A d X A plus mu B d X B and thus integrating this we can easily get G at constant temperature pressure is equal to mu A X A plus mu B X B ok.

So, these 3 things, one is this is the fundamental equations at the bar at the top equation number 1 equation number 2 as well as the conditions that, X A plus X B equal to 1 in a binary system. So, therefore, d XA is equal to minus d XB we can write down d XA plus d XB equal to 0 1 is a constant. So therefore d XA is equal to minus d XB we can actually use these 3 equations or this 3 equations to arrive at that mu A and mu B, can be easily derived as a tangent to the free energy curve and this I leave it to you to derive it.

Because I have given you the equations, you can do at a part of homework in your in the course and derive this very simple as I as you can see here simply, you have to plug in these equations and the master equation that is G P T is equal to mu A plus XA plus mu B. Just do that differentiate it you will find out the mu A and mu B expressions and mu A expressions then you will find out they are given by the tangent to the curve. So, tangent to the curve is basically that is what we have been discussing, suppose this is my free energy versus composition plot this is x or X B whatever you can define to pure A end pure B end.

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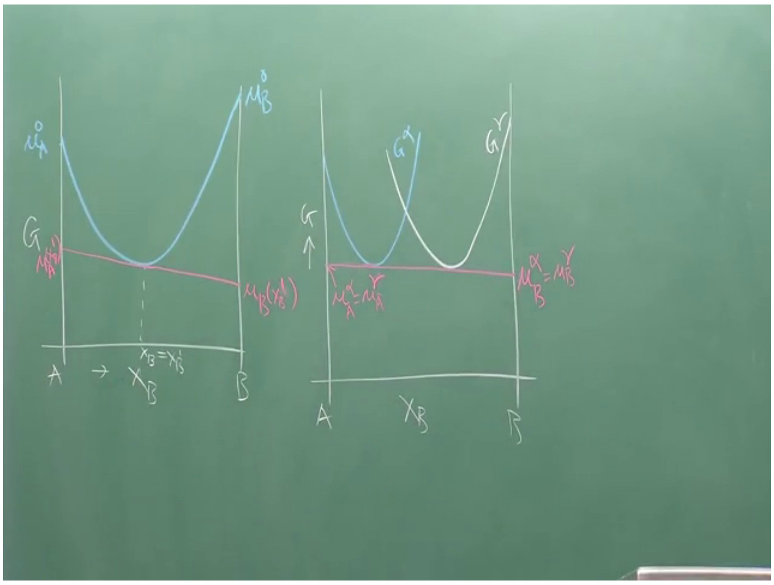

Now I will draw using a colored chalk so that is become very easy for you to follow. So, suppose this is my free energy curve and so that means this point is equal to mu A0, this point equal to mu B 0 right. So, if I want to derive the equilibrium condition or the sorry not equilibrium condition; rather the mu A mu B for the solutions suppose this is equal to X B equal to X B 1. So, at this point what I do is I draw a tangent to the curve, this is what I was telling in this tangent will get equation easily, will from these derivations the tangent will be extended toward the A end and the B end. So, if I extend to the A end I get mu A for X B 1 similarly I will get mu B for X B 2, oh sorry X B 1 not 2 because this X B 1 is the composition at which you derive it.

That is the way actually the tangent to curve rule applies or it is getting applied. So, for 2 phase mixture as I told in that last lecture, again I am doing it for your understanding for 2 phase mixture. The same suppose I have alpha phase, this is G alpha let me write down otherwise and this is suppose G of gamma as we discussed. So, we have to find out the equilibrium conditions, we need to draw a common tangent between these 2 and this common tangent obviously, is to both the curves and that is why the free energy the sorry chemical potentials will be like this, chemical potential of mu B in the alpha is same as chemical potential in mu B in the gamma.

Similarly here the A end this point here mu A alpha is equal to mu A beta sorry mu A gamma. So, that you can clearly see that this is the fundamental aspects in the phase stability or phase equilibrium, if I have 2 or then 3 phases the similar rule will apply that will see in eutectic phase diagram. So, eutectic or eutectoid systems we will apply the same rules that is what I am discussing so much on this time spending so much time on these. Now up on knowing all these aspects you must have an fair amount of idea that, you know these chemical potentials of the phases can be written like this is graphical representation.

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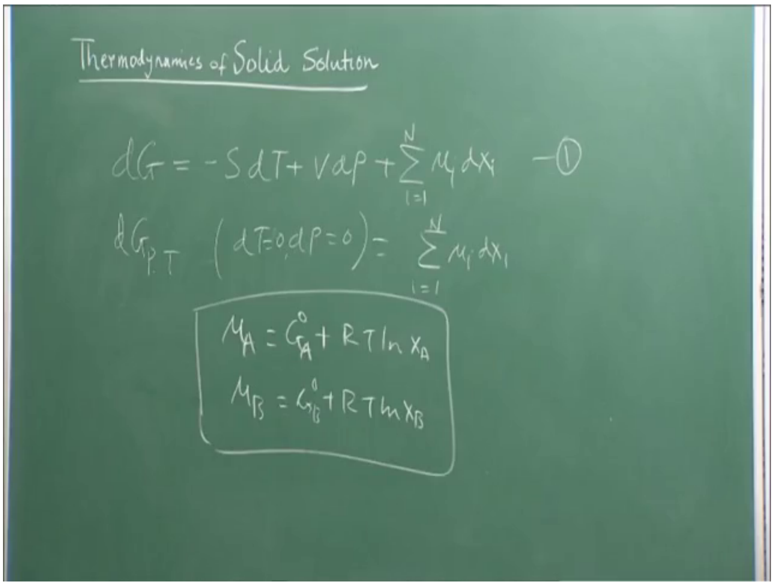

Thermodynamics of Solid Solution

$$dG = -S\,dT + V\,dP + \sum_{i=1}^{N} \mu_i\, dX_i \quad -①$$

$$dG_{P,T} \; (dT=0, dP=0) = \sum_{i=1}^{N} \mu_i\, dX_i$$

$$\boxed{\begin{aligned} \mu_A &= G_A^0 + RT\ln X_A \\ \mu_B &= G_B^0 + RT\ln X_B \end{aligned}}$$

So, I can write down the chemical potentials for the binary system as mu A equal to G A 0 plus R T log of X A and mu B is G B 0 plus R T log of X B. So, that is the derive equations on the chemical potentials, but most of the cases we will not like to apply these equations algebraically, but will apply their constructions very simple constructions ok.

So, that is the recap from the last lecture for the last few minute 7, 8 minutes I talked about it, now let us move on to the aspects, which I told you at the beginning that most of the solutions in the real life are not ideal. So therefore, delta h mixes in the free energy equation, delta H mix is not equal to zero. So therefore, we have to find out a model which will allow us to calculate what is the delta h mix.

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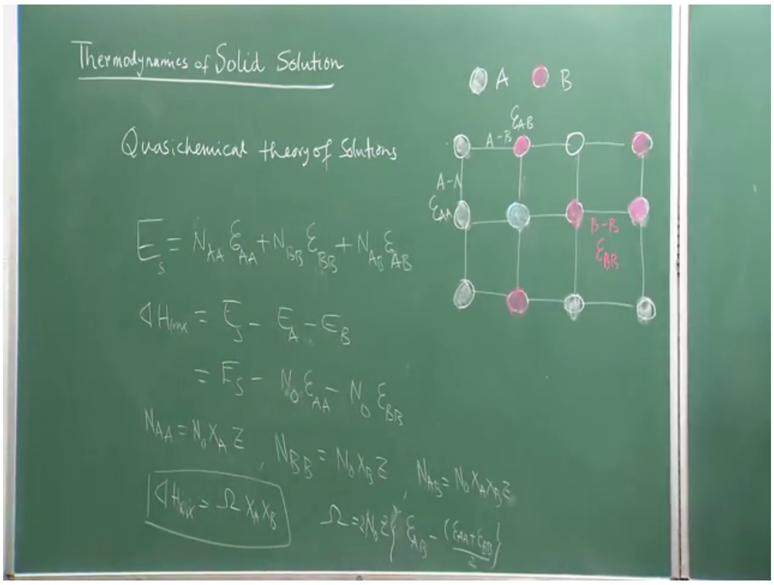

Thermodynamics of Solid Solution

Quasichemical theory of Solutions

$$E_s = N_{AA}\varepsilon_{AA} + N_{BB}\varepsilon_{BB} + N_{AB}\varepsilon_{AB}$$

$$\Delta H_{mix} = E_s - E_A - E_B$$

$$= E_s - N_0\varepsilon_{AA} - N_0\varepsilon_{BB}$$

$N_{AA} = N_0 X_A Z$, $N_{BB} = N_0 X_B Z$, $N_{AB} = N_0 X_A X_B Z$

$$\boxed{\Delta H_{mix} = \Omega X_A X_B} \quad \Omega = 2N_0 Z\left\{\varepsilon_{AB} - \frac{(\varepsilon_{AA}+\varepsilon_{BB})}{2}\right\}$$

So, carry over on this aspects, let us first draw a simple 2 dimensional lattice of atoms, this is 2 dimensional lattice of atoms and let us suppose this is my B atom So and this is my A atom let us put it white so that you can see. So, I do it for many. So, these are all A atoms. So, for your understanding let me write at the top, this I call A atoms and this I call B atoms. So, if in a solid solution like this, I have a atomically mixed atoms some are A some are B. So, I could clearly see if I draw the points suppose these lines indicates type of bonds as you see there are 2-3 types of bonds here, one is between A and A other one is between A and B and third one is between A B and B. Let us see there any B-B bonds let us make it if there is no this is B-B bonds.

So, there are 3 types of bonds present in a solid solutions, now this approach which I am going to discuss in the next lecture also carry over is known as Quasi chemical theory of solutions. Basic idea purpose is to find out expression for delta H mix, I have discussed in to that delta G mix is depends on 2 things one is delta H mix minus T delta S mix and delta x mix expression I have already derived. So, for the ideal solutions we assume that delta H mix equal to 0. So, this was the expression for delta G mix, but in the real solution delta H mix is not equal to 0. So, basic purpose of this construction is to find out the delta H mix, the assumption is that in this theory that delta H mix is solely depend up on the bond energies.

That is the basic assumptions it is also to some extent correct that, this enthalpy of mixing or the even change of enthalpy of mixing is a direct functions of the bond energies. Now as you see the binary solid solutions like this, when you have A bottoms A bonds A-B bonds and B-B bonds, there are change of bond characteristics compared to pure A and pure B-B then A-B. So, what is a change? Change is that if I assume the bond strengths of A suppose is like this, bond strengths of B-B to be like this epsilon B-B and bond strengths of A-B like that. So, therefore, a total bond energies of the system is nothing, but number of bonds A bonds multiplied by the bond energies of AA plus number of bonds of B-B multiplied by the bond energies of B-B plus number of bonds of AB multiplied by the bond energies of AB correct. So, if delta H mix is solution to E suppose this is e of solid E of solution, minus E of AA means pure A minus E of B.

Then we can clearly see this is nothing but we can clearly right that, this is E A E S minus the bond and the number of bonds some AA obviously, this will be equal to in a 1 mole this will be equal to Avogadro number N 0 multiplied by AA number of AA bond energy, Avogadro number of atoms in a pure B multiplied by bond energies of pure B that is what you will get. So, we have to find out, the expression for N AA, N B-B N AB N AB for the binary solid solutions. So, this can be easily done by simply assuming that, the number of bonds is nothing but proportional to the mole fractions of A or B or AB type of bonds. So, suppose for N A I can write down if the I have 1 mole of solid solutions. So, then I have total number of atoms is abrogated number A 0, multiplied by the mole fractions of A multiplied by the coordination number of A.

Obviously, a coordinates number means A atom suppose, I have a B atom with a surrounded by 1 A atoms 2 A atoms 3 A atom and 4 A atom and then others or let us assume this A atom it is surrounded by 1 A atom, 1 another A atom here and another B atom B atom, B atoms, these nearest neighbors actually 1 2 A and 3 B. So, in 2 dimensional scales it has a z value of 5, but in 3 d it will be more. So, that is why in general we put Z, so that means what? This is the number of Avogadro number multiplied by the mole fractions of A multiplied by the Z is a coordination number for that. Similarly N B-B is nothing but N 0 X B Z and N AB is nothing but N 0 X A X B Z0. As you know in a binary systems actually, this is what you will get these are the probabilities of the systems.

Now if I do the complete maths what I will find is like this, delta H mix and that I leave it to you complete maths means you can rearrange the equations, you can plug in this values N AA, N B-B, N AA and get the ES and then subtract this what you will get delta H mix is equal to sigma XA multiplied by X B, while sigma has a value of I think N 0 Z in to epsilon which is all other let us write epsilon AB minus epsilon AA plus epsilon B-B by 2 and this will be multiplied by 2 normally, but many times this 2 is absorbed within a. So, thus I get an expression of delta H mix like this, value is completely depend up on the bond energy differences between AB bond and B-B bonds.

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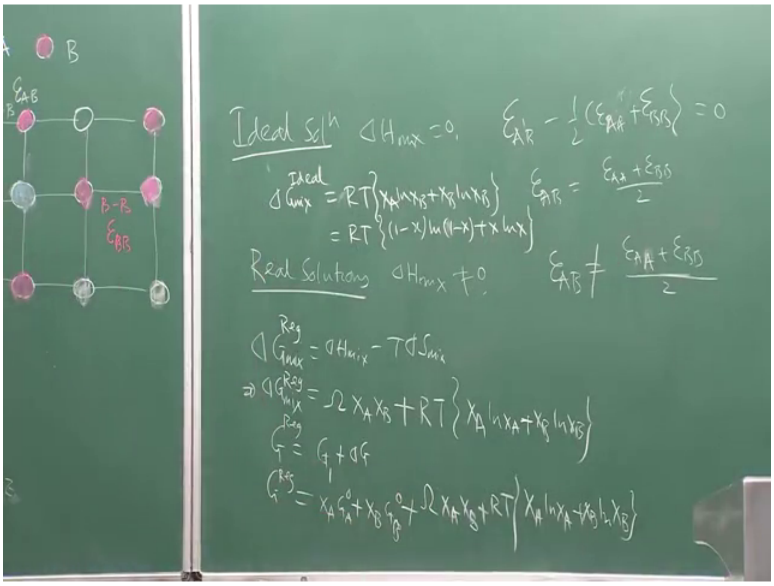

For a ideal solution we assume that delta H mix is 0 for ideal solutions we assume ideal solution we assume delta H mix equal to 0; that means, that the E AA minus half of E B-B at E AB AA plus E B-B equal to 0. That means, E AA is equal to E AA plus B-B divided by 2. So, the bond energy between AB is average sum of bond energies of AA and BB.

So, that is there is not much change of bond charac bond energies when the solution forms, but for the real solutions this is not true. Delta H mix is not equal to 0 that clearly tells you E AA, AB is not equal to EAA plus E B-B by 2. That will be the factors which will play a role in determining the actual value of omega because omega strongly depends on these parameter. N 0 is a Avogadro number, that is fixed 6.0232 to the power 10 to the power 3 and Z is a coordination number.

So, if we have a FCC solid solution Z is equal to 12, if it is a BCC solution Z is equal to 8 otherwise these are not changing much, what is going to change is a dependent type of atoms AB or AA or B-B energies this value is going to be changed drastically and then you can get different values of delta H mix. So, this is in a nutshell although I have not discussed in details about the aspects, this is in a nutshell simple way you can derive delta H mix. Remember the major assumption in deriving this is that we assume that the bond energies are actually contributing to the enthalpy of mixing. So that means, the n type of mixing and the bond energies are actually equivalent, but there will be other aspects which will come to clear to you other factors which contribute to delta H mix, those we will discuss in future whenever required.

So, in a simple mystic fashion I say I would say that we discuss first the case of ideal solutions and then we are going to discuss the real solutions. So, now, if I know delta H mix I can write down delta G mix is equal to delta H mix minus T delta H mix. So, that is means delta G mix is equal to omega X A in to X B plus R in to T, remember delta H mix is nothing but minus R X A l n X A plus X B l n X B. So, therefore, if I multiply with minus T that is become plus T; this is what is actually the real expression of delta G mix for regular solution, for ideal solutions we know that delta G mix is ideal, is nothing but R T XA l n XA plus XB l n XB and I wrote these things in the last lecture as like this.

So, this is also correct 1 minus X A l n x 1 minus X A or 1 minus x l n 1 minus x plus x l n x mix because if we assume x as a mole fraction of B, then 1 minus x will be mole fraction of A as X A plus X B equal to one. So, that this change over from these to this is basically to facilitate your understanding that, excuse me that these 2 parameters the mole fractions of a and X A and X B must be visible separately. So, that you do not forget it that is why I made a changeover.

So, now, if I know this I can simply calculate G, G of regular solution is nothing, but G of G when I say step one. So, therefore, I remember last class I have written step 1 plus delta G, so that means, this is equal to X A G A 0 plus X B G A G B 0 plus this term this is sigma X A plus X B plus RT X A log of X A plus X B then log of XB. So, finally, we get an expression of G for regular solution. Now we will see how this G will depend up on temperature depend upon sigma, depend upon X A or X B correct. So, for that we need to plot the data and obviously, we cannot change all the parameters together when you plot the data. So, what you will see in the next when I make the plots, what I am going to tell you I will discuss it in this lecture the case where sigma is equal less than 0 remember if sigma is less than equal to 0 what does happen?

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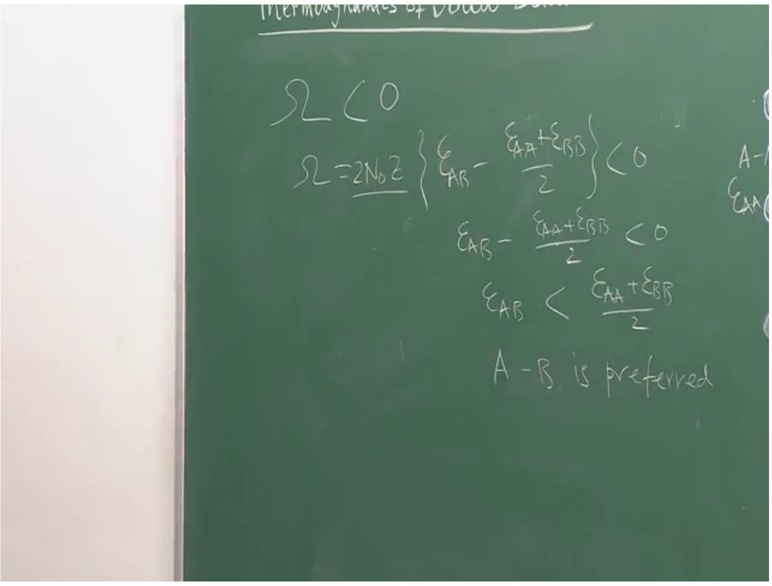

$$\Omega < 0$$

$$\Omega = 2N_0 Z\left\{\varepsilon_{AB} - \frac{\varepsilon_{AA}+\varepsilon_{BB}}{2}\right\} < 0$$

$$\varepsilon_{AB} - \frac{\varepsilon_{AA}+\varepsilon_{BB}}{2} < 0$$

$$\varepsilon_{AB} < \frac{\varepsilon_{AA}+\varepsilon_{BB}}{2}$$

A - B is preferred

Sigma was sigma is a strong function of this is N 0, Z multiplied by bond energies of AB minus bond energies of AA plus B-B by 2 and that we assumed less than 0. This parameter cannot be making any change the sign of this sigma. So, therefore that means, epsilon AB epsilon AA plus B-B by 2 is less than equal to 0. That means, AB is energy is less than equal to average of the bond energies of a B-B AA and BB, that means, AA if bond is preferred because it is a lower more energies.

So, they will prefer over AA and B-B bonds, so this is equivalent to saying that solid solutions will be promoted because solid solutions will have more number of AB bonds than AA and B-B bonds. So, therefore, whenever sigma is equal to less than 0, you will clearly understand that G will be for a solid solutions will be lower than the individual mixtures that is the thing. So, now how do I plot? So obviously we can plot 2 cases here.

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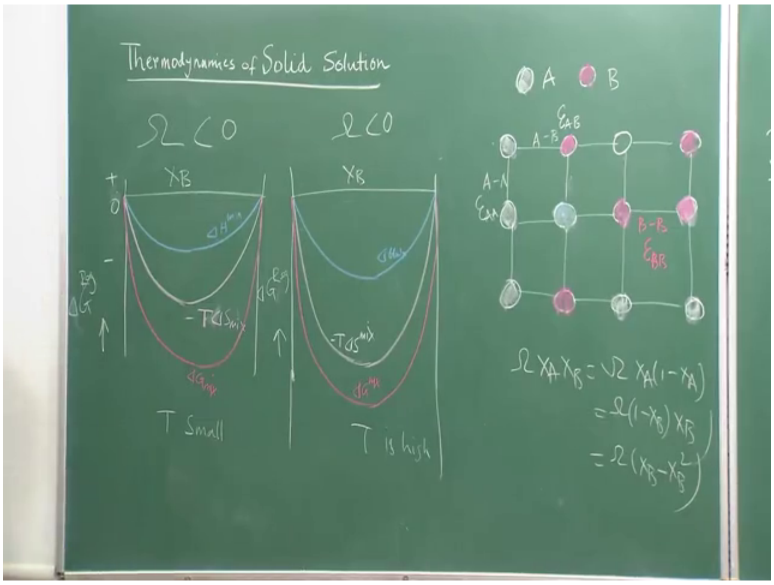

When sigma is equal to less than equal to 0, one when the temperature is low other 1 is the temperature is high because as I said temperature is a factor and all this plots, we are going to plot as a function of X B-B right. So, this is 0, this is minus this is plus. So, here I am going to plot T small, when T is small means their room temperature less than room temperature and here I am going to plot again same thing G, this is remember this is G vertical axis is G regular solution as a function of X B when T is high.

So, there I will use different colored chalks to facilitate it to you understand these things, first let us plot obviously, because sigma is less than 0 and I have we have seen that then this value sigma is negative. So, this value is negative, sigma X A is positive X B is positive only thing sigma is negative. So, therefore, this fellow is negative and we know that entropy term is always negative. So, what will happen because of that delta H mix I think it is better we plot delta G mix, that is better than it is easy to fall it let us change it delta G because delta G is also same as delta G only difference is that constant term is added.

So, this is for my delta H mix I write down delta H mix. So, minus of T delta S mix will be also inverted parabola, why these inverted parabolas I have told you because if I expand this it looks like a parabola. This is already a parabola this is because sigma in to X A X B; that means, X A in to 1 minus X A. So, therefore, this is X A square and that is why it is a inverted parabola, but if you are not understanding I can write it down sigma

X A 1 minus X A. So, I can write down sigma is a X A minus X A square. So that means, r let us do it other way because we are plotting X B it will be similar, x sigma 1 minus X B multiplied by X B, x equal to sigma X B minus X B square.

So, anything wherever you have a square term on the for the variable that is a equation of parabola. SO that means, G delta G will be also looking the same kind of plot. So, this is delta G mix. So, that any value of X B the solid solutions is preferred, that is what we discussed when sigma is less than equal to 0 for any value of X B, any value of the compositions on the on this pure a to pure b solid will be preferred a b bond will be preferred.

So, similarly for high temperatures what will what happen high temperature? Entropy term will increase further, that is what is going to happen nothing else is going to change. So, enthalpy will be slightly increasing because bond energies will slightly change let us let me increase a little further. So, this is here it is, this is delta H mix now entropy will also increase further, because temperature term is there and so similarly your delta G term will increase. So, this is T delta S mix and this is delta G mix. So, whatever may be the value of sigma value of X B with temperature whether point sigma is less than 0, solid solution is always preferred.

So, we do not see any changes from ideal to regular when sigma is less than equal to 0, for a sigma more than equal to 0. We will discuss in the next class since it will be changing when the value will be more than 0.