Heat Treatment and Surface Hardening (Part-II)

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Lecture - 12
Expressions for equilibrium of two phases - I

Let us continue our discussion on Phase Diagram from Thermodynamic Principles. And this is lecture number lecture 12.

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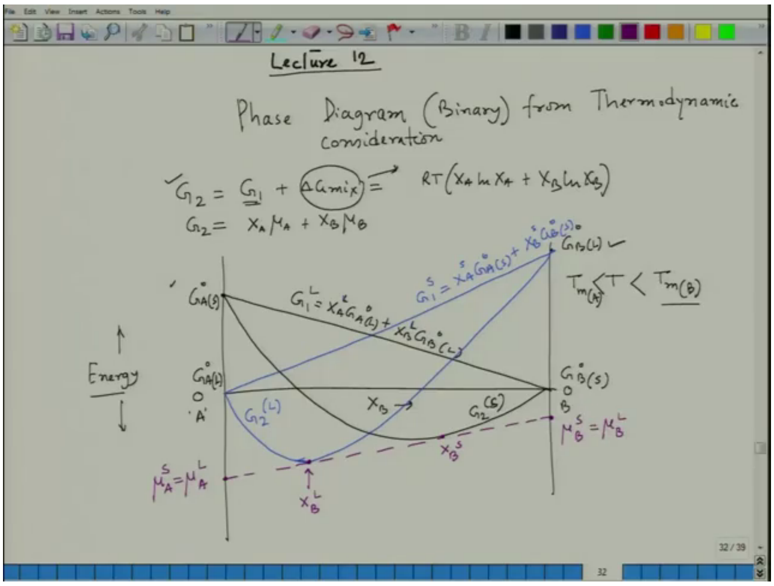

Lecture 12

Phase Diagram (Binary) from Thermodynamic consideration

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

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

In last few lectures we have seen that how free energy curve of solid solution or liquid solution varies with compositions at a particular temperature. And of course, if you change the temperature accordingly, the graph would change its position; we will see that particular part later on.

But few concepts we have learned from previous discussion. So would continue our discussion on phase diagram, and that to binary from thermodynamic consideration. What we have learned that for any binary ideal solution whether it is a solid or liquid, this is my final expression and that can be written in the form of chemical potential, which is X A mu A plus X B mu B G 2; whether it is a solid solution or liquid solution that would be decided by the superscript whether we are writing solid or liquid. And remember we are working from the point of ideal solution form.

Also we have drawn a diagram where we have seen that zero point is basically the energy axis I can say energy axis, and if this is pure A and this is pure B, then I can also place the standard free energy of pure liquid and pure solid whether it is A or B in this particular axis with composition X B. And what we have considered that T the temperature, where we are considering solution formation is greater than T m of A and less than of T m of B. And arbitrarily if we choose 0 to be our reference state, then this point would definitely be this is G A's of liquid because. And also I can decide what where should I have my G A 0 solid. Since temperature is greater than melting point of A, then standard free energy for pure a in liquid form must have lower free energy than that of the solid.

So, its meeting these criteria; so that means, G A S standard value is greater than G A of liquid and that standard value. But if I go to the other end, which is pure B and the temperature of our consideration is less than the melting point of pure B. So, this point should be G B of solid, because at that temperature solid B must have lower free energy than liquid B. So, if I put this is my G B of liquid 0, then immediately I could get the G 1 for liquid and as well as G 1 for solid before mixing. And that would be if I make different color for solid and liquid solution, if I put blue color for liquid solution so, this will be a straight line connection between these two points, because this is standard free energy of liquid A and this is the standard free energy of liquid B.

And similarly if I put black color for solid before mixing, then that line would be this one this is G 1 solid, and this is G 1 liquid, so this is before mixing. So, I can put it in this form this would be equal to X A G A 0 liquid plus X B G B 0 liquid, whereas this would be equal to X A G A 0 solid plus X B G B 0 solid, and remember we are looking at either solid or liquid.

So, this composition what we are considering X A and X B, they would also be in solid state in the case of solid, and this would be also in the case of liquid, it would be liquid. Now we can also get to the point of mixing free energy which is del G mix and this del G mix is nothing but, if we consider this term only which we can write in the form of RT X A l n X A plus X B l n X B, and if we can add this particular quantity to G 1 either for solid or liquid, I would get the parameter the free energy which is G 2.

So, in case of liquid if I try to do that this would might go like this, would be like this, and in case of solid if I try to see it would follow this track. So, this is G 2 for solid this is G 2 liquid, so we have this situation. Now once we have this situation from our previous understanding we know that the common tangent tells you, tells us that what that equilibrium condition. Now if I draw the common tangent, if we draw this common tangent, so it is meeting at this point as well as at this point meeting the solid G 2 line as well as liquid G 2 line.

So, these are two compositions which is let us say this is X B of liquid this is X B of solid, and also we have understood from our previous discussion that at this point, we know that chemical potential of A in solid is equal to chemical potential of A in liquid, similarly at this point we have chemical potential of B in solid equal to chemical potential of B in liquid, this is the equilibrium condition. Now if I try to continue now from our equilibrium concept, this is one; criteria this is another criteria, and also we get the equation for G 2 as for solid as well as liquid.

Now, if I try to understand the equation for this particular line, I can get this line equation from change in free energy from solid to liquid, in case of B or change in free energy for A from solid to liquid.

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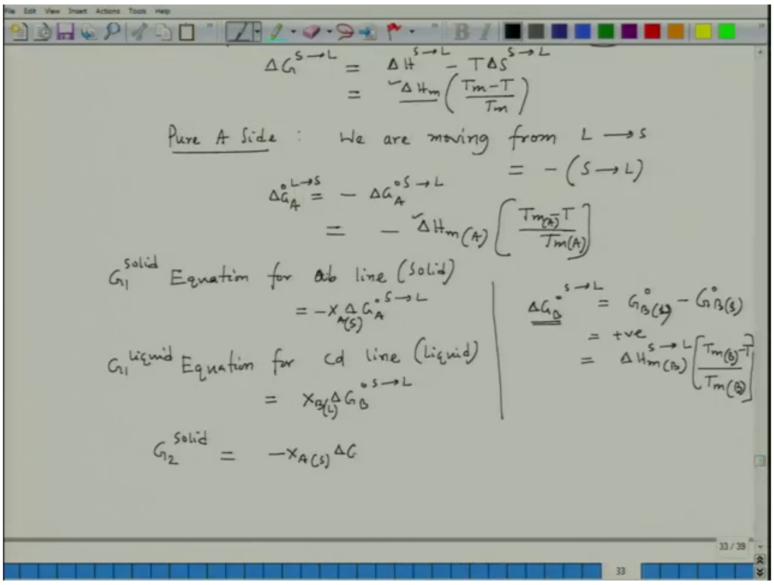

$$\Delta G^{S\to L} = \Delta H^{S\to L} - T\Delta S^{S\to L}$$
$$= \underline{\Delta H_m}\left(\frac{T_m - T}{T_m}\right)$$

Pure A Side : We are moving from L → S
$= -(S \to L)$

$$\Delta G_A^{\circ L\to S} = -\Delta G_A^{\circ S\to L}$$
$$= -\Delta H_{m(A)}\left[\frac{T_{m(A)} - T}{T_{m(A)}}\right]$$

G_1^{solid} Equation for ab line (Solid)
$$= -X_{A(S)}\Delta G_A^{\circ S\to L}$$

G_1^{liquid} Equation for cd line (Liquid)
$$= X_{B(L)}\Delta G_B^{\circ S\to L}$$

$$G_2^{\text{solid}} = -X_{A(S)}\Delta G$$

$$\underline{\underline{\Delta G_B^{\circ}}}^{S\to L} = G^\circ_{B(L)} - G^\circ_{B(S)}$$
$$= +ve$$
$$= \Delta H_{m(B)}^{S\to L}\left[\frac{T_{m(B)} - T}{T_{m(B)}}\right]$$

If we assume that every time we consider melting that means, in that case I can get some idea about this expression. Now, we know that delta G solid to liquid is nothing but delta

H solid to liquid minus T delta S solid to liquid, and this also can be written in the form of delta H m T m minus T by T m we have already understood this particular equation how would we get it from our phase one lectures you just refer to our phase one lecture.

Now, in case of A if we consider pure A if we consider that time the stable condition is liquid. So, if I try to and this enthalpy of melting, I can also have it for pure A or I can have it for pure B. Now if I try to see the difference between these two lengths, these two particular segments, here the stable condition is liquid so that means, liquid has to be taken to solid because we are considering the solid line. So, I have to go this way, but I have already said that every time will consider melting that means solid to liquid, but in case of pure A side we are moving from liquid to solid.

So, it will be just like negative of solid to liquid, since we are considering that solid to liquid is to be considered every time, whenever we consider some value. In this case the value we are considering is delta, which is the enthalpy of melting. So, in this case delta G 0 of A is nothing but minus of which is liquid to solid because, if I have to reach to solid line I have to go this way, if I have to go to solid line liquid to solid that, then only we can reach to this point. So, then this is nothing but minus of delta 0 A solid to liquid.

So, this also I can write in this form minus of delta H m A T m minus T by T m, and remember we are not putting any superscript like solid to liquid in this particular situation, because we are already assuming that every time it would be solid to liquid. So, if I put the superscript, so it should be solid to liquid, but all the time we will be considering the same thing. So, that is what I can just remove this it will not make our equation cluttered.

Now, if I have to get the equation for this particular straight line that means, the straight line let us say I put some point notation which is let us say this is a, this is b, this is c and this is d. So, the equation for a b line would be delta G A 0 solid to liquid X A minus. So, if I consider X B this direction, X A should be considered in this direction. So, this by this particular a c by c d I can consider, so I can put this equation as minus because these minus is coming since we are taking liquid forcefully to the solid condition, even we see that the liquid standard free energy for pure a is lower than the standard free energy for pure solid A, at the temperature where we are looking for the solution formation.

Similarly, I can also get the equation for c d line and that equation for c d line can be found out through the same principle. So, here already we know that the solid pure B in standard condition is the stable condition, because temperature where we are doing this particular treatment is below the melting point of B, and here in order to reach to this particular c d equation, I just need to take the free energy from solid to liquid. So, if this is solid to liquid and liquid free energy is higher than the solid free energy, so my delta G B is 0 solid to liquid, should be G B it liquid 0 minus G 0 B solid which is positive quantity is equal to delta H m B solid to liquid T m and here, I miss that particular notation this is for A T m B minus T divided by T m B.

So, that case these line equation this c d line equation could be can be written in the form of X B and delta G B. So, this equation would be X B delta G B 0 solid to liquid, and it would be positive because I could see that for melting my free energy change would be positive. Now remember this we are considering for liquid line, and this is for solid line, before mixing so, this is G 1 solid this is G 1 liquid, I can simply put this is as liquid this is a solid.

Now, if I try to get G 2 of solid it would simply be G 2 of solid means at any point let say at any point if I consider at this point if we consider, this would be this one this particular G 1 point, plus this del G mix for solid solution. So, this would be equal to just a minute, I am considering liquid this is for liquid and in case of solid. Let us say if I try to see for solid, so if I try to see the composition here so the solid line, I had get to this point. So, I just add del G mix first I think we made a mistake here, this should be solid, just we have reversed this particular thing. So, this would be liquid; and liquid just you have to make little change there.

So, in case of G 2 solid is nothing but, minus X A solid delta G A 0 solid to liquid, I am just making it proper because we just gave the notation wrong otherwise things are all right so, I am changing the notations because we are considering this is for solid, because it is only connecting the solid free energy lines. G 2 solid with this plus RT X A solid l n X A solid plus X B solid l n X B solid this is what; this is G 1, and this part is nothing but delta G mix for solid this is for solid that means we are absolutely right.

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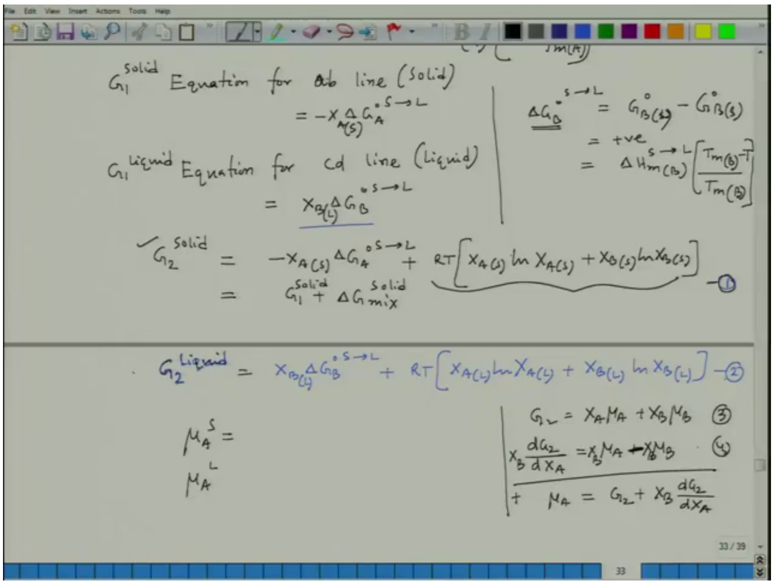

G_1^{solid} Equation for ab line (Solid)

$$= -X_{A(S)}\Delta G_A^{\circ S\to L}$$

G_1^{liquid} Equation for cd line (Liquid)

$$= \underline{X_{B(L)}\Delta G_B^{\circ S\to L}}$$

$$\Delta G_B^{\circ S\to L} = G^{\circ}_{B(L)} - G^{\circ}_{B(S)} = +ve = \Delta H_{m(B)}^{S\to L}\left[\frac{T_{m(B)}-T}{T_{m(B)}}\right]$$

$$\checkmark\ G_2^{Solid} = -X_{A(S)}\Delta G_A^{\circ S\to L} + \underbrace{RT\left[X_{A(S)}\ln X_{A(S)} + X_{B(S)}\ln X_{B(S)}\right]} \quad -①$$

$$= G_1^{Solid} + \Delta G_{mix}^{Solid}$$

$$G_2^{Liquid} = X_{B(L)}\Delta G_B^{\circ S\to L} + RT\left[X_{A(L)}\ln X_{A(L)} + X_{B(L)}\ln X_{B(L)}\right] \quad -②$$

$\mu_A^S =$

μ_A^L

$$G_2 = X_A\mu_A + X_B\mu_B \quad ③$$

$$X_B\frac{dG_2}{dX_A} = X_B\mu_A - X_B\mu_B \quad ④$$

$$+ \quad \mu_A = G_2 + X_B\frac{dG_2}{dX_A}$$

Now, for G 2 of liquid if we try to plot, then simply we have to for example this is my liquid line the blue line, and if I consider this particular composition. So, we have to simply add this G 1 at this composition for liquid, and the delta G mix for the liquid, at that particular composition. So, we already have decided what is my G 1 liquid, which is the equation for the line c d, so it will be simply X B delta G B 0 S to liquid plus R T X A liquid l n X A liquid plus X B solid l n X B solid, sorry this is liquid; this is liquid, so this is equation 1 this is equation 2.

Now, we can also get the equation for mu A solid as well as mu A liquid, now equation form mu A solid and mu A liquid how to find out we have previously checked, if G 2 is equal to X A mu A plus X B mu B, then equal to mu A minus mu B, then if I multiply with X B and then add this one and put it as equation 3 and this is equation 4 see if we add them, then we would get mu A equal to G 2 plus X B G 2 d X A same concept we will put it up in this current context.

So, if I try to find out mu A solid, we have to also get to the equation 1, and get the value for d G 2 d X A for solid, and if I try to get to mu A liquid we have to go to equation 2 equation 2 for liquid where we have to also follow the same concept here.

So, we will stop here, in the next lecture will continue on this particular topic, how to find out mu A S and mu A L and subsequently. We will also try to see what are this is the equilibrium concept on one end, and on the other end there is a equilibrium concept mu

A mu B solid is equal to mu B liquid we have to find out their values. So, these two things will just continue in our next lecture.

Thank you.