Heat Treatment and Surface Hardening - II
Prof. Kallol Mondal
Prof. Sandeep Sangal
Department of Material Science & Engineering
Indian Institute of Technology, Kanpur

Lecture - 10
G-X diagrams (Part- II) and concept of chemical potential (μ) from G-X diagrams

Hello everyone. Today we have lecture 10. And we will continue our discussion on free energy composition diagram for binary ideal solution. And we started with solid solution and we had seen in our discussion in the previous lecture that the final free energy of solid solution is nothing but G 1 S plus R T l n rather G 1 S del G mix. And where this superscript we are just adding to indicate whether it is a solid solution or a liquid solution.

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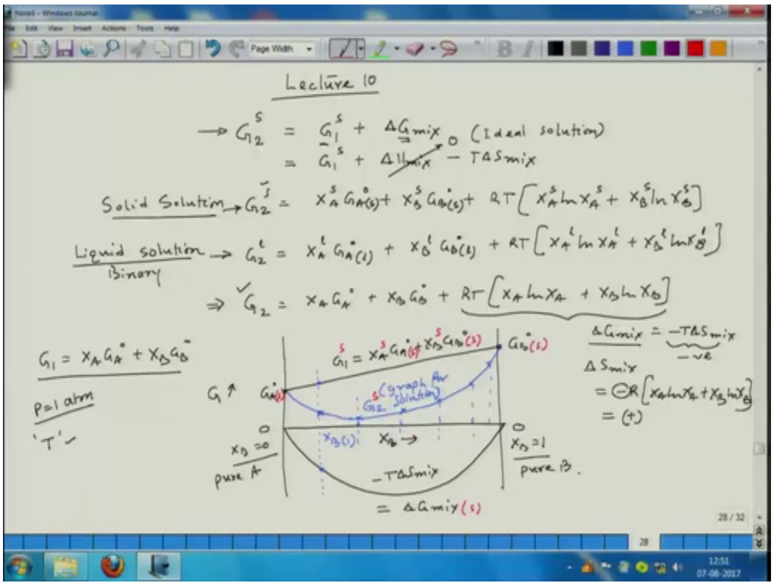

Lecture 10

$\rightarrow G_2^S = G_1^S + \Delta G_{mix}$ (Ideal solution)

$= G_1^S + \cancel{\Delta H_{mix}}^{0} - T\Delta S_{mix}$

Solid Solution $\rightarrow G_2^S = X_A^S G_{A(S)}^0 + X_B^S G_{B(S)}^0 + RT[X_A^S \ln X_A^S + X_B^S \ln X_B^S]$

Liquid solution Binary $\rightarrow G_2^l = X_A^l G_{A(l)}^0 + X_B^l G_{B(l)}^0 + RT[X_A^l \ln X_A^l + X_B^l \ln X_B^l]$

$\Rightarrow G_2 = X_A G_A^0 + X_B G_B^0 + \underbrace{RT[X_A \ln X_A + X_B \ln X_B]}$

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

P = 1 atm

'T' ✓

$\underline{\Delta G_{mix}} = \underbrace{-T\Delta S_{mix}}_{-ve}$

$\Delta S_{mix} = \ominus R[X_A \ln X_A + X_B \ln X_B] = (+)$

And remember we are looking into the binary system. Now, if it is ideal solution then it can be written as G 1 S plus del H mix minus T del S mix where this term goes to 0 since its ideal, and we have also seen that the final expression is X A G A 0 plus X B G B 0 plus R T X A l n X A plus X B l n X B. And since we are indicating there it is a solid solution, then we can also indicate this things as solid solution this is for solid this is also for solid. So, every time we are looking at a particular state of the matters, whether it is a pure A or pure B and even after forming solution they will also have their concentration in solid form. So, this superscript in case of solid its S in case of liquid you will see that it is L.

So, if I try to write the same expression for liquid, I simply change the superscript it will become l and this all those things will have superscript and subscript accordingly. So, this is 0 l plus X B l G l plus R T X A L l n X l plus X B L l n X B L. So, this is for liquid solution, and since we are considering binary, so it is basically binary system and here is also solid solution, and we can have a generalized equation whether it is a solid solution or liquid solution it does not matter the generalized equation would become fine.

Now if I try to from graphic point of view the symmetrically if I try to see how these parameters are changing. So, it would give us a physical significance of this G 2, let us look into that, now I can have a plot like this, where let us say this is my 0 point; that means, this is G axis and this is composition axis if I consider X B is varying in this direction, so here X B equal to 0 and here X B equal to 1; that means, here it is a pure B and here it is pure A ; that means, X A equal to 1 and this is pure B.

Now, if we see this term this is nothing but del G mix at the same time, so this is del G mix which is equal to minus T del S mix del S is del S mix is basically the entropy change due to solution formation or due to mixing of X A amount of a and X B amount of B, and if I try to see the expression of del S mix only which is nothing but, minus R X A l n X A plus X B l n X B since X A and X B both are fractions. So, logarithm of l n of X A and l n of X B both will be negative, and there is a negative sign outside. So finally it would become positive. That means, whenever there is a solution formation due to mixing the entropy of the system goes up. So, it is a positive quantity, but if we try to see del G mix since there is a negative term, then these term would become negative.

So, if I try to see the plan also you see that this is symmetrically varying weight X B, so the plot of so, this is my T del S mix which will be negative this is nothing but del G mix, now on the other hand. So, G 1 that the generalized equation could be written as X A G A 0 plus X B G B 0. And this 0 superscript we have already explained that this talks about the standard state, since the pressure is kept at 1 atmosphere at the temperature of our consideration so; that means, this is at temperature T and the pressure is 1 atmosphere, that is what we call it as a standard state.

Now we can see that if at that T temperature, this can be the pure A has got a free energy G A 0, which is a more of energy as we have discussed in our last class this is G B 0. Now if I try to plot this 1 then it will be nothing but, a straight line connection between this point and this point, and this we can write it as G 1 equal to X A G A 0 plus X B G B 0, and now if I try to see this particular equation which is the free energy of the solution at a particular concentration of B or a this is nothing but, the addition of G 1 addition of G 1 and plus addition plus del G mix.

So, if I try to consider a concentration this, which is let us say X B 1. So, that time G 1 is this and G 2 will be decided by the addition factor of this term and this term, because at X B 1 concentration, my del G mixes staying at this position so, I can just add this since this is negative we have considered this as a 0 axis 0 point, so this term is coming like here. So, similarly I can consider different concentration and I can get the value of G 2 at that concentration and accordingly I can get those G 2 points, so I can get this like this.

So, if I connect them I would get a plot like this, so this point is G 2 points, and since we are connecting all those G 2 points at all the concentration from pure A to pure B. So, we are getting this is this graph is basically the graph for G 2, or graph for solution. Now whether it is a liquid solution or solid solution that will be decided by the superscript, now if I try to put the superscript value I try to say this is the solid solution, then we will start with solid, solid, solid and similarly for liquid those superscripts and subscripts will be changed to liquid.

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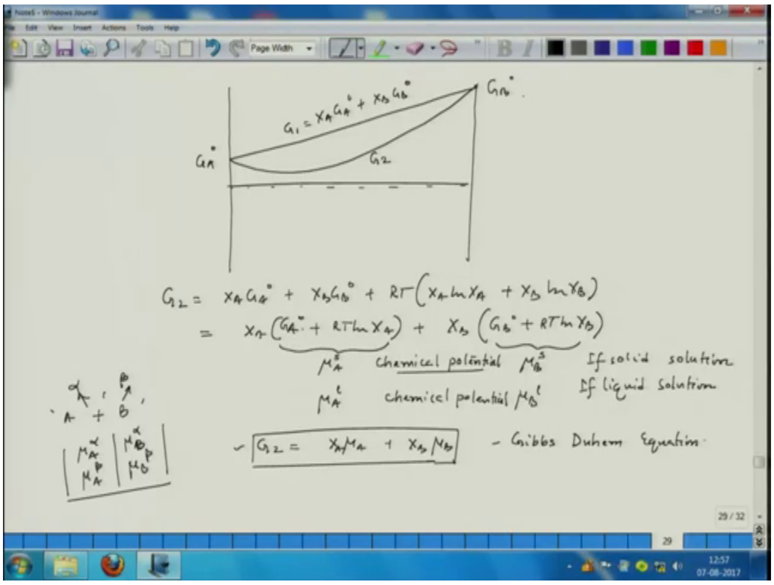

$$G_2 = X_A G_A^\circ + X_B G_B^\circ + RT(X_A \ln X_A + X_B \ln X_B)$$

$$= X_A \underbrace{(G_A^\circ + RT\ln X_A)}_{\mu_A^s} + X_B \underbrace{(G_B^\circ + RT\ln X_B)}_{\mu_B^s}$$

chemical potential μ_B^s If solid solution

μ_A^l chemical potential μ_B^l If liquid solution

$\boxed{G_2 = X_A \mu_A + X_B \mu_B}$ – Gibbs Duhem Equation

α, β, A + B

μ_A^α μ_B^α

μ_A^β μ_B^β

Now, we see that the common nature of this G to curb, this is my G A 0 G B 0 G 2 without giving any superscript of subscript, we can say that this is the generalized equation for ideal solution. So, I can write G 2 equal to X A G A 0 plus X B G B 0 plus R T X A l n X A plus X B l n X B, so I can write X B.

Now from our basic thermodynamic understanding for a dilute solution I can simply replace it with mu A and this one, I can replace with mu B, and this mu is nothing but, chemical potential chemical potential. Now whenever we try to see this chemical potential of a particular constituent in a solution, we have to also mention in what phase, now this is a generalized equation if it is solid that; that means, if we are forming solid solution, then this mu A, I can write simply as mu A of solid solution, and mu B of solid solution if it is solid; if solid solution, and if liquid solution, then it would become mu A liquid and this would become mu B liquid.

And this chemical potential always let us get it clear that chemical potential of a constituent in a solution, or that particular element in that solution all let us say if we consider alpha phase and beta phase both of A and B atom. So, they can form alpha phase or beta phase, if I would like to term their chemical potential in alpha and beta, then I can write it as mu A alpha it means the chemical potential of A in alpha phase, and in case of beta I can write mu A beta means chemical potential of A in beta phase.

So, accordingly I can also write mu A mu B alpha, and mu B beta, so this is the notation convention what will be taking the phase would be superscript and the element or the constituent of that particular solution would be subscript. So, it would be X A mu A plus X B mu B, this is a very important equation, this has a similarity this is also an equation which can be derived and this is 1 of those equations of Gibbs Duhem, so this is 1 of those Gibbs Duhem equation. So a little bit of brasher from elementary thermodynamics can help, so please visit some of those thermodynamic books, and try to see how this gives to n equations are derived.

Now, in our case this particular equation would be very important because finally, we would be looking at the equilibrium of 2 phases, since during phase transformation and finally during heat treatment, we are looking at the phase transformation mostly, and that is why we need to also see the equilibrium condition. Now let us use this factor and try to see how we attain equilibrium. Now if I try to look at this particular equation rather let us continue on this particular slide. I can delete this all those term I can continue with this let us say I need to measure the G to point.

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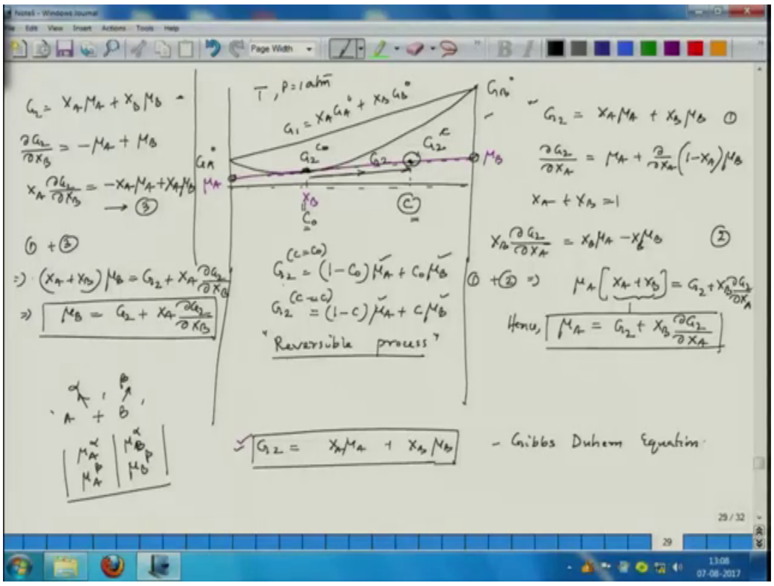

$G_2 = X_A\mu_A + X_B\mu_B$

$\frac{\partial G_2}{\partial X_B} = -\mu_A + \mu_B$

$X_A\frac{\partial G_2}{\partial X_B} = -X_A\mu_A + X_A\mu_B \rightarrow$ ③

① + ③

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

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

$\alpha, \beta,$

A + B

μ_A^{α} | μ_B^{α}

μ_A^{β} | μ_B^{β}

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

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

"Reversible process"

$\boxed{G_2 = X_A\mu_A + X_B\mu_B}$ - Gibbs Duhem Equation

$G_2 = X_A\mu_A + X_B\mu_B$ ①

$\frac{\partial G_2}{\partial X_A} = \mu_A + \frac{\partial}{\partial X_A}(1-X_A)\mu_B$

$X_A + X_B = 1$

$X_B\frac{\partial G_2}{\partial X_A} = X_B\mu_A - X_B\mu_B$ ②

① + ② $\Rightarrow$ $\mu_A[\underbrace{X_A + X_B}] = G_2 + X_B\frac{\partial G_2}{\partial X_A}$

Hence, $\boxed{\mu_A = G_2 + X_B\frac{\partial G_2}{\partial X_A}}$

Now, G 2 point if I draw a tangent on this particular point, if I do it with a different color this is that point, and this equation is nothing but this so; that means, this must be mu B this is mu A and at this point which is composition X B. Now if I try to see the value of mu A and mu B whether we can find it from the slope understanding of the slope as well as this particular G 2 value we can get some important equations, and those equations will be useful while we try to see the local equilibrium as well as the global equilibrium to find out the phase diagram.

Now, if we see this G 2 equal to X A mu A plus X B mu B and also remember that we are not putting any specific to any particular solution this will be valid for all the solutions, so, that is what we are looking at the generalized equation. Now I can get the slope X A equal to mu a plus, so then this is X and also we know that X A plus X B equal to 1 for binary solution. So, I can retain write it as X mu B. So, this is at a particular temperature T and pressure equal to 1 atmosphere. So, then it becomes mu B can multiply with X B.

Now this is equation 1, this is equation 2, if I add this to equation I get equation 1 plus 2 I get mu A X A plus X B equal to G 2 plus X A and this is nothing but, 1. So hence mu A equal to G 2 plus X B X A this is 1 major equation which will be useful while we try to see the equilibrium condition, and similarly I can also have an equation for mu B 2, so G 2 equal to X A mu A plus X B mu B similar way G 2 X B minus mu A plus mu B.

Now, I can multiply with X A plus, now I can this is equation let us say this is equation 1 and if we consider this is equation 3, so 1 plus 3, I would get these 2 term will get cancelled so finally, we are left with X A plus X B mu B equal to G 2 plus X A G 2 X B. So, this is mu B equal to G 2 plus X A G A 2 I dou X B, this is another important equation, so these 2 equations remember we need to use this in the next couple of lectures.

Another important part we need to complete in this section, so it can be this particular diagram can be referred, let us say I am here at this point. And now just take this composition as C 0 and on this line if I try to go to this particular composition C. So, what will be the situations, in that particular G 2 equation, and since X be equal to C 2 C 0 and here this is a new X B equation, now at this point what will be my equation G 2 equal to 1 minus C 0, since X A equal to 1 minus X B. So, hence it will be X A would be 1 minus C 0 mu A plus C 0 mu B.

Now, this is at concentration C equal to C 0, now I can also have equation for c equal to c these 2 n these 2 values are not changing that chemical potential of mu A and chemical potential of B in that particular solution. So, they are fixed these 2 points are fixed these point; and these, point both are fixed. So, the only change would be 1 minus C mu A plus

C mu B, so these 2 terms are not changing only this composition is changing. So that means we are arriving at another G 2 prime which is different than this particular G 2. That means, I can write it as G 2 c and I can write it as G 2 c 0 and this superscript c 0 means this is considered at concentration C 0, and this superscript C means this is considered at concentration C; that means, with reference to concentration of B.

Now, how can I reach from here to this place, so I need to go this way how can I move, and at the same time I maintain the equilibrium condition. That means, if these 2 conditions are to be in equilibrium at the same time the change is also taking place, only 1 way that can be possible that is the reversible process.

So, now, the amount of B is increasing, if I move from C 0 to C so; that means, the B has to be added to the concentration C 0 reversibly; that means, such an infinite decimal amount of B we would be adding to C 0 concentration, and that would take the free energy from G 2 C 0 to G 2 c and at the same time since c has got low concentration of A at the same time we are taking out infinite decimal amount of a gradually from concentration C.

So, it is a 2 way methods, 1 way is we are adding be in way infinite decimally to maintain reversibility, as well as taking out A reversibly so; that means, infinite decimal amount of a should be taken out infinite decimal amount of A B should be added up. So, I can change the free energy from here to there in a reversible fashion. So this is another important aspect which will be used for determining way why we go for common tangent in order to decide the equilibrium between 2 phases at 2 different concentrations.

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

Thank you.