Heat Treatment and Surface Hardening - II
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Lecture - 11
Concept of common tangent for equilibrium between two phases

Let us continue our discussion on equilibrium for two phases. Now as we have seen in the last lecture; lecture 10 we have seen that how we can find out the chemical potential of a particular component in a particular phase with the help of slope of G 2 line. So, in this lecture- which is lecture number 11.

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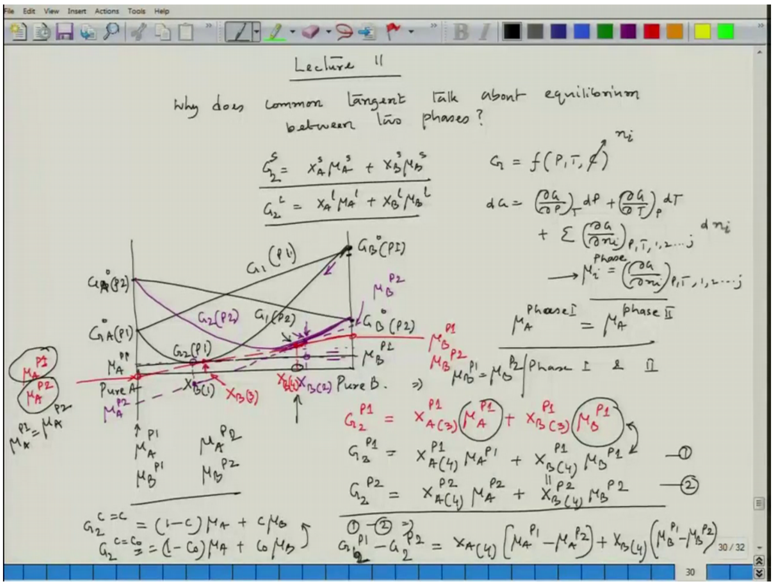

Lecture 11

Why does common tangent talk about equilibrium between two phases?

$$G_2^s = x_A^s\mu_A^s + x_B^s\mu_B^s$$

$$G_2^L = x_A^L\mu_A^L + x_B^L\mu_B^L$$

$$G = f(P, T, \overset{n_i}{\cancel{x}})$$

$$dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT + \sum \left(\frac{\partial G}{\partial n_i}\right)_{P,T,1,2\ldots j} dn_i$$

$$\rightarrow \mu_i^{\text{phase}} = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,1,2\ldots j}$$

$$\mu_A^{\text{phase I}} = \mu_A^{\text{phase II}}$$

$$\Rightarrow \mu_B^{P1} = \mu_B^{P2} \Big| \text{Phase I \& II}$$

$$\mu_A^{P1} = \mu_A^{P2}$$

μ_A^{P1} μ_B^{P1} μ_A^{P2} μ_B^{P2}

$$G_2^{P1} = x_{A(3)}^{P1}\mu_A^{P1} + x_{B(3)}^{P1}\mu_B^{P1}$$

$$G_2^{P1} = x_{A(4)}^{P1}\mu_A^{P1} + x_{B(4)}^{P1}\mu_B^{P1} \quad \text{—①}$$

$$G_2^{P2} = x_{A(4)}^{P2}\mu_A^{P2} + x_{B(4)}^{P2}\mu_B^{P2} \quad \text{—②}$$

$$G_2^{c=c} = (1-c)\mu_A + c\mu_B$$

$$G_2^{c=c_0} = (1-c_0)\mu_A + c_0\mu_B$$

$$① - ② \Rightarrow G_2^{P1} - G_2^{P2} = x_{A(4)}\left[\mu_A^{P1} - \mu_A^{P2}\right] + x_{B(4)}\left(\mu_B^{P1} - \mu_B^{P2}\right)$$

We would see that why common tangent talks about equilibrium between two phases or rather why does if I write talk about equilibrium between 2 phases.

Now, we have seen in the our last lecture that at any point on G 2 line, we can get an equation for G 2 which is G 2 equal to XA mu A plus XB mu B. Now in case of solid solution, it would be solid and in case of liquid solution it would be liquid. Now whenever we talk about equilibrium and that to when we have composition as a variable, now that time we can write G in the form of function of P T and composition. And this compositions can be written in the form of n i and that time we can write it as del G equal to plus summation of j. And this is basically nothing but mu i of number of components.

So, this is the i th component chemical potential of particular phase; this is phase or solution whatever you saying. Now if pressure and temperature are kept constant, then the entire equilibrium situation is decided by these particular term chemical potential. If we have pressure constant means it has already attained mechanical equilibrium, temperature constant means thermal equilibrium. But if we see that the chemical potential of a particular component in a phase 1 is same of that particular phase chemical potential in the second component then we will say that the system is in chemical equilibrium.

So, the concept of chemical equilibrium is mu A phase 1 equal to mu A phase 2 and that time we say that phase 1 as well as 2 both have component A. And similarly if we try to see the chemical potential of all the elements of phase 1 and 2 in these 2 different phases are saying we and say that the system is in equilibrium or the chemical equilibrium. This same concept can be valid here. Now let us try to see the concept what we have just now stated. And here we are trying to plot chemical potential GA 0 P 1 and this is GB 0 P 1 and now I can put it as this one as GB 0 phase 2 and this is as GB 0 phase 2; sorry, this should be A because this is pure A side, this is pure A and this is pure B.

Now, we can get the G 1 plot for both the phases this is G 1 of P 1 and this is G 1 of P 2 and correspondingly, we get the G 2 values of phase 1 the this is my G 2 phase 1 and if I try to plot it in a different color, this is my G 2 phase 2 G 2 phase 2. And we see that they are not lying on the same free energy line same free energy values. So, they have 2 different free energies.

Now, I can draw a tangent at different points on this particular line and accordingly can get the chemical potential mu A phase 1 mu B phase 1 mu A phase 2 and mu B phase 2. So, you can get all those values for example, if I try to see a tangent on this particular line. So, this is the composition this is let us say XB 1 and that time this becomes mu B phase 1, this becomes mu A phase 1. Similarly I can try to get if I try to plot the tangent at this point which is let us say XB 2 I can get the chemical potential values also this is A mu A phase 2, this is mu B phase 2 and from our previous discussion we can also change the concentration reversibly from one point to another.

So, actually if I am here, I can go to this particular point by adding B atom reversibly to this particular concentration XB 1 or on the other hand, I can also start with this particular concentration I can go to this particular concentration by taking out B reversibly from this composition from this composition or adding A to this composition to this composition so; that means, all the time I can have this reversible process in order to maintain the system is in dynamic equilibrium.

Now, as we take this particular tangent this particular tangent this particular tangent and if I try to shift it like if I try to rotate that tangent over this particular curve I will come across at certain situation where I will get a tangent which will become tangent to this point as well as on this graph this point. So, this is that point and this is the point and the composition let us say here the composition is with a red color, I can mention it as XB 3 and at this point, the composition is composition will be little on the left side sorry this is this composition would be little on the left side. So, this is that composition this is XB 4.

Now, let us look at these 2 points; one interesting fact is at this point I see that mu A phase 1 and mu A phase 2 phase 2; they are marching on a particular point at this point similarly at this point, I see that mu B phase 1 and mu B phase 2, they are at the same point. Now at this composition which is XB 3 I can have an equation for G 2 G 2 an for what phase P 1 phase P 1 phase 1 can write it as XA 3 phase 1 mu A phase 1 plus XB 3 since we are considering only this phase 1 phase 1 and mu B phase 1.

Now, if I try to change this particular concentration of phase 1 to this composition which is phase composition which is XB 4, I have to simply add B into this composition reversibly. So, as we have seen in your last lecture where we have considered this particular equation which is G 2 C equal to C is nothing but 1 minus C mu A plus C mu B and that was changed from. So, in order to go from this to this, I just had to add B reversibly to this composition C 0. So, if I try to change this composition of that phase 1 to this particular concentration XB I can simply write phase 1 equal to because I am not changing this term and this term because they are fixed.

So, I simply can write it as XA 4 of phase 1 because I am not changing the phase, I am just changing the concentration phase remains the same mu A phase 1 plus XB 4 P 1 mu B P 1. So, I have not change this particular term this particular term remains fixed because these 2 points on those 2 pure metal sides are fixed because I am going along that particular free energy line and I am doing it doing this change reversibly now at this point, I can write G 2 of phase 2 is equal to a XA 4 P 2 mu A P 2 plus XB 4 P 2 mu B this will be P 2, because now I am considering for phase 2.

So, if I; this is equation one this is equation 2, I would see that at this particular concentration at this particular concentration I do get 2 phases. That means, P 1 and P 2 where I could see that their chemical potentials are marching at a single point on the pure metal sites for example, if I consider pure A, I see that these 2 particular values are marching at the points. That means, mu A P 1 equal to mu A P 2 and here also its mu B P 1 equal to mu B P 2. So, if I 1 minus 2, if I do that then I do get this equation P 1 minus sorry; this is G 2 equation for solution G 2 P 2 equal to since the composition is same XA; I simply write XA 4 because the composition is same at this at this point compositions are same.

And also I have taken the phase 1 to this composition by adding B reversely into the P 1 of composition XB 3 I can write mu A P 1 minus mu A P 2 and similarly these 2 compositions are same, so XB 4 mu B P 1 minus mu B P 2.

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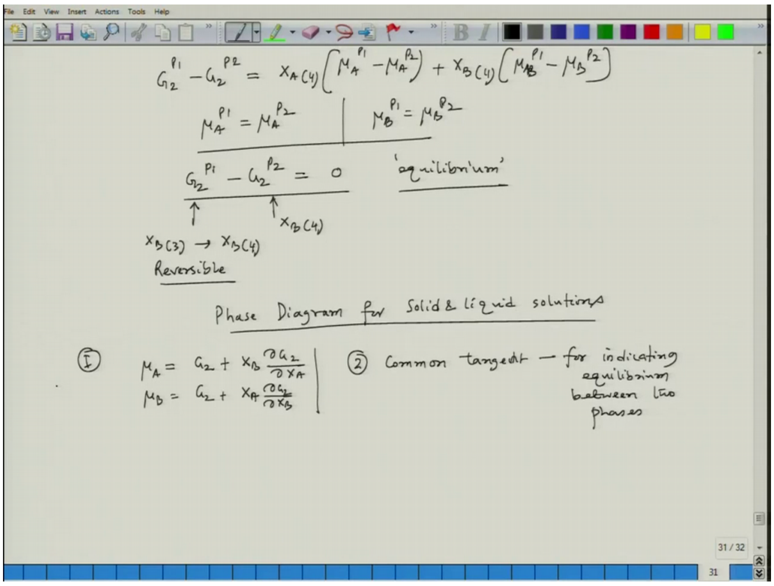

$$G_2^{P1} - G_2^{P2} = X_{A(4)}\left(\mu_A^{P1} - \mu_A^{P2}\right) + X_{B(4)}\left(\mu_{AB}^{P1} - \mu_B^{P2}\right)$$

$$\mu_A^{P1} = \mu_A^{P2} \quad \Big| \quad \mu_B^{P1} = \mu_B^{P2}$$

$$G_2^{P1} - G_2^{P2} = 0$$

'equilibrium'

$$\uparrow \qquad \uparrow X_{B(4)}$$

$$X_{B(3)} \rightarrow X_{B(4)}$$

Reversible

Phase Diagram for Solid & liquid solutions

Ⓘ $\mu_A = G_2 + X_B \frac{\partial G_2}{\partial X_A}$

$\mu_B = G_2 + X_A \frac{\partial G_2}{\partial X_B}$

② Common tangent — for indicating equilibrium between two phases

So, if I go to this value so; that means, G 2 P 1 minus G 2 P 2 equal to XA four; that means, composition mu A phase 1 minus mu A phase 2 plus x B 4 mu mu B P 1 minus mu B P 2, since we have seen that mu A of phase 1 equal to mu A phase 2 as well as mu B phase 1 equal to mu B phase 2; that means, G 2 P 1 minus G 2 P 2 equal to 0.

And remember this we have achieved by reversible transformation from composition XB 3 to XB 4 and this one, we are maintained at XB 4. So, this is reversible transformation; that means, that phase 1 and phase 2 both are at equilibrium because the free energy of these two phases at that particular composition which is XB 0 are same. So, this is equilibrium now we understand that why this common tangent indicates the equilibrium of two phases at 2 different concentrations.

So, these particular clue we will again use it for drawing phase diagram for solid liquid. So, now, we are using we will be using several concepts what we have learnt till now one concept is we can get the chemical potential of a particular component at a particular point on the G 2 line or G 2 curve of a phase by simply getting the slope at that point; that means, we can get mu equal to G 2 plus XB XA which is a and similarly mu B equal to G 2 plus XA XB. So, these 2 equations as well as we got the knowledge of common tangent for indicating equilibrium between two phases this is concept number 2 this is concept number one. So, these 2 concepts will be essential in order to get a phase diagram and phase diagram is always done as for our current understanding from the equilibrium criteria.

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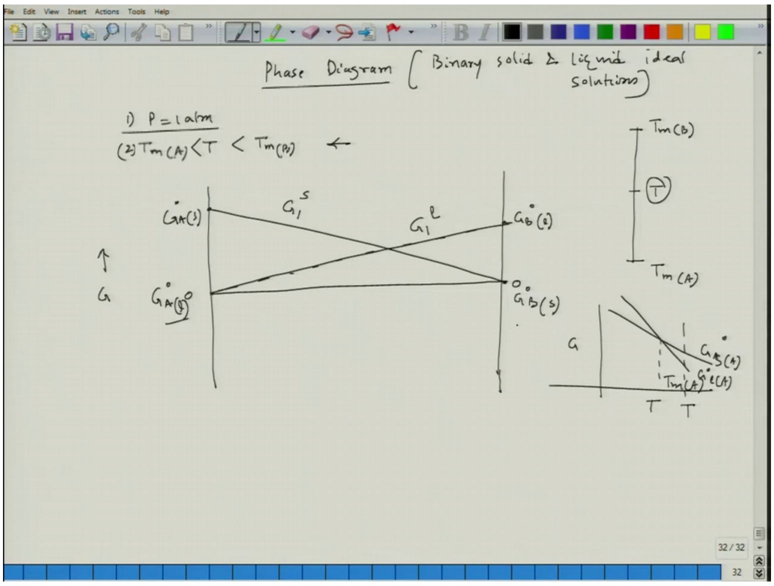

Phase Diagram (Binary solid & liquid ideal solutions)

1) P = 1 atm

(2) $T_m(A) < T < T_m(B)$ ←

Let us get into the phase diagram and that to binary solid as well as liquid ideal solution now when we try to get to the phase diagram we have to physically see; where are those critical points. For example, the standard state for solid as well as liquid whether the temperature what we are considering is higher than one particular pure component and lower than the other pure component and also their positions. So, let us first consider the pressure is one atmosphere.

So, we do not have to worry about it and second consideration let us say the T which we are considering the temperature at which we are trying to see the equilibrium between solid and liquid solutions that T is less than the melting point of pure b, but greater than tm with the melting point of a it means that if I try to see the melting point axis this is my tm a and this is my tm B if it is if that T is here. So that means, at this t; that means, that particular temperature a should remain in liquid condition because this temperature is higher than pure a melting point and B should remain in solid form because this pure B melting point is higher than the temperature of our consideration.

So, if we try to see the plot now at the same time i can choose the reference point and let us say, I choose the reference point as 0; that means, the free energy standard free energy value in the and also whether it is a standard or non standard it does not matter this is the free energy axis. Now if I take these 2 points as 0 and since as per this particular criteria pure a should remain in liquid condition; that means, pure a free energy in liquid state must be lower than the free energy of pure solid because if we try to see the melting point G versus temperature plot.

So, this is my tm a and this is GA, this is G of solid A and this is G of liquid A and the temperature what we are considering is lying somewhere here so; that means, standard free energy of pure a in liquid form should be lower than the standard free energy of pure solid at that particular temperature. So, if I take it as a reference. So, this is GA 0 liquid. So, then GA 0 solid would lie higher,, but on the other side, it is just reverse because this temperature is lower than the melting point of pure B.

So, at this temperature solid B would be the stable state so; that means, the solid B standard free energy should be lower than the standard free energy of pure liquid B. So, if I take it as arbitrarily if I choose it as B of solid. So, somewhere GB 0 liquid will be lying above and we can immediately get the G one lines of this is G one of solid and this is G 1 of liquid.

Let us stop here, we will continue this discussion in our next lecture, but at least you should understand that why we are considering zero point to be GA 0 of liquid and this is

GB 0 of solid, because we can arbitrarily choose the reference point according to our convenience. And that is what we always talk about standard state, because standard state is taken from the convenience part of convenient part of it and which is talking about the reference condition.

Thank you. So, let us stop here.