

Heat Treatment and Surface Hardening (Part-II)

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Lecture - 13

Expressions for equilibrium of two phases - II

Let us continue the concept what we have been doing for the last few lectures. And in lecture 12, we have come to the particular point that how to get equation for liquid solution as well as solid solution. And that equation contains delta G value in pure condition for both A and B. And also it contains the entropy of mixing term along with temperature term. So that means, which is nothing but delta G mix. So we will have our lecture 13.

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Lecture 13

$$G_2^S = -X_{A(s)} \Delta G_A^0(s) + RT \left[X_{A(s)} \ln X_{A(s)} + X_{B(s)} \ln X_{B(s)} \right] \quad (5)$$

$$X_B^S \frac{dG_2^S}{dX_A^S} = -X_{B(s)} \Delta G_A^0(s) + RT \left[X_{A(s)} \ln X_{A(s)} - X_{B(s)} \ln X_{B(s)} + 1 - 1 \right] \quad (6)$$

Equation (5) and (6) (Addition) $\left[\frac{d}{dX_{A(s)}} (X_{A(s)} \ln X_{A(s)}) = -\ln X_{A(s)} - 1 \right]$

$$\mu_A^S = G_2^S + X_B^S \frac{dG_2^S}{dX_A^S} = -\Delta G_A^0(s) + RT \ln X_{A(s)} \quad (7)$$

$$\frac{dG_2^S}{dX_{A(s)} dX_{B(s)}} = X_{A(s)} \Delta G_A^0(s) + RT \left[\frac{-X_{A(s)} \ln X_{A(s)} + X_{A(s)} \ln X_{B(s)}}{-1 + X} \right] \quad (8)$$

$$\left. \begin{array}{l} G_2 = X_A \mu_A + X_B \mu_B \quad (9) \\ X_A \frac{dG_2}{dX_B} = -X_A \mu_A + X_B \mu_B \quad (10) \end{array} \right\} \text{Equation (8) and (10) (Addition)}$$

$$\mu_B^S = G_2^S + X_{A(s)} \frac{dG_2^S}{dX_{B(s)}} \quad (11)$$

And in this lecture we will try to see the equilibrium condition along the common tangent for solid line and liquid line. In order to do that we will just go back to the picture what we have drawn, in our last lecture 12. This is the picture what we have drawn. And then finally after doing lot of calculations, lot of equation development we have reached to this particular situation. And also you have seen that in order to find mu A for a solution I can make use of this equation, of course we can also develop equation

how to find the chemical potential of B, and let us start that part. I know G_2^{solid} is equal to μ_A^{solid} plus.

Now G_2^{solid} is equal to μ_A^{solid} plus $RT \ln X_A^{\text{solid}}$ minus $\ln X_B^{\text{solid}}$ and then, from this part it would come 1 and from this part it would come minus 1 both would get cancelled. So, if I multiply with X_B^{solid} then it would be minus. So, this is equation let us say 5, and this is 6. If I continue from the equation number what we have done in the previous lecture. So, there we ended equation number 4, but now we have to start with equation number 5 and 6. So, if we add equation 5 and 6, then we get G_2^{solid} plus $X_B^{\text{solid}} G_2^{\text{solid}}$; you see that these 2 if we add this 1 and this 1 so it becomes 1, this is μ_A^{solid} . Here also, if we add this quantity and this quantity they would cancel, and if we add this and this quantity they will become 1. So finally, we would get $RT \ln X_A^{\text{solid}}$, so this is equation 7.

And this is nothing but μ_A^{solid} . Similarly, I would get μ_B^{solid} ; that means, chemical potential of B in solid solution the similar line so I can try to get another equation for μ_B . And just to follow up what we have done in lecture number 11, if G_2 is equal to $X_A \mu_A$ plus $X_B \mu_B$ then X_B be equal to μ_A plus μ_B , and then if I multiply with X_A , and then add this is let us say 8 equation this is 9, if we add them we would get μ_B equal to G_2 plus $X_A G_2$ divided by X_B . Since this one and this one if we add they, will be 1.

Soon then, dG_2^{solid} equal to μ_A^{solid} plus $RT \ln X_A^{\text{solid}}$ plus $\ln X_B^{\text{solid}}$ this would be minus 1, and here it would be plus 1. So, it would get cancelled because derivative of $\ln X_A^{\text{solid}}$ term in to minus 1 if we multiply this term again because X_A plus X_B equal to 1.

So now, $d \ln X_B^{\text{solid}}$ of X_A^{solid} could be equal to $\ln X_A^{\text{solid}}$ minus one. Then if we multiply this 1 with X_A^{solid} , so this is X_A^{solid} this equation is let us say 10, see if we add equation this is addition, equation 5 and 10 addition we would get μ_B as equal to G_2^{solid} plus $X_A^{\text{solid}} G_2^{\text{solid}}$ is equal to $RT \ln X_B^{\text{solid}}$.

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Solid and liquid
 (1) Component B in solid & liquid

$$\mu_A^S = \mu_A^L$$

$$\mu_B^S = \mu_B^L$$

$$G_2^L = X_{B(L)} \Delta G_{B(L)}^0 + RT \left[X_{A(L)} \ln X_{A(L)} + X_{B(L)} \ln X_{B(L)} \right] \quad (12)$$

$$\mu_A^L = G_2^L + X_{B(L)} \frac{dG_2^L}{dX_{A(L)}} \quad \mu_B^L = G_2^L + X_{A(L)} \frac{dG_2^L}{dX_{B(L)}}$$

$$X_{B(L)} \frac{dG_2^L}{dX_{A(L)}} = -X_{B(L)} \Delta G_{B(L)}^0 + RT \left[X_{A(L)} \ln X_{A(L)} - X_{B(L)} \ln X_{B(L)} + 1 - X \right] \quad (13)$$

Add Equation (12) & (13)

$$\mu_A^L = RT \ln X_{A(L)}$$

$$X_{A(L)} \frac{dG_2^L}{dX_{B(L)}} = X_{A(L)} \Delta G_{B(L)}^0 + RT \left[X_{A(L)} \ln X_{A(L)} + X_{B(L)} \ln X_{B(L)} - 1 + X \right] \quad (14)$$

Add Equation (12) and (14)

$$\mu_B^L = G_2^L + X_{A(L)}$$

So, this is equation number 11, for equilibrium for component A in solid and liquid is nothing but mu A solid equal to mu A liquid. So, what we have calculated is nothing but mu A in solid phase, and mu B in solid phase. Now you have to also calculate mu A in liquid phase, now for equilibrium same of component B in solid liquid it will be mu B solid equal to mu B liquid and we have calculated these 2 quantities, we have to calculate this as well as this, and for this we have to make use of G 2 of liquid solution

now we can write the G 2 of liquid solution is equal to X B liquid delta G B 0 I can simply write liquid plus R T X A liquid l n X A liquid plus X B liquid l n X B liquid and it would follow the same way of calculating mu A as well as mu B in the liquid phase in case of mu A which is nothing but G 2 L plus X B liquid d G 2 l T X A L whereas, for in case of mu B liquid it would be G 2 L plus X A L dg 2 l d X B L.

Now, d G 2 L L equal to since this is in terms of B, so it would be minus delta G 0 B L plus R T l n X al it minus l n X B L plus 1 minus 1 this is coming because of derivative of logarithmic term, and as well as there is a multiplication factor which is X by L on X B L

So, if I multiply this 1 with X B L the way we have done it here, then this is X B L X B L X B L; that means, in the liquid phase. So, this equation let us say I term it as 12 and this is 13, if I add equation 12 and 13, we would get mu A liquid equal to, so this would get cancelled this term and this term would get cancelled. So, we would get R T l n X A L.

Similarly if I try to find out $\mu_{B,L}$, so this is $G_{2,L} + dG_{X_{B,L}}$ equal to $\Delta G_{B,0,L} + RT \ln X_{A,L}$ plus $\ln X_{B,L}$ minus 1 plus 1, and then if I multiply with $X_{A,L}$ this is $X_{A,L}$ then this term, and then if we add, this is equation 14 add equation 12 should be 14. Then we would get $\mu_{B,L}$ equal to $\Delta G_{B,L}$ so, $0_L + RT \ln X_{P,L}$.

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The image shows a handwritten derivation on a whiteboard. At the top, it states $\mu_A = RT \ln X_{A(L)}$. Below this, it derives the chemical potential of A in the liquid phase: $\mu_{A(L)} = G_{A(L)} + RT \ln X_{A(L)}$. It then adds equation (12) and (13) to find $\mu_{B(L)} = G_{B(L)} + RT \ln X_{B(L)}$. The next part shows the equality of chemical potentials between solid and liquid phases: $\mu_A^S = \mu_A^L$, leading to $-\Delta G_{A(S)} + RT \ln X_{A(S)} = RT \ln X_{A(L)}$ (Equation 15). Similarly, $\mu_B^S = \mu_B^L$ leads to $RT \ln X_{B(S)} = \Delta G_{B(S)} + RT \ln X_{B(L)}$ (Equation 16). A phase diagram on the right shows the chemical potentials of A and B in solid and liquid states as a function of composition. The diagram shows two sets of curves: one for solid (S) and one for liquid (L). The solid curves are higher than the liquid curves. The intersection points represent equilibrium conditions. The diagram also shows the relationship $X_{A(L)} = 1 - X_{B(L)}$ and $X_{A(S)} = 1 - X_{B(S)}$.

Now, I can use these equilibrium conditions. So, now, my equilibrium conditions are $\mu_{A,solid}$ equal to $\mu_{A,liquid}$, I can get $\mu_{A,liquid}$ equation as this one. So, $\mu_{A,liquid}$ equation $RT \ln X_{A,L}$ is equal to I have already calculated $\mu_{A,solid}$ which is this 1. So, I can put that equation as minus which is minus ΔG_A plus $RT \ln X_{A,S}$ this is equation which is let us say equation 15. And similarly for another equilibrium μ_B is equal to $\mu_{B,L}$ that case it would be $\mu_{B,L}$ we have calculated it is nothing but $\mu_{B,S}$ if I consider $\mu_{B,S}$ is this 1. So, this is $RT \ln X_{B,S}$ equal to and $\mu_{B,L}$ is basically this one, which is $\Delta G_{B,L} + RT \ln X_{B,L}$ [laughter], just cross checking $\mu_{B,S}$ is this $\mu_{B,S}$ is this, and then $\mu_{A,L}$ is this and $\mu_{B,L}$ is this. So, I am getting equation 16.

So, now these 2 equations if we see carefully, we have 2 unknowns because if we know ΔG_m for pure A and ΔG_m for B, then we can easily calculate ΔG_0 of a solid and ΔG_0 of B for liquid. (Refer Time: 09:10)

Now, here if we see this term, $X_{A,S}$ and $X_{A,L}$ if I try to plot that miniature plot, so this is $\mu_{A,S}$ equal to $\mu_{A,L}$ this is $\mu_{B,S}$ equal to $\mu_{B,L}$. Now I am pointing

these 2 lines, these 2 points, at this point I can have μ_A solid μ_B solid this particular composition, and this critical and this is for I think this equation if I go back to that particular plot, this is for solid, this is for liquid.

So, these 2 compositions I can term in the form of X_A or X_B both the time they are liquid, this some touch some time it becomes a little confusing, and this is X_A solid X_B solid. Now I can term X_A liquid so, these compositions; and these compositions, I can term X_A liquid equal to 1 minus X_B liquid. And this 1 I can write X_A solid equal to 1 minus X_B solid, so actually we are having 2 unknown 2 equations.

So, now we can solve this particular, and to solve this we have to just express either liquid or solid composition with reference to a particular component either A or B let us do it from the point of liquid pure A ok, from the point of A.

So, now if I try to does a little bit of simplifications here, so $\ln X_A$ liquid by X_A solid I can write it minus ΔG^0_{AS} , then I can write X_A^L equal to X_A^S exponential minus ΔG^0_{AS} divided by RT , this is equation 17. Similarly from this equation I can write $\ln(1 - X_A^L)$ minus $\ln(1 - X_A^S)$ equal to minus ΔG^0_{BS} then.

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The image shows a digital whiteboard with handwritten mathematical derivations. The top part shows the derivation of equation 17 and equation 18. Equation 17 is $X_A^L = X_A^S \exp\left(-\frac{\Delta G^0_{AS}}{RT}\right)$. Equation 18 is $1 - X_A^L = (1 - X_A^S) \exp\left(-\frac{\Delta G^0_{BS}}{RT}\right)$. The bottom part shows the final expression for X_A^S as $X_A^S = \frac{1 - \exp\left(-\frac{\Delta G^0_{BS}}{RT}\right)}{\exp\left(-\frac{\Delta G^0_{AS}}{RT}\right) - \exp\left(-\frac{\Delta G^0_{BS}}{RT}\right)}$.

$$\Rightarrow X_A^L = X_A^S \exp\left(-\frac{\Delta G^0_{AS}}{RT}\right) \quad \text{--- (17)}$$

$$\ln(1 - X_A^L) - \ln(1 - X_A^S) = -\Delta G^0_{BS} \quad \text{--- (18)}$$

$$\Rightarrow \frac{1 - X_A^L}{1 - X_A^S} = \exp\left(-\frac{\Delta G^0_{BS}}{RT}\right)$$

$$\Rightarrow 1 - X_A^L = (1 - X_A^S) \exp\left(-\frac{\Delta G^0_{BS}}{RT}\right) \quad \text{--- (18)}$$

$$\Rightarrow \text{Solve equation (17) and (18)}$$

$$X_A^S = \frac{1 - \exp\left(-\frac{\Delta G^0_{BS}}{RT}\right)}{\exp\left(-\frac{\Delta G^0_{AS}}{RT}\right) - \exp\left(-\frac{\Delta G^0_{BS}}{RT}\right)}$$

I can write $1 - X_A^L$ equal to $\frac{\Delta G^0_{BL}}{RT} - \exp(1 - X_A^S)$ then it would become $1 - X_A^L$ equal to $1 - X_A^S \exp(-\frac{\Delta G^0_{BL}}{RT})$ so, we have equation 18.

Now interestingly you can see that equation 17 and 18 can be solved because we have 2 unknowns, this is $1 - X_A^L$ and this is another unknown. So, we can solve this solve equation 17 and 18 and the solution, if we see that solution becomes I can solve this, so now, I can get X_A^S I can get equal to $1 - \exp(-\frac{\Delta G^0_{BL}}{RT})$ divided by $1 - X_A^L$. Similarly X_A^L equal to $1 - X_A^S \exp(-\frac{\Delta G^0_{BL}}{RT})$. So, we have both these compositions we have found out what is my X_A composition and X_A comp X_A composition for solid and liquid state.

So, let us stop here. We will continue in our next lecture, that why these two solutions for compositions at two different points, where the phases are at equilibrium leads to a phase diagram and that to binary phase diagram.

Thank you.