Phase Equilibria in Materials (Nature and Properties of Materials -II)
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Lecture-08
Phase Stability in Binary Solution

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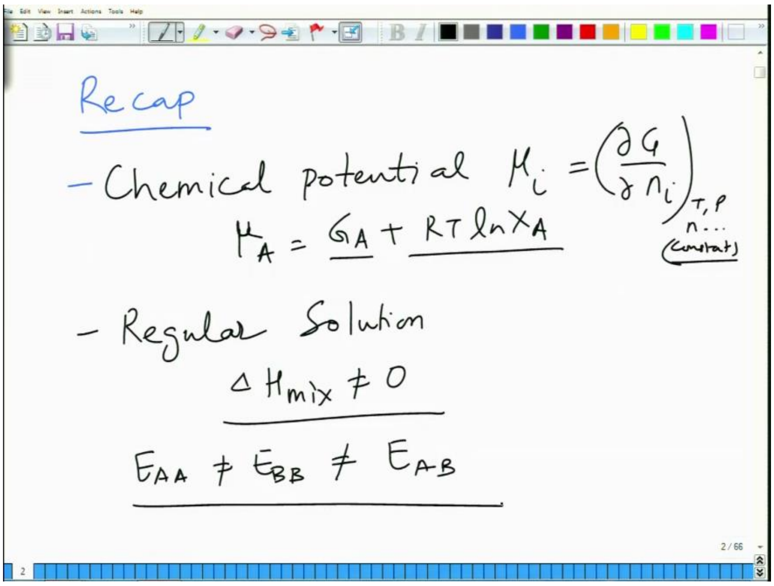

Recap

- Chemical potential $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n\ldots \text{(constant)}}$

$\mu_A = G_A + RT \ln X_A$

- Regular Solution

$\Delta H_{mix} \neq 0$

$E_{AA} \neq E_{BB} \neq E_{AB}$

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So, we start a new lecture again. Let me just give you a brief recap of last lecture. In the last lecture, we talked about; we introduce the topic of Chemical Potential, and which is nothing but μ_i for a given substance, and this is nothing but

$$\mu_i = \left(\frac{\partial G'}{\partial n_i}\right)_{T,P,n} \qquad \text{when T, P and n are constant}$$

So, basically it is an incremental change in the free energy, when you change the; when you make a small change in the composition of a phase, without altering the composition, significantly.

And then, we looked at; introduced regular solutions. And here also we saw that μ_A for a given substance

$$\mu_A = G_A + RT \ln X_A$$

So, chemical potential, which is also called as partial molar free energy of A is equal to molar free energy of A in that phase plus this term $RT \ln X_A$, we can see that this term is going to be negative. So, partial molar free energy of A is going to be; it basically depicts the influence of addition of extra A into the phase with respect to changes in the overall molar free energy of that particular substance. You can see that; if you know A, X_A =0, then $G_A = \mu_A$.

So, now, sorry when X_A = 0, then it is asymptotic on the y-axis, but when X_A = 1, then obviously this $\mu_A = G_A$. And then, we introduced regular solutions. Regular solutions are not ideal solutions for which $\Delta H_{mix} \neq 0$, see that greater and equal to 0 or smaller and equal to 0, making it is an exothermic or endothermic process of solution formation. And in this context the only difference; the only assumption that we are making is that

$E_{AB} \neq E_{AA} \neq E_{BB}$. And other things remain fairly the same as we discussed.

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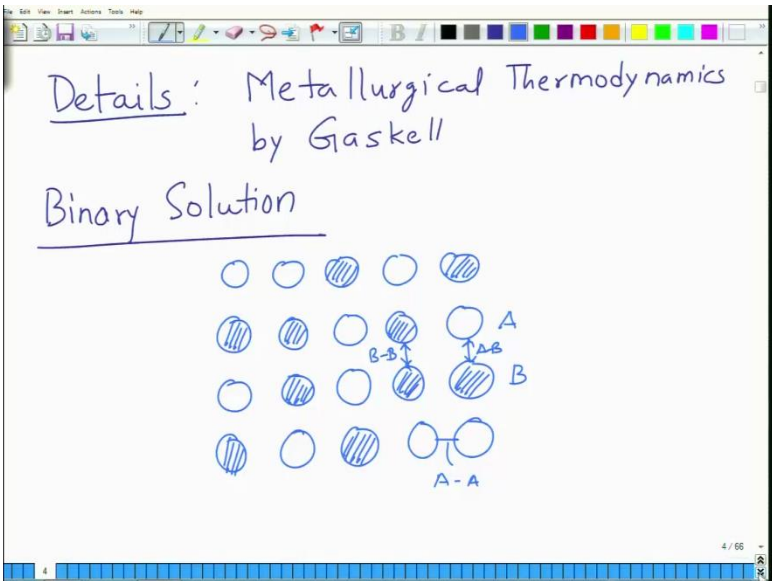

Details: Metallurgical Thermodynamics
by Gaskell

Binary Solution

So, what is; so, now let us draw a schematic picture of a binary solution. By the way if you want to get into details of this; so, details can be read from metallurgical thermodynamics by Gaskell. So, the authors name is; let me just check, I have given this name in the introductory information on the course. So, basically this is the book. If you google it, you will find this book.

So, basically now let us move to what is a binary solution schematic. So, I draw here lattice alright. Some of these atoms are A, some of them are B. So, let us say; so these are let us say the B atoms ok. So, this is A, this is B. So, we can see here that this is B-B bond, this is A-B bond, and this would be A-A bond. So, depending upon the bond energy of each of these bonds, there will be a preference for a particular type of bond.

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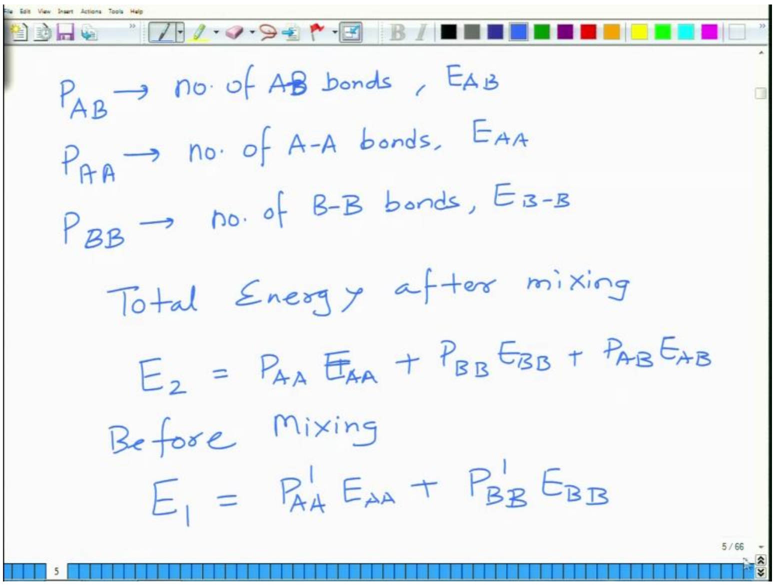

$P_{AB} \rightarrow$ no. of AB bonds , E_{AB}

$P_{AA} \rightarrow$ no. of A-A bonds, E_{AA}

$P_{BB} \rightarrow$ no. of B-B bonds, E_{B-B}

Total Energy after mixing

$$E_2 = P_{AA} E_{AA} + P_{BB} E_{BB} + P_{AB} E_{AB}$$

Before mixing

$$E_1 = P'_{AA} E_{AA} + P'_{BB} E_{BB}$$

So, we have let us say; so, we can define that we have P_{AB} as a number of A-B bonds, with bond energy E_{AB}. Similarly, we have P_{AA} bonds, number of, with bond energy E_{AA}, then we have bond energy of P_{BB}; P_{BB} is a number of B-B bonds, with bond energy E_{BB}. So,total energy after mixing

$$E_2 = P_{AA}E_{AA} + P_{BB}E_{BB} + P_{AB}E_{AB}$$

And what was it before mixing, before mixing you only had AA and BB kind of bonds, so it was

$$E_1 = P'_{AA}E_{AA} + P'_{BB}E_{BB}$$

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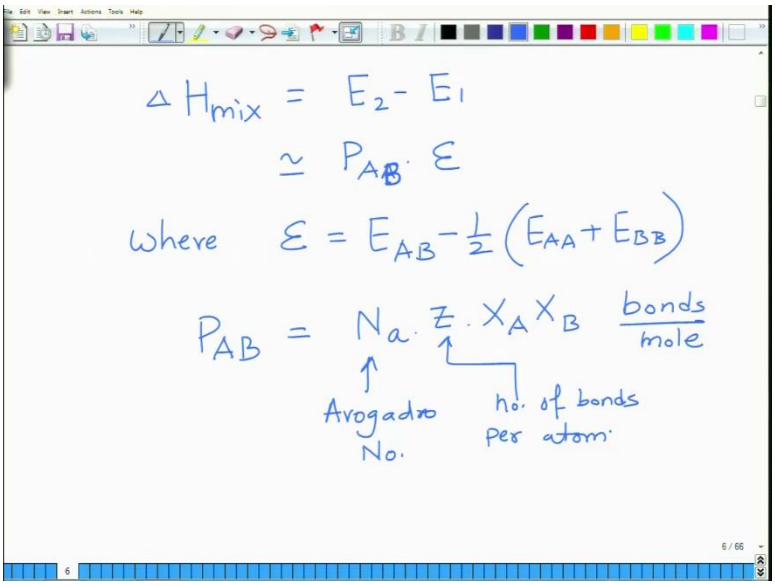

$$\Delta H_{mix} = E_2 - E_1$$

$$\simeq P_{AB} \cdot \mathcal{E}$$

where $\mathcal{E} = E_{AB} - \frac{1}{2}(E_{AA} + E_{BB})$

$$P_{AB} = N_a \cdot Z \cdot X_A X_B \quad \frac{\text{bonds}}{\text{mole}}$$

Avogadro No.

no. of bonds per atom.

Now, we will not get into detailed analysis, but this ΔH_{mix} detailed analysis can be found in Gaskell; so, if you go to Gaskell, you will find it there, it is nothing but

$$\Delta H_{mix} = E_2 - E_1$$

$$\cong P_{AB}\ \varepsilon$$

$$\varepsilon = E_{AB} - \frac{1}{2}(E_{AA} + E_{BB})$$

So, number of A-B bonds in the mixture, multiplied by some average energy, this average energy is difference between E_{AB}, the boundary of AB bonds minus the average of bond energy of AA and BB bonds, so E_{AB} minus half of E_{AA} plus E_{BB}.

Now, it turns out that

$$P_{AB} = N_a Ƶ X_A X_B$$

Basically, it is nothing but bonds per mole of mixture, where N_a is Avogadro number, Ƶ is the number of bonds per atom, and X_A and X_B are the mole fractions of A and B.

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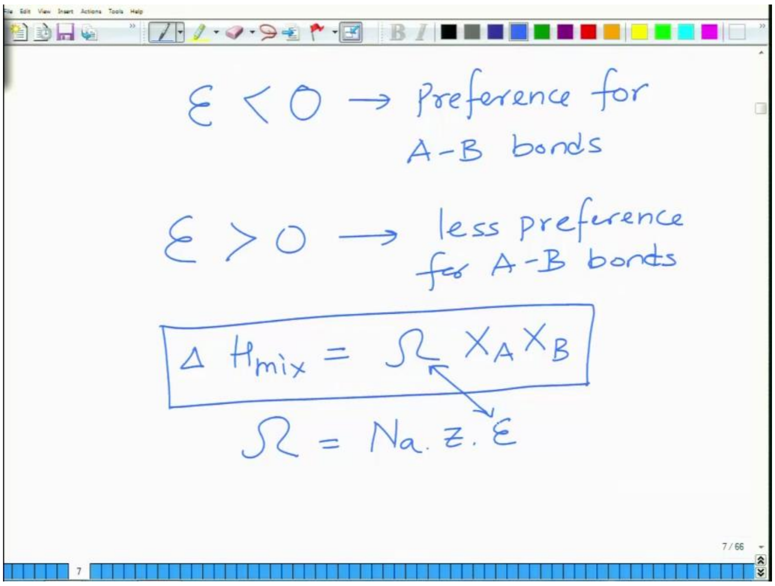

$\varepsilon < 0 \rightarrow$ preference for A-B bonds

$\varepsilon > 0 \longrightarrow$ less preference for A-B bonds

$$\boxed{\Delta H_{mix} = \Omega X_A X_B}$$

$$\Omega = Na . z . \varepsilon$$

So, we; from this it is obvious that if apps; this is this energy $\varepsilon < 0$, then we have preference for A-B bonds, whereas if $\varepsilon > 0$, then less preference for; then of course, what you would expect in a ideal solution. So, when epsilon, when $\varepsilon < 0$, you have higher preference for A-B bond in a random solid solution, so which means A and B would like to be close to each other. And when you have $\varepsilon > 0$, there is less preference for A and B bonds as compared to what you would expect in a random solid solution, so which means A and AA BB would be preferred over a AB kind of configuration.

So, using this formalism, we define the

$$\Delta H_{mix} = \Omega X_A X_B$$

where this $\Omega = N_a Ƶ\ \varepsilon$

So, this is the; and depending upon the magnitude of this term $N_a Ƶ\ \varepsilon$, where the sign of this term will be determined by the sign of; so, this will be dependent on that. So, sign of this term omega is going to be governed by sign of ε, which is dependent upon what is the preference of bonding in a given phase. And this will determine what kind of free energy of; what kind of change in enthalpy of mixing that you would obtain for a given system.

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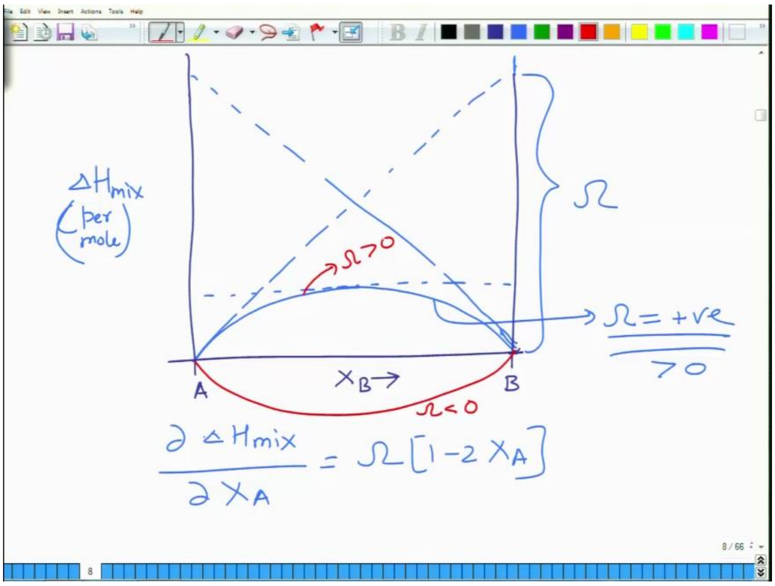

$$\frac{\partial \Delta H_{mix}}{\partial X_A} = \Omega[1-2X_A]$$

So, when you plot this now; so, what we are plotting here is basically delta H mix, which of course per mole, all these quantities are plotted as per mole. And this plot goes as vectors. And if you make a tangent to this, tangent makes an intercept here; similarly, if you make a tangent here, so if I extend this, this will make; so, this will cut on the y-axis with the magnitude on both sides.

So, we can see that in the middle, now you can work out the slope ok. So, if you do $\frac{\partial \Delta H_{mix}}{\partial X_A}$ let us say, so you will obtain basically ok, and so, you can calculate the values of different values of X_A. So, what will; what this tells you is that the intercept value is omega at the ends, and in between at point 5 composition, when they are equal in proportions, in that case this slope is equal to 0. So, it goes through a flat region in between.

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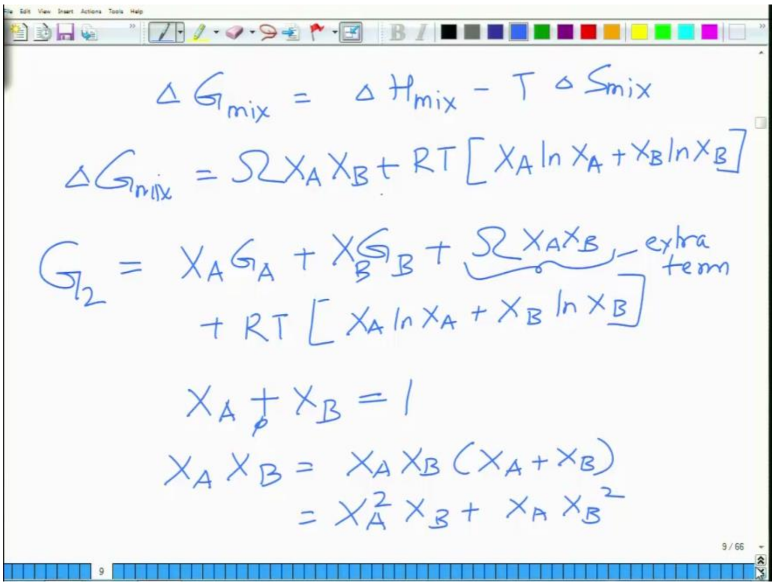

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

$$\Delta G_{mix} = \Omega X_A X_B + RT[X_A \ln X_A + X_B \ln X_B]$$

$$G_2 = X_A G_A + X_B G_B + \underbrace{\Omega X_A X_B}_{} \text{ — extra term}$$
$$+ RT[X_A \ln X_A + X_B \ln X_B]$$

$$X_A + X_B = 1$$

$$X_A X_B = X_A X_B (X_A + X_B)$$
$$= X_A^2 X_B + X_A X_B^2$$

Now, what is this mean, in terms of free energy of mixing. So,

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

$$\Delta G_{mix} = \Omega X_A X_B + RT[X_A \ln X_A + X_B \ln X_B]$$

And so, G 2 which is the free energy after; free energy of the solution can be written as

$$G_2 = X_A G_A + X_B G_B + \Omega X_A X_B + RT[X_A \ln X_A + X_B \ln X_B]$$

You can see now, that this is the extra term, which was not present in, which was not present for ideal solution. So, this is the term, which has been added now, after considering non-ideality in the system, which means that is a regular solution. So, what it; you can further distinguish it. So, you know that, so we can do some trick to calculate what is μ_A and μ_B here. So, we know that $X_A + X_B = 1$, and so we can write

$$X_A X_B = X_A X_B (X_A + X_B)$$

$$X_A X_B = X_A^2 X_B + X_A X_B^2$$

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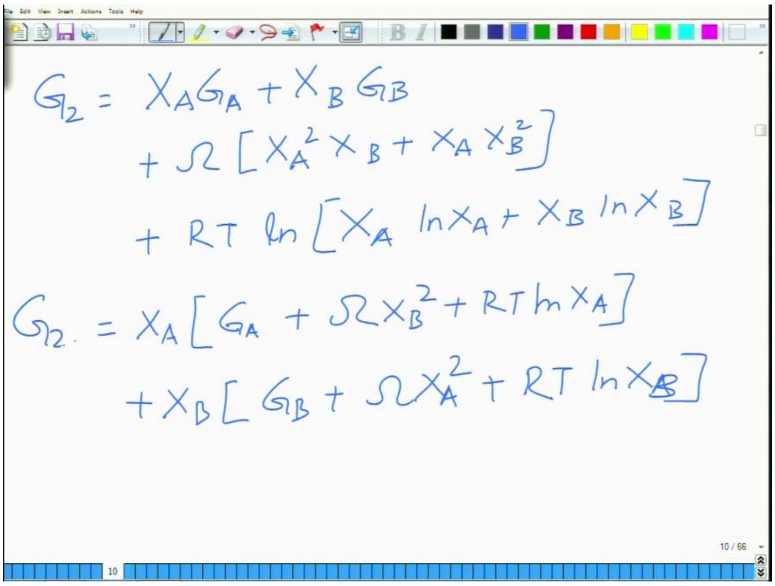

$$G_2 = X_A G_A + X_B G_B$$
$$+ \Omega [X_A^2 X_B + X_A X_B^2]$$
$$+ RT \ln [X_A \ln X_A + X_B \ln X_B]$$

$$G_2 = X_A [G_A + \Omega X_B^2 + RT \ln X_A]$$
$$+ X_B [G_B + \Omega X_A^2 + RT \ln X_B]$$

Now, let us make this change in the above equation. So,

$$G_2 = X_A G_A + X_B G_B + \Omega[X_A^2 X_B + X_A X_B^2] + RT[X_A \ln X_A + X_B \ln X_B]$$

$$G_2 = X_A[G_A + \Omega X_B^2 + RT \ln X_A] + X_B[G_B + \Omega X_A^2 + RT \ln X_B]$$

you can now modify this little further.

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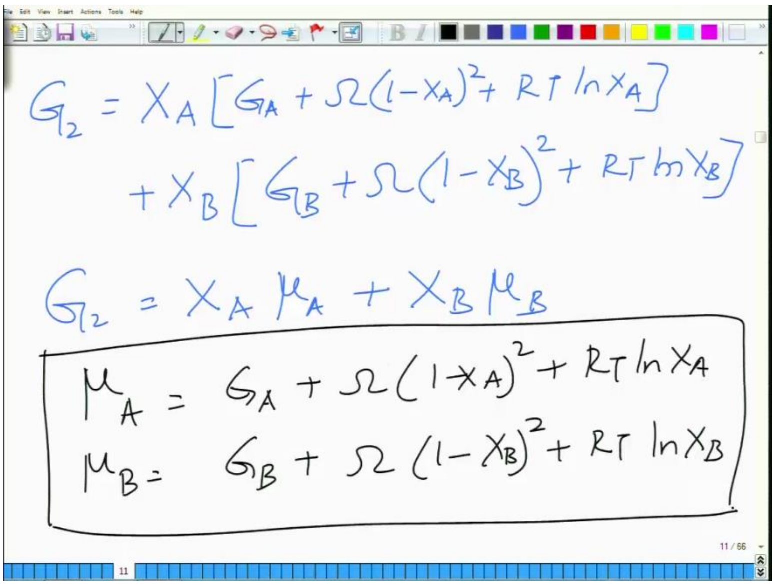

$$G_2 = X_A [G_A + \Omega (1 - X_A)^2 + RT \ln X_A]$$
$$+ X_B [G_B + \Omega (1 - X_B)^2 + RT \ln X_B]$$

$$G_2 = X_A \mu_A + X_B \mu_B$$

$$\boxed{\begin{aligned} \mu_A &= G_A + \Omega (1 - X_A)^2 + RT \ln X_A \\ \mu_B &= G_B + \Omega (1 - X_B)^2 + RT \ln X_B \end{aligned}}$$

So, X_B can be written as $(1 - X_A)$.

$$G_2 = X_A[G_A + \Omega(1 - X_A^2) + RT\ln X_A] + X_B[G_B + \Omega(1 - X_B^2) + RT\ln X_B]$$

Now, what is this equal to; this is this is nothing but

$$G_2 = X_A\mu_A + X_B\mu_B$$

So,

$$\mu_A = G_A + \Omega(1 - X_A^2) + RT\ln X_A$$

$$\mu_B = G_B + \Omega(1 - X_B^2) + RT\ln X_B$$

These are now the modified terms for chemical potential of A and B. Vice versa, what you obtained in case of ideal solution. So, this is the difference that we obtained after considering the known ideality into the system that is regular system basically, which; regular solution in which $\Delta H_{mix} \neq 0$.

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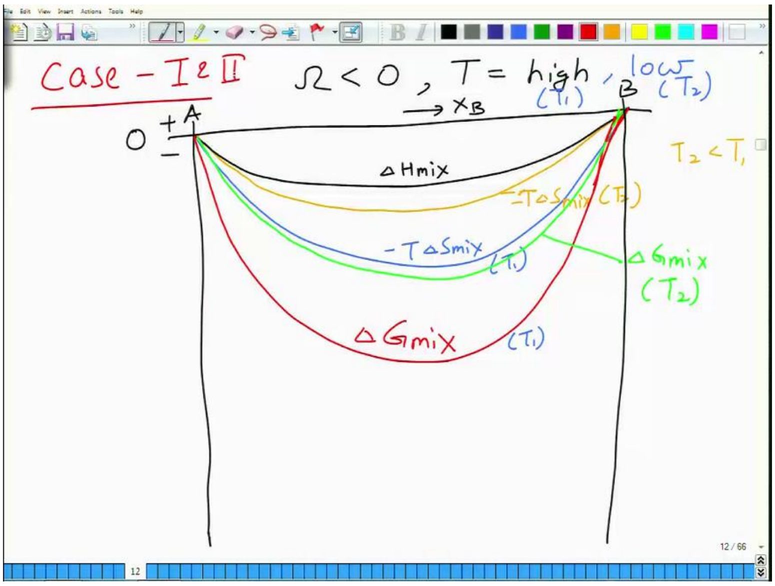

So, now let us plot this ok. So, we first make case I, in which this interaction parameter omega is less than 0, which means it is negative, ΔH_{mix} is negative, and temperature is high. So, actually we are going to start from; so, since we have this omega less than 0, and we already known that ΔG_{mix} is in case of ideal solution was negative, so we will have to plot from negative scale, so this is let us say 0. And here we are going from pure A to pure B, so this is, as a function of X_B.

So, we first plot ΔH_{mix}, ΔH_{mix} is going to be like this, this is ΔH_{mix}. Now, let us plot what is $-T\Delta S_{mix}$, this is $-T\Delta S_{mix}$. Since, both of them are negative, the free energy is going to be even, so just let me use a different color. So, this is going to be the, sorry, pardon me for little bit of mistake there. But, this is ΔG_{mix}. So, when you have $\Omega < 0$, interaction parameter less than 0, which means the bond energy is for A-B bonds is preference, there is a preference for A-B bonds.

In this case, the bond, basically the bond energy of A-B bonds is lower than average bond energy of AA and BB bonds, and the temperature is high, we know already know what is the effect of high temperature, high temperature provides you higher driving force for solution making.

So, in this case, when the interaction parameter is also negative that delta G mix will be even further lower as compared to ideal solution, because in case of ideal solution, this ΔH_{mix} was 0. So, now, you have this extra added term, which is of negative nature to delta G mix, making it further down. So, this will, this will be good for, this will, this will make the solution; making AB solution formation even more preferable as compared to the ideal solution, when the interaction between A and B is high, that is the bond energy of A-B bonds is lower.

What will happen, when you have a lower temperature? In case of lower temperature, so this is high. So, let us say if I want to plot on the same thing for low temperature, so delta H mix will undergo some change as function of temperature, but let us say it does not change too much. What will change is $-T\Delta S_{mix}$, so this $-T\Delta S_{mix}$ at lower temperature will be this. So, this is $-T\Delta S_{mix}$ at, let us say T_2, with T_2 being smaller than T_1. So, this is for let us say for T_1 alright. So, high is T_1, low is T_2 ok.

So, what will happen to now the free energy, the free energy correspondingly will also be lower. I mean these are related positions, so do not worry about the exact this thing. So, this is now $\Delta G_{mix}^{T_2}$. So, the driving force will be lower at lower temperatures, because we know that this $T\Delta S_{mix}$ term is going to govern that. So, you can see when the interaction parameter is negative, there is propensity for the formation of A-B bonds. As a result, it is more likely to form AB solid solution, as compared to the ideal scenario, when $\Delta H_{mix} = 0$. So, ΔH_{mix} negative favors the formation of AB solid solution, even with higher driving force.

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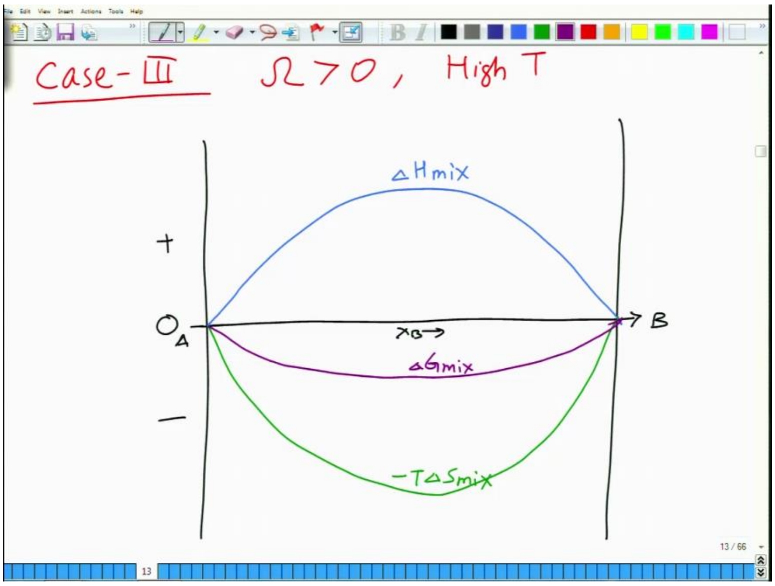

Case- III $\Omega > 0$, High T

Now, let us let us take another case. So, in this case, we have considered case I and II that is of high and low temperature. Now, let us go to case III. Case III is that of, let us say, your interaction parameter is positive, which means there is less preference for A-B bonds, or A-B bond energy is higher, but at high temperature. So, what might turn out in such a cases, again we plot, make the same plot. Now, in this case since interaction parameter is greater than 0, the delta H mixing will not be negative, it has to be positive.

So, now we will, have to choose our scale properly. So, let us say this is the axis, this is B, this is A, and this is X_B, and this is 0. So, this is plus, this is minus. We are going to plot various energies here. So, first we plot the ΔH_{mix}, ΔH_{mix} will be something like this. So, this is ΔH_{mix}. So, just to clarify in the previous plot, in this plot, when we plotted this ΔH_{mix}, in this case this interaction parameter was positive that is greater than 0. So, when it is greater than 0, it undergoes so, if I just make a slight modification in that plot, so if it was greater than 0, it was like this; if it was less than 0, it would have been like this.

So, this is for, and this is for. So, ΔH_{mix} now has this kind of behavior, when it goes through a maximum at certain, at in the middle of AB composition that is half A and half B. Now, when you now plot $T\Delta S_{mix}$, that $T\Delta S_{mix}$ again goes to a similar fashion, this is -T. So, let me just make it little bit more deeper. Since, it is high temperature, at high temperature; it is likely to be very deep; so it will be something like this. So, this is $-T\Delta S_{mix}$.

So, since at high temperature $-T\Delta S_{mix}$ term dominates over ΔH_{mix} term, which is positive, your G the plot of G will be somewhere like this. So, this will be ΔG_{mix}. So, at high temperature, even though there is less preference for AB kind of bonds, there is a propensity to form AB solid solution because of domination of the entropy factor, that is $-T\Delta S_{mix}$ term dominates over the enthalpy term, giving rise to still lower free energies or complete solid solubility of A and B into each other, to make a solid solution.

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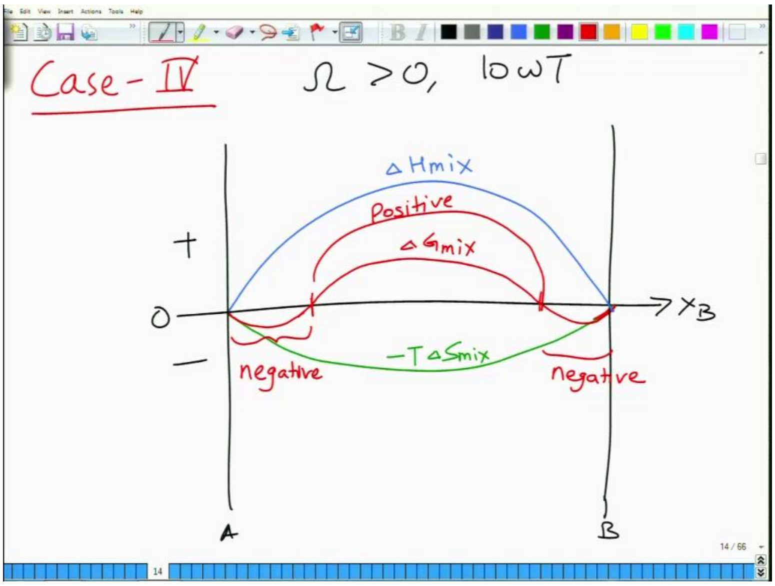

What happens, when we go to lower temperature? So, when we go to lower temperature, let us say case IV. In this case, the scenario is slightly different. So, again the interaction parameter is positive, temperature is lower ok. Again we make this plot. So, we have pure A and pure B. You start somewhere in between, so this is 0, this is plus, this is minus, and this is basically X_B. So, ΔH_{mix} is like this, this is ΔH_{mix}. Now, we are at lower temperature, which means this, so, this $-T\Delta S_{mix}$ term is not very deep, it is rather shallow.

So, when we plot the resultant free energy; turns out, that the resultant free energy follows a plot, which is like this, something like that, this, is. So, what this tells you is that below these, whereever you see a change in the, whereever you see a negative curvature or change in the slope. So at these points there is a change in the slope. When you have change in slope, the free energy goes from negative to positive, ΔG_{mix} is negative within this regime, so it is negative, in this regime it becomes positive, and in this regime it becomes again negative.

So, what this tells you is that, now the boundaries will shift depending upon the relative increase in, relative values of $\Delta H_{mix} - T\Delta S_{mix}$, what this tells you is that, even though ΔH_{mix} is positive that is less preference for A-B bonds at lower temperature, you can go to 0 Kelvin. When you go to 0 Kelvin, this curve will become so very close to 0 Kelvin, this curve will become almost flat.

But, even then there will be slight solid solubility of B in A or A in B, so what it means is that, when you add, so there is a preference for impure system over the pure systems. So, when you add little bit of B into A or A into B, the free energy tends to decrease. There is a negative phase of mixing, which tends to prefer the formation of impure phase than the pure phase. We look in the reasons of this in the next slide, in the next class; we do not have time. But, this is what that the message is that lightly impure solids are preferred thermodynamically over the pure solids as long as temperature is higher than 0 K. So, nothing is perfectly pure in nature because of thermodynamic reasons.

Thank you very much. We will finish here.