# Heat Treatment and Surface Hardening - II
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## Lecture – 20
## Graphical representation of ΔGmix, ΔHmix, and -TΔSmix for real solutions and evolution of eutectic phase diagram from the G-X plots

Hello. Today we have lecture 20.

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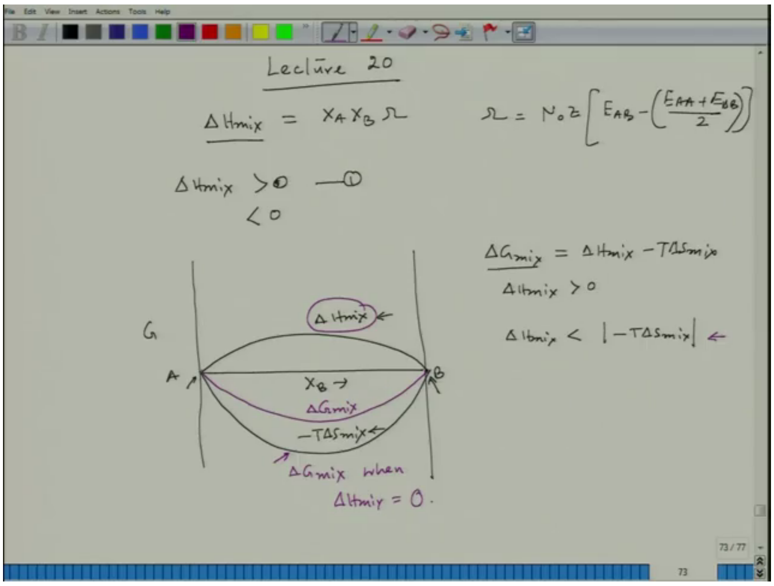

Lecture 20

$\Delta H_{mix} = X_A X_B \Omega$ $\qquad \Omega = N_0 z \left[ E_{AB} - \left( \frac{E_{AA} + E_{BB}}{2} \right) \right]$

$\Delta H_{mix} > 0$ — ①
$< 0$

$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$
$\Delta H_{mix} > 0$
$\Delta H_{mix} < |-T\Delta S_{mix}|$ ←

We have already seen that del h mix equal to XA XB omega and omega is N0 z e a B minus EAA plus BB by 2. This is my omega now when we consider ideal solution this del Hmix is 0, but if we consider non ideal situation that time del Hmix can have value greater than 0 or it can have value less than 0.

Now, we started working on the situation which is the first situation where delta h mix is 0, that time we saw that if the situation is like if this is my minus T del Smix. and if this is my del Hmix and XB this is pure A and B. this is G now del Gmix is del Hmix minus T del Smix and here del Hmix greater than 0, but if we compare this value as well as this value at all the concentration level from this concentration to this concentration, I could see del Hmix is less than minus T del Smix the mod of this value. So, that case del h del Gmix would be all the time negative over the entire composition from 0 percent B to 100 percent B. So, my del Gmix would have value between del Hmix and minus T del Smix. And since this condition is valid for all the concentration from 0 to 100 percent B, then del Gmix would also be negative this would be my del Gmix.

So, situation is not changing much if we compare the situation where del Hmix is 0 had this been 0 had this been 0 only difference would have been this line would have been del Gmix, when del Hmix is equal to 0; that means, only difference is the how stiff is going to be the del Gmix. If it is positive then the stiffness of; that means, the negativeness of del Gmix would reduce, but situation would be little complicated.

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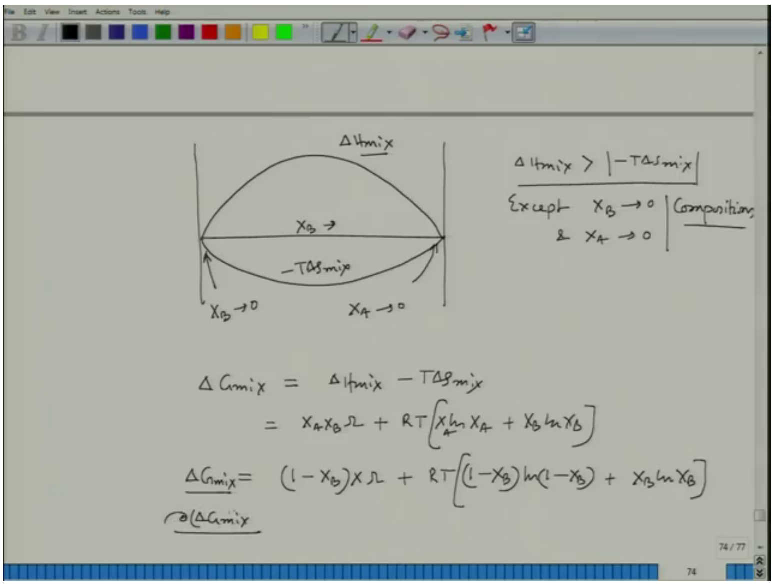

$\Delta H_{mix} > |-T\Delta S_{mix}|$

Except $X_B \rightarrow 0$ & $X_A \rightarrow 0$ | Composition

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

$$= X_A X_B \Omega + RT\left[X_A \ln X_A + X_B \ln X_B\right]$$

$$\underline{\Delta G_{mix}} = (1 - X_B) X \Omega + RT\left[(1 - X_B)\ln(1 - X_B) + X_B \ln X_B\right]$$

$\underline{\partial(\Delta G_{mix}}$

If we have a situation when the graph nature is like this. This is my del Hmix XB, but minus T del Smix, if the condition is del Hmix is greater than minus T del Smix except XB tends to 0, and XA tends to 0 these 2 compositions except these compositions. all other compositions this condition is valid. So, if I try to see the minus T del s plot from this picture it is seemingly observed that del Hmix is all the time greater than minus T del Smix, the mod of that minus T del Smix value at all the concentration for all the concentration XB equal to 0 to XB equal to 100, but the situation is not like that.

Now, if I try to see the slope of this line slope of this line at XA tends to 0, and here XB tends to 0 it would lead to some exciting situation. Now we see that del Gmix is equal to del Hmix minus T del Smix, which can be written as XA XB ma plus RT XA ln XA plus

XB ln XB. I can write it as 1 minus XB, XB plus RT 1 minus XB. I just convert in everything every composition in terms of XB.

Now, if I try to find out the slope of this del Gmix plot, then with reference to XB it would be 1 minus 2 XB.

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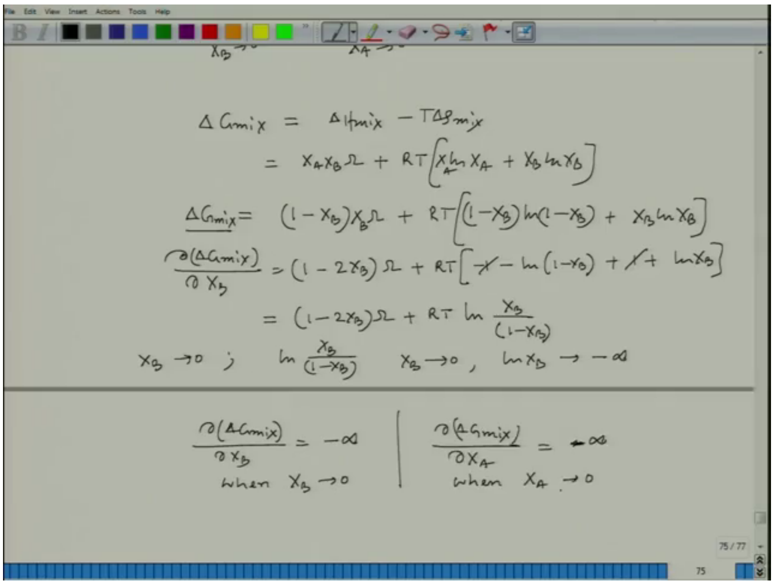

$X_B \to$ $X_A \to$

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

$$= X_A X_B \Omega + RT\left[X_A \ln X_A + X_B \ln X_B\right]$$

$$\underline{\Delta G_{mix}} = (1 - X_B)X_B\Omega + RT\left[(1-X_B)\ln(1-X_B) + X_B \ln X_B\right]$$

$$\frac{\partial(\Delta G_{mix})}{\partial X_B} = (1 - 2X_B)\Omega + RT\left[\cancel{-1} - \ln(1-X_B) + \cancel{1} + \ln X_B\right]$$

$$= (1-2X_B)\Omega + RT \ln \frac{X_B}{(1-X_B)}$$

$X_B \to 0$ ; $\ln \frac{X_B}{(1-X_B)}$ $X_B \to 0$ , $\ln X_B \to -\infty$

$\frac{\partial(\Delta G_{mix})}{\partial X_B} = -\infty$ when $X_B \to 0$ | $\frac{\partial(\Delta G_{mix})}{\partial X_A} = +\infty$ when $X_A \to 0$

Plus RT plus it would become now, when XB tends to 0 what happens to ln XB 1 minus XB down. Actually x if XB tends to 0 ln XB would be equal to minus infinity. Hence d del Gmix dx B would be minus infinity when XB tends to 0.

Similarly, if I consider in this plot we have considered the slope at this point on del Gmix curve is minus infinity same way I can prove we can prove that tends to 0. So, this is the slope of del Gmix on 2 extreme ends.

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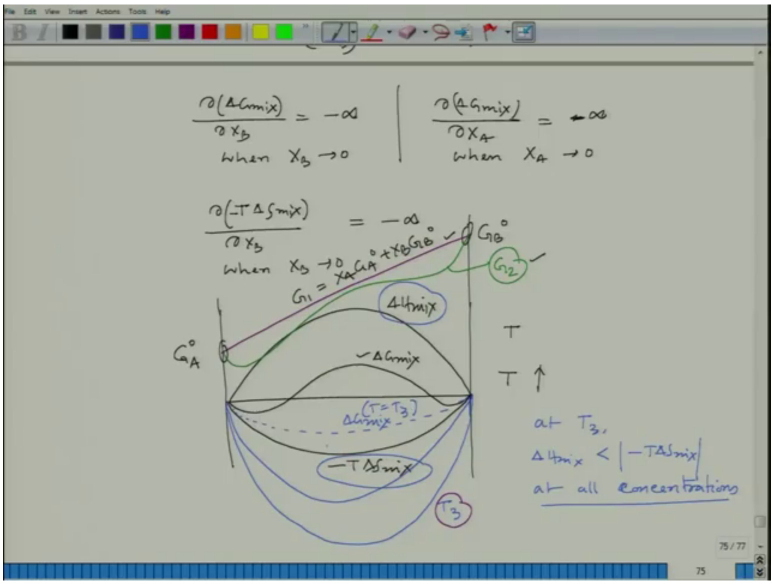

$\frac{\partial(\Delta G_{mix})}{\partial X_B} = -\infty$ when $X_B \to 0$

$\frac{\partial(\Delta G_{mix})}{\partial X_A} = -\infty$ when $X_A \to 0$

$\frac{\partial(-T\Delta S_{mix})}{\partial X_B} = -\infty$ when $X_B \to 0$

$G_1 = X_A G_A^0 + X_B G_B^0$

at $T_3$, $\Delta H_{mix} < |-T\Delta S_{mix}|$ at all concentrations

Now, similarly if I try to find out the slope of minus T del Smix XB when XB tends to 0, it would be also minus infinity. Therefore, it is very clear that the slope around this point and around this point for this particular line minus T del Smix is minus infinity. So, whatever could be the value of del G del Hmix; that means, the finite value of del Hmix. around this zone this condition would not be valid rather when XB tends to 0 as well as XA tends to 0 T del Smix is greater than del Hmix for this situation.

Of course, as we go towards the right here or towards left this condition would start prevailing. So, minus my del Gmix which is this expression would look like this. So, there will be dip around a pure range side on both the sides, when XB is very low and when XA is very low. Whatever could be the situation, since these value is always finite and these value is becoming minus infinity on pure metal science.

Now, if we have a situation like this, my del Gmix is this one, this is del Hmix this is minus d del Smix. Now if I try to see what would happen to the G 2 line this was my this is G a 0 this is G B 0. This is G1 equal to XA GA 0 plus XB GB 0. We have to just add this value with this value and here also the situation would be same around this zones there will be dip in G 2 line and then there will be again upward momentum G 2 line. So, if my G 2 line would be like this. So, this would be my G 2.

Now, final solution free energy line would have a situation like this. So, now, if let us say this is the effect at any temperature T, but if let us say the temperature goes up increases and if it increases, then that change would be not here rather it will be change would be here. So, these lines would start going down because as the temperature goes up these 4 thing would go like this.

So, at some point of time, let us say this is a temperature, T 3 at T 3 del Hmix would be less than minus T del Smix at all concentrations all concentration. So, that time these G 2 line would also keep on changing because, if it is, if it is T 3 then my G del Gmix would be gradually would go down, because del Gmix is nothing but this is del Gmix when T equal to T 3. So, everything would go down this entire line would go down and it would come to this place. So, that time my new G 2 line would be simply this would be my T 2 T equal to T 3.

So, these 2 conditions can be possible; that means, at low temperature, we have a situation this at high temperature we have a situation like this. in those cases where del Hmix is positive.

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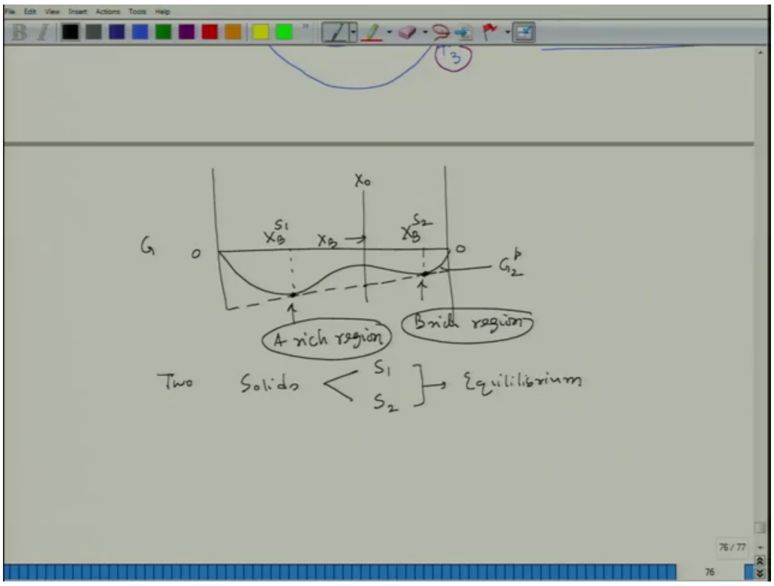

Now if I try to deal with only the G 2 line let us say I have drawn the this is 0 point G value. So, if the situation is like this, this is G 2 of some solution some phase some phase. Then I could see that the common tangent can be drawn and that common tangent passes through these 2 points. And if these 2 points are passing through that common tangent; that means, these 2 compositions will be in equilibrium. And interestingly if we see this is my XB, at this point it is more of a rich region and this is B rich region.

Now, there is a possibility, that these 2 phase would appear interestingly initially we have considered that both the A and B pure metals have same crystal structure and the solution resultant solution is also having the same crystal structure that time we are getting this G 2 line to be continuous from 0 to 100 percent B. and we are having 2 solids, 2 solids one with a composition XA of solid one and then this is x or XB, I can put it in terms of XB this is XB solid 2 solid one, and solid 2 they are in equilibrium, and actually 2 different solids are forming with the same crystal structure, but having 2 different compositions. And these composing for example, if we try with a composition this which is x 0 initial composition these initial composition will be distributed into these 2 solids of different compositions and when these 2 solids are forming we are getting an equilibrium and one solid is having richer in a the other solid is having richer in B.

So, this is called phase separation and because of this particular situation we get to see eutectic.

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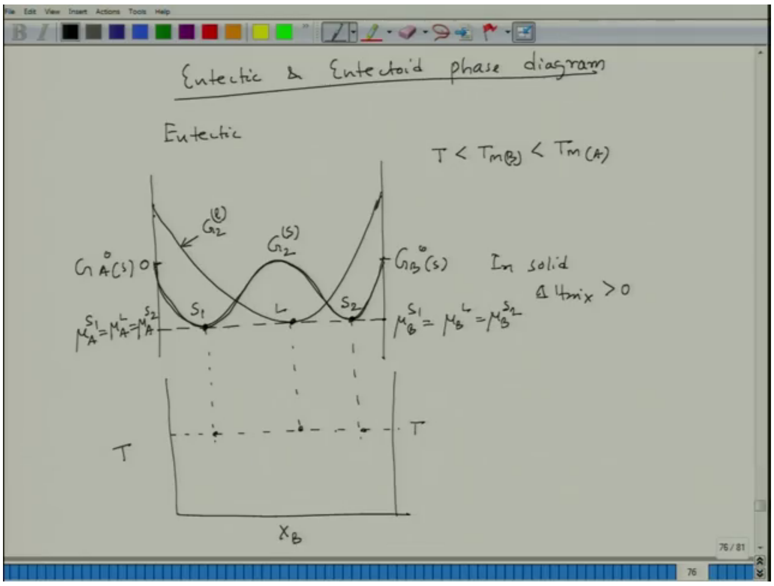

As well as eutectoid phase diagram. let us consider eutectic. here also the 2 sides to pure metal sides are having same crystal structure the resultant is also giving resultant solution is also giving the same crystal structure. So, if we have a situation free energy composition situation like this, let us say this is 0 and if the temperature is less than tm B and less than TMA. So, I would get this is liquid and then this is GA 0 of solid this is GB 0 of solid. and this one are we are taking it as a reference so that means, 0 value and now we could see that and this this shape is coming due to this particular shape is coming because in solid condition in solid condition del Hmix is greater than 0 and this is G 2 of solid and this is G 2 of liquid. Now we could see that there could be a common tangent which will connect this point this point and this point. So, I can mention the equilibrium condition mu A, and this would be then solid one this would be solid 2 solid one equal to mu A liquid equal to mu A solid 2. and similarly here I can write B solid one equal to mu B liquid equal to mu B solid 2.

See if I try to see the plot on T XB T versus x B. So, if this is my temperature T, where I could just drop down these points. And I could get these 3 points on this equilibrium points on this temperature. And where liquid and 2 different solids structure are same, but they have different composition, one is a rich another one is B rich. So, they are in equilibrium.

Now, if I try to see a temperature which is greater than let us say this temperature is TE.

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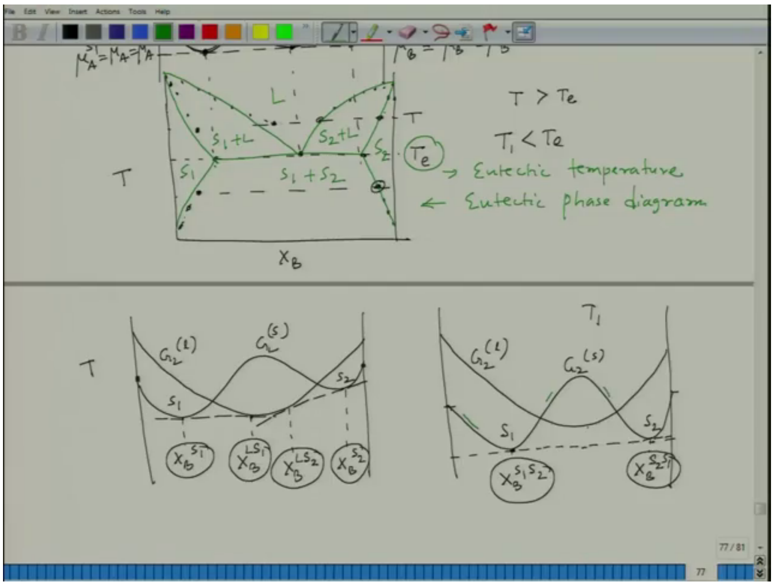

Then situation could be like this. So, here I have a common tangent and there is one more common tangent. So, this is solid one this is solid 2 this is G 2 solid and this is G 2 liquid. So, this is XB solid one this is XB liquid with in equilibrium with solid one and this composition would be XB liquid in equilibrium with solid 2 and this is XB solid 2.

Now, this at this temperature, if I try to see this temperature which is greater than T then I can have those points. So, let us say this is my point, these are those points, and those are those equilibrium points. This is this composition, and this point is this composition this corresponds to this composition. And this corresponds to these compositions and if we have a situation like this this is at T, if the situation is like this is G 2 liquid, this is G 2 solid. So, the only I could get a common tangent like this with is this one would be solid one this one would be solid 2 with a composition XB solid one.

Now this is in equilibrium with solid 2 and here it is XB solid 2 in equilibrium with solid one. and that time we can also see this we can plot these 2 points and if the temperature this is let us say T 1, T 1 is less than T e that time we are getting this situation where liquid line moves up that is where the liquid line is always above this particular common tangent, this common tangent between S1 and S 2. That is why the liquid cannot be formed liquid would become Meta stable the stable phases would be S1 and S 2. So, we are getting 2 different regions this is this point is correspond to this and this point corresponds to this composition.

So, now if I try to continue these points as with the temperature, I would get those locus is like this and on this side this locus should be like this. And here also I get these points and here also this points and so if we combine those I would get a phase diagram. So, this is my liquid this is solid one this is solid 2 this is S1 plus s 2, this is solid one plus liquid this is solid 2 plus liquid. So, these are the equilibrium phases and this diagram is nothing but eutectic phase diagram and where this is eutectic temperature and it indicates that because of this particular nature of this particular G 2 S which is because of del Hmix in the solid state is greater than 0, we are getting an eutectic phase diagram.

Let us stop here. We will continue our discussion in our next lecture.

Thank you.