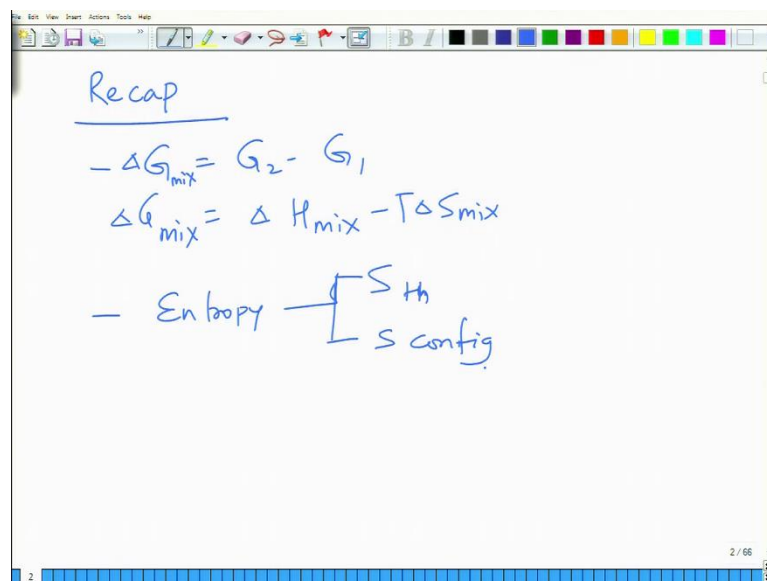


Phase Equilibria in Materials (Nature and Properties of Materials- II)
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Lecture - 06
Calculation of Configurational Entropy

So, we start a new lecturer again, lecture 6. So, we just first do a bit of a recap of what we saw earlier.

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So, in the previous lecture we basically started with the mixing of 2 components; A and B. Because in practical systems, we are dealing with impure system, which consists of more than 2 or more elements. So, we start with binary solutions consisting of 2 elements. So, we looked at the free energy ΔG_{mix} that happens by mixing 2 elements. And this was basically $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$. So, for G_2 ; for G_2 to be lower than G_1 which means the free energy, if solution is a stable then G_2 has to be lower than G_1 . And this ΔG_{mix} term which is the free energy change upon mixing, that is free energy of mixing is nothing but $\Delta H_{mix} - T\Delta S_{mix}$. So, ΔH_{mix} is the change in the enthalpy or the heat content of system, and ΔS_{mix} is the change in the entropy of the system before and after mixing. And we first started with regular solution, which means that for regular solution we assume that $\Delta H_{mix} = 0$, which means there is no change in enthalpy after mixing. And it remains the same which means ΔH is 0, but there is a change in configurational entropy, there is a

change in entropy which we were working out; we are also; and then we moved on to entropy.

And we said that entropy is thermal and configurational. And we have chosen to ignore the thermal contribution to entropy because of; if there are if there is no substantial, if there is no; if there is very negligible change in the heat in the in the temperature of volume of the system, then we can say yes thermal is negligible. Especially in the solid state, and we only work with the configurational entropy.

So now let us see how we evaluate the configurational entropy.

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Calculation of Configurational Entropy :

$$S = S_{\text{config}}$$

Before mixing

Pure A } $S_1 = 0$
Pure B }

$$k_B \ln W = k_B \ln(1) = 0$$

So we say, alright; so, we said that we will ignore thermal entropy. So, $S = S_{\text{config}}$. So, before mixing, so, we had pure A and pure B. And for both of these S_1 so, $S_1=0$, because whether you had pure A and pure B, the number of ways in which; because it is equal to $k_B \ln W$ and W is 1 as long as it is pure A and pure B. As a result

$$k_B \ln W = k_B \ln(1) = 0$$

So, for both these states, the entropy was equal to 0. So as a result, if you take their waited sum then that will also be equal to 0. So, $S_1 = 0$.

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After mixing

$$S_2 = k_B \ln W_2$$

$$W_2 = \frac{(N_A + N_B)!}{N_A! N_B!}$$

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 ●○○○○ ~ A (X_A)
 ○●○○○
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 B (X_B)

●○○○○
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$N_A \rightarrow$ No. of A atoms
 $N_B \rightarrow$ " " B "
 $N_A + N_B = N$
 $\frac{N_A}{N} = X_A, \frac{N_B}{N} = X_B$

What about S_2 which is after mixing? So, after; now we will look at after mixing, $S_2 = k_B \ln W_2$, ok. So, what is W_2 ? W_2 ; now what is the lattice like; you have; now let me draw the lattice here. You had situation like this. Now some of these are; frequency, this is A, this is B. So, A is in proportion X_A , B is in proportion X_B , but as far as; as long as it is a random solid solution which means position of A and B cannot be fixed. The A and B can be randomly distributed.

If they can be randomly distributed, there are multiple ways you can arrange A and B and each manner can be different. So, this is one possible manner, in another possible manner you can have situation like this; just count the number of atoms; I have marked 5 atoms as grey. This is another configuration. So, you can have configuration. So now, this is only about you know, 16 atoms that I have taken, but our system has much more large number of atoms. If we take one mole, it will have 6 into 10 to the power 23 atoms. So, which means you have numerous ways of making distinct configurations of atoms by mixing A and B.

So, if that is the case, then W can be defined as

$$W_2 = \frac{(N_A + N_B)!}{N_A! N_B!}$$

$N_A =$ No of A atoms and $N_B =$ No of B atoms

So, this gives me the total number of possible distinct configurations in which I can arrange; it should be N_B . I can arrange A and B in a solid solution of AB distinctly. So, this N_A is the number of A atoms and B is the number of B atoms.

$$N_A + N_B = N(\text{total no of atoms})$$

$$\frac{N_A}{N} = X_A \text{ and } \frac{N_B}{N} = X_B$$

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For 1 mol of AB

$$N_A = X_A \cdot N_a \rightarrow \text{Avogadro's no. } (6.023 \times 10^{23} \text{ atoms})$$

$$N_B = X_B \cdot N_b \rightarrow \text{"}$$

$$W_2 = \frac{(N_A + N_B)!}{N_A! N_B!}$$

$$S_2 = k_B \ln W_2$$

And if you take for 1 mole of solution, if I take 1 mole of AB, then

$$N_A = X_A N_a \text{ and } N_B = X_B N_b$$

where, N_a is nothing but Avogadro's number which will mean 6.023×10^{23} atoms per mole. So, we are just going to take for 1 mole because a free energy is a molar quantity and that will be simpler later on as you will see.

So now to solve this expression, we have seen that

$$W_2 = \frac{(N_A + N_B)!}{N_A! N_B!} \text{ and } S_2 = k_B \ln W_2$$

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$$S_2 = k_B \ln \frac{(N_A + N_B)!}{N_A! N_B!}$$

Sterling's approximation
$$\ln X! = X \ln X - X$$

Gas Constant
$$R = N_A \cdot k_B$$

Which means,

$$S_2 = k_B \ln \frac{(N_A + N_B)!}{N_A! N_B!}$$

To solve this, we need a approximation which is called as sterling's approximation, which says that $\ln X! = X \ln X - X$ and another thing that you may; and we can also define gas constant as $R = N_A k_B$, which is product of Avogadro's number and Boltzmann constant is R , which is gas constant. So now, when you do that?

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$$S_2 = k_B \left[\ln(N_A + N_B)! - \ln N_A! - \ln N_B! \right]$$

$$S_2 = k_B \left[(N_A + N_B) \ln(N_A + N_B) - (N_A + N_B) - (N_A \ln N_A - N_A) - (N_B \ln N_B - N_B) \right]$$

$$S_2 = -$$

Now,

$$S_2 = k_B [\ln(N_A + N_B)! - \ln N_A! - \ln N_B!]$$

$$S_2 = k_B [(N_A + N_B) \ln(N_A + N_B) - (N_A + N_B) - (N_A \ln N_A - N_A) - (N_B \ln N_B - N_B)]$$

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A screenshot of a digital whiteboard showing a handwritten derivation. The word "Replace" is underlined. The equations are: $N_A = X_A N_a$, $N_B = X_B N_a$, $S_2 = -R_B N_a [X_A \ln X_A + X_B \ln X_B]$, $= -R [X_A \ln X_A + X_B \ln X_B]$, and $\Delta S_{mix} = S_2 - S_1 = -R [X_A \ln X_A + X_B \ln X_B]$. The final equation is enclosed in a red box. The whiteboard interface includes a toolbar at the top and a status bar at the bottom showing "9/66".

And if you solved it

$$\text{Replace } N_A = X_A N_a \text{ and } N_B = X_B N_b$$

you will get

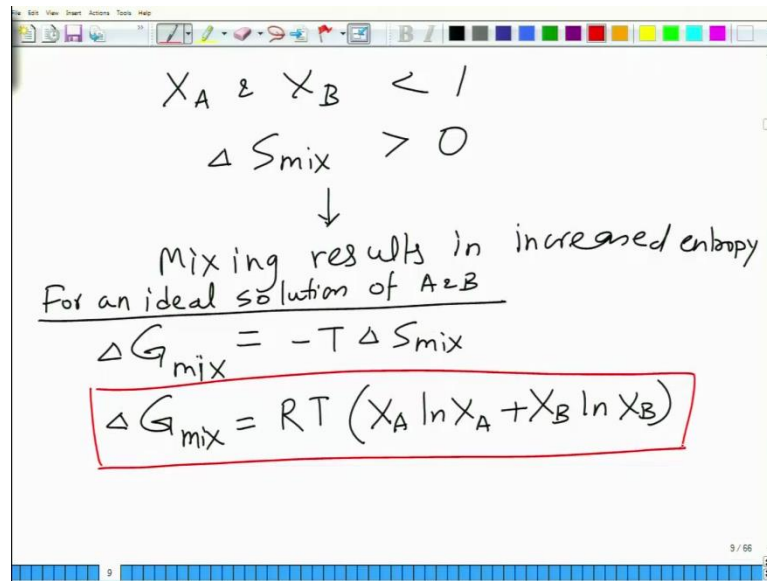
$$\begin{aligned} S_2 &= -k_B N_a [X_A \ln X_A + X_B \ln X_B] \\ &= -R [X_A \ln X_A + X_B \ln X_B] \end{aligned}$$

As a result,

$$\Delta S_{mix} = S_2 - S_1 = -R [X_A \ln X_A + X_B \ln X_B]$$

So, this is the free energy of mixing that you get after applying; after working out the expression for configurational entropy, assuming that thermal entropy change is equal to 0.

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So, you can see here, since

$$X_A \text{ and } X_B < 1,$$

$$\Delta S_{mix} > 0$$

So, you can see in the above expression; since $X_A < 1$, $X_B < 1$; log of these are going to be negatives; as a result negative negative will become positive. And as a result, $\Delta S_{mix} > 0$; so which means that entropy increases after mixing. So, mixing results in increased entropy, ok.

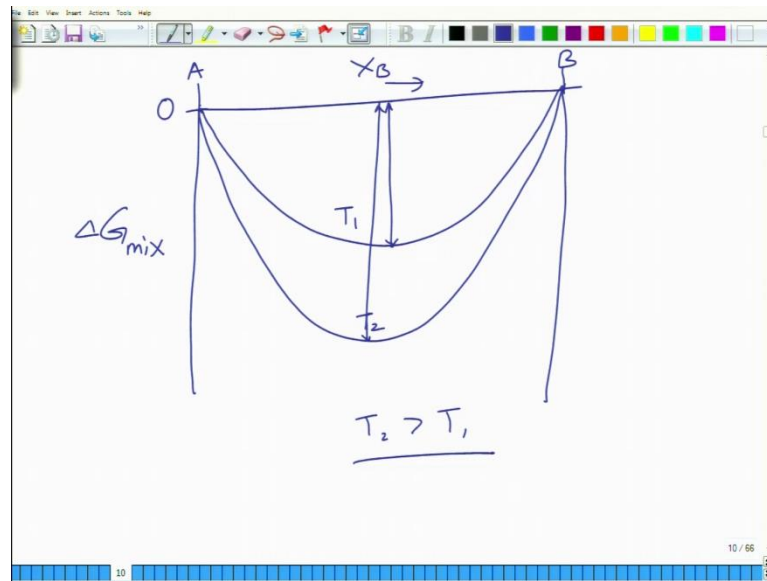
So, we can write now; the expression for ΔG_{mix} , for a regular solution because ΔH_{mix} was; so, for a regular; for a; sorry not for a regular solution I am sorry, for ideal solution of A and B; for an ideal solution of A and B,

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

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

This is delta G mixing.

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So now, if you plot it; you can also plot it. We can see from the above expression that since X_A and $X_B < 1$, lower than 1, ΔG_{mix} is going to be negative. So, as a result I am going to plot this below 0. So, this is 0, this is pure A, this is pure B and this is change in X_B . So, if you plot ΔG_{mix} as a function of X_A and X_B . So, if I put ΔG for; So, you can see that ΔG_{mix} for $X_A = 1$ is 0.

And it is also 0 for $X_B = 1$. So, actually it is not exactly going to touch the; So, it is not going to exactly be equals to 0 it will be actually asymptotic, but nevertheless because if you take the gradient the gradient will not be equal to 0. So, basically it; for a schematic, it will be something like that. So, this is at fixed temperature T_1 . If you increase the temperature T_2 , it will go to; because it is; this is T_2 . So, $T_2 > T_1$ leads to higher; So, you can see that this is; this depth has increased as the temperature increases. So, we can see the ΔG_{mix} of phase you are mixing, becomes more and more negative at higher temperatures.

So, that explains why things are mixed better at higher temperatures than at lower temperatures. Of course, there are kinetic arguments as well but thermodynamically, a free energy of mixing is more negative at higher temperature than at low temperatures and mixing is preferred at higher temperatures as compare to lower temperatures.

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$\Delta G_{mix} \rightarrow$ Driving force for mixing

$$G_2 = G_1 + \Delta G_{mix}$$
$$G_2 = X_A G_A + X_B G_B + RT(X_A \ln X_A + X_B \ln X_B)$$

↓
negative

So, let us now move on to; so, basically this free energy of mixing, ΔG_{mix} ; you can say is the driving force for mixing, ok. And this is very obvious I mean we try to mix for example, very simple things like sugar and water or salt and water, they mix far more easily at high temperature than low temperature; of course, there are solid solubility arguments as well. But let us say we are in the solubility limit; even then; and kinetic arguments; leaving aside the kinetic arguments, the mixing is; mixing has higher driving force at higher temperature than at lower driving force, and that is why you see them in practice as well.

So, the actual free energy now; we said,

$$G_2 = G_1 + \Delta G_{mix}$$

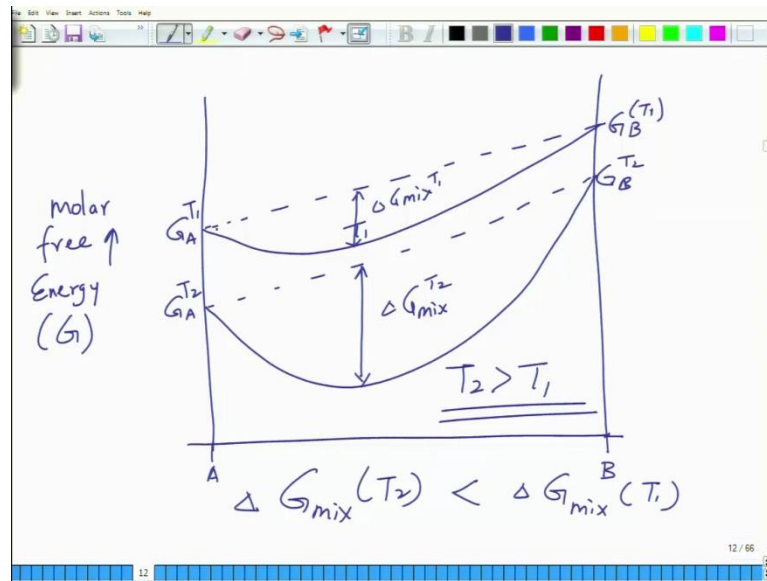
And this

$$G_1 = X_A G_A + X_B G_B$$

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

and this has an additional term now, $RT[X_A \ln X_A + X_B \ln X_B]$. So, this is the overall free energy of the solution, and you have to appreciate that this term actually is negative. And that is what makes the free energy of mixed solution lower than the pure solutions.

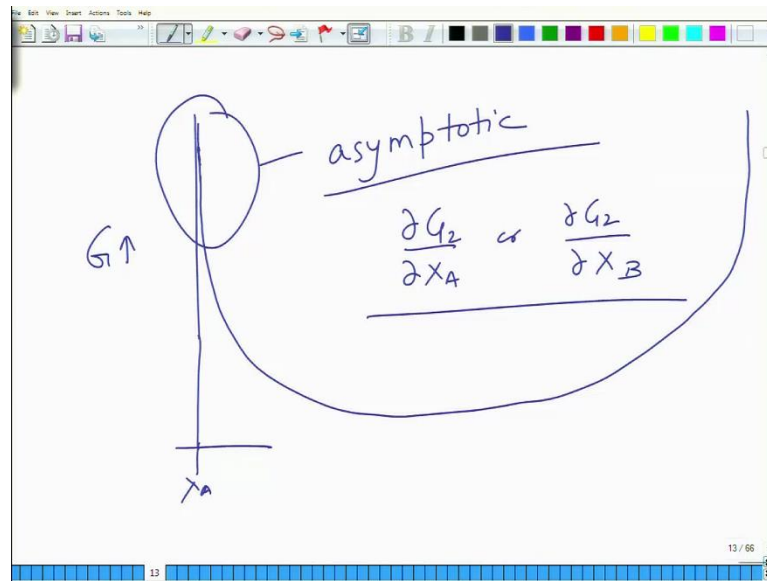
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If I now plot it; so, on; so, this is molar free energy G , ok.; So, if I plot for example, at a given temperature, the free energy follows this kind of behavior. This is G_A , this is G_B , and if I; so, let us say this is a temperature T_1 , if I do the same now at temperature T_2 which is higher. Now free energy of course, has decreased so, this is at T , T_1 this is at T_1 , this is at T_2 , this is at T_2 . And this will be the; now the free energy of; so, you can see that this is the $\Delta G_{mix}^{T_1}$, this is $\Delta G_{mix}^{T_2}$ which is higher. So, $\Delta G_{mix}^{T_2}$ is; so, higher means it is more negative. So, it is; so, $T_2 > T_1$

So, one thing that; that you have to note is that the intercepts on the; on the; on the y axis; they are not exactly intercepts; the curves, the free energy curves actually go tangential to the y axis at X_A and X_B . And that you can verify by; so, if you look at the free energy expression, take $\frac{\partial G_2}{\partial X_A}$ and $\frac{\partial G_2}{\partial X_B}$. You will see that it will not be; it has to be asymptotic which means the curve goes on X and Y axes as if it touches.

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So, if you zoom it what you should obtain is basically; if I just zoom it; let us say this is X_A , and the curve will go like this, show in that, ok. So, it does not actually intercept, it just goes parallel to; so, this is G . So, here it is; you can say asymptotic. And for this you can just take

$$\frac{\partial G_2}{\partial X_A} \text{ or } \frac{\partial G_2}{\partial X_B}$$

and you can see, the gradient will be will be infinity. So, it is not exactly cutting the y axis.

So; now let me summarize this particular point once again. So, we started with; let me go; let us go; this is a very complex, this is interesting thing to understand. So, we started with calculation of configurational entropy. So, configurational entropy is basically about the number of ways in which you can arrange the atoms within a lattice. So, before mixing it is pure A and pure B. So, there is only one way of identifying the mix; there is only one configuration in which you can see the atoms. As a result, $S_1 = 0$ for both A and B, as a result the net entropy before mixing is equal to 0.

After mixing; however, you can have different configurations, if A and B are randomly distributed in the lattice. And as a result if you have N_A number of A atoms and N_B number of B atoms. Then the W_2 , the parameter of randomness is nothing but

$$W_2 = \frac{(N_A + N_B)!}{N_A! N_B!}$$

where N_A and N_B are nothing but; if you have 1 mole of solid solution, then $X_A N_A$ and $X_B N_B$, which is Avogadro's number. So, W_2 can be further modified using Stirling's approximation. And what we will get is entropy which is; so, if you do analyze it, we get S_2 as

$$= -R[X_A \ln X_A + X_B \ln X_B]$$

And as a result, the delta S of mixing

$$\Delta S_{mix} = S_2 - S_1 = -R[X_A \ln X_A + X_B \ln X_B]$$

So, we can see that here since X_A and $X_B < 1$, the entropy change is always positive. So, when you are going from pure A and pure B to AB state, the entropy change actually is positive. So, basically we are saying that mixing results in a positive increase in entropy. So, for an ideal solution of A and B,

$$\Delta G_{mix} = -T\Delta S_{mix} = RT[X_A \ln X_A + X_B \ln X_B]$$

And when you plot this ΔG_{mix} as a function of temperature, what we see is that, for pure A and pure B; of course, there is no mixing so, $X = 0$. But for any intermediate composition range, there is a decrease in free energy of mixing which means there is a negative free energy of mixing which results in; which is what makes the; makes mixing possible. If it was not negative, you would not have mixing happening. And as you increase the temperature, the ΔG_{mix} also decreases further, which means the driving force for making a solution increases as you increase the temperature. And this is what is important to understand. So, ΔG_{mix} is nothing but driving force behind mixing.

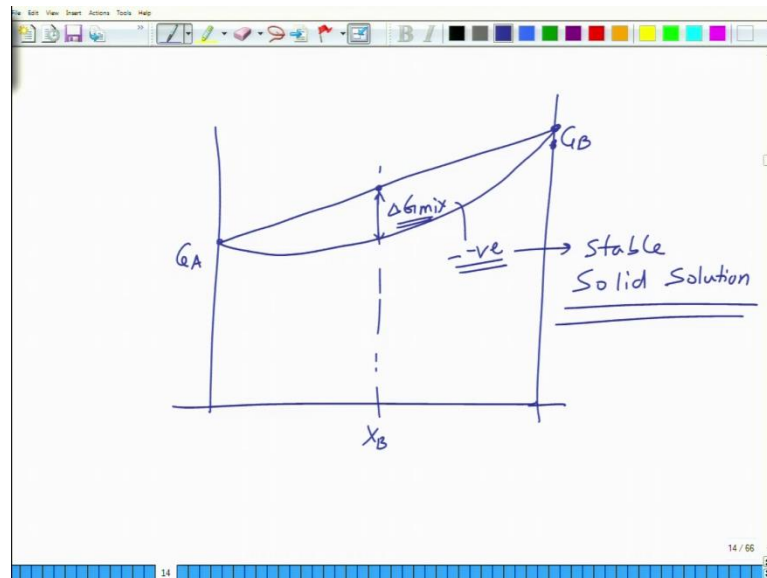
And G_2 is basically nothing but

$$G_2 = G_1 + \Delta G_{mix}$$

G_2 is $X_A G_A$ plus $X_B G_B$, this is the original component before mixing, and what you have added the third term is $RT[X_A \ln X_A + X_B \ln X_B]$. And this term is negative and this and so, this is this is what is true for most systems. Though which are; which make a stable solid solution that when you mix them together, it results in a free energy where ΔG of mixing is negative.

And if you plot now the overall free energy, the molar energy. The molar free energy shows this kind of trend. So, you can see that you were somewhere here, and you; now you have gone somewhere here. So, this is what is the driving force.

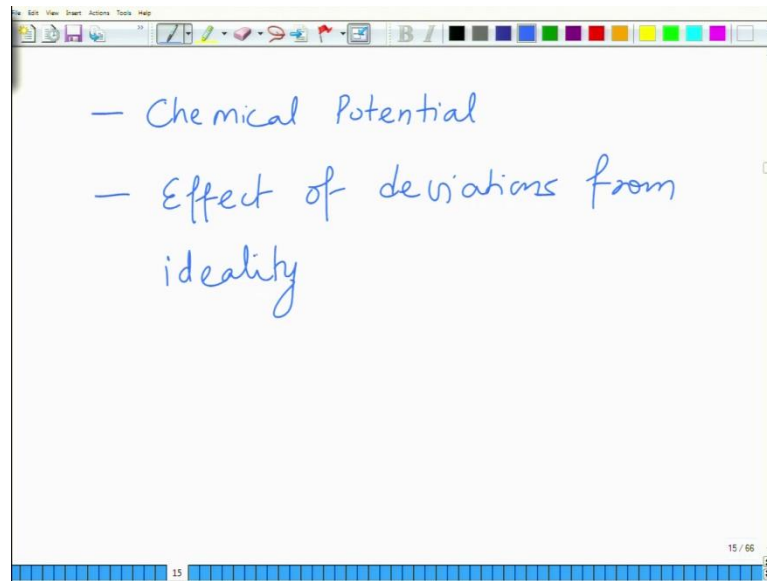
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So, if I draw in a separate plot, this is delta; this is G_A , this is G_B , and if I just take the weighted average, sorry this is G_B . So, if I take a composition X_B , this is what is the weighted average. Now weighted average basically says that I am at a free energy which is higher than that of A. Now it does not; so, you cannot really mix.

The mixing is made possible only because you had a decrease in the free energy from this state to that state. And this is ΔG_{mix} . And this is basically negative. And that is what makes the mixing possible, because now you are in a free energy state, which is lower than the free energy of the mixture. As a result, you have a stable solid solution. So, this will make stable solid solution.

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We will see later on. Now so, what we will do next is, not today, but in the next few classes we will; in the next few lectures we will look at the concept, such as chemical potential, which is necessary to understand the effect of compositional changes in the regular solutions. Because what we have talked about until now is the ideal solution. And now we will look at the chemical potential; we will look at the regular solutions. In the regular solutions, we will study chemical potential; we will study the effect of deviation from ideality. And that will make us understand what happens in reality. In reality, whether what makes a solution stable or unstable, because not everything is mixable; so, not everything makes a stable solid solution. So, we will see that in next lecture as to what do we mean by; what are the practical implications of deviation from ideality. So, we will do that in the next class.

Thank you.