Heat Treatment and Surface Hardening (Part-II)

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Lecture - 14
Expressions for equilibrium of two phases - III

Hello everyone. Today we will continue our discussion on phase diagram from thermodynamic principles. We are concentrating on binary phase diagram and that to for solid and liquid ideal solutions, and today's lecture is lecture 14.

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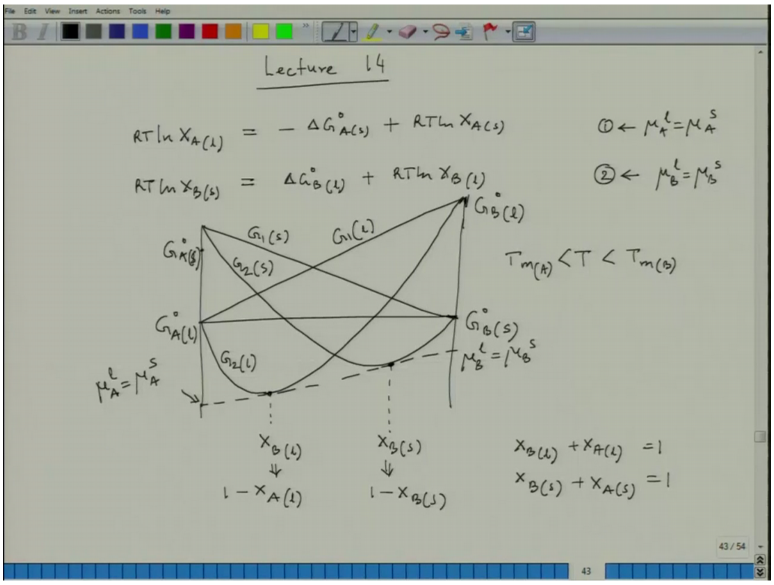

Lecture 14

$RT\ln X_{A(l)} = -\Delta G^{\circ}_{A(s)} + RT\ln X_{A(s)}$ ① $\leftarrow \mu_A^l = \mu_A^s$

$RT\ln X_{B(s)} = \Delta G^{\circ}_{B(l)} + RT\ln X_{B(l)}$ ② $\leftarrow \mu_B^l = \mu_B^s$

$T_{m(A)} < T < T_{m(B)}$

$X_{B(l)} + X_{A(l)} = 1$

$X_{B(s)} + X_{A(s)} = 1$

In our lecture 13, we derived 2 equations from the equilibrium concepts that is chemical potential of a particular element in a phase, when it is equal to the chemical potential of that particular element in other phase at a particular temperature and pressure we call it as chemical equilibrium. And that time we had 2 equations; the equations are written as equal to minus delta G 0 A solid plus RT ln X A s, this is one equation which was derived from the chemical potential of A in both the phases; that means, liquid and solid. And another equation was there is RT term RT ln X B solid equal to delta G 0 B liquid plus RT ln X B liquid.

And these 2 equations were G A 0 which is a pure condition for liquid and this is G A 0 for solid this is G B 0 solid and this is G B 0 liquid and our temperature was less than T

M B and T M A the temperature is less than melting point of pure B and greater than melting point of pure A. So, that case. So, we got these two conditions this is G 1 of solid this is G 1 of liquid and then we had this is for G 2 of liquid this is G 2 of solid.

Now, this 2 equations; this is equation 1, this is equation 2 were up 10, when we had a common tangent passing through these two points on liquid and solid lines and this is corresponding to X B of liquid this is corresponding to X B of solid which can also be written in the form of X A liquid 1 minus and this one can be written as 1 minus X B solid since X B liquid plus X A liquid equal to 1.

Similarly X B solid plus X A solid equal to 1 and at this point, at this point, mu A of liquid equal to mu A of solid and here mu B of liquid equal to mu B of solid. So, this expression was drawn from this concept of mu B of liquid equal to mu B of solid and this one was derived by using this particular concept equal to mu A solid. So, this is clear.

So, now we see that we have X B X A solid liquid as well as X B liquid and X A solid, but everything can be converted in the form of one particular component. So, we can convert this into one particular component for example, if we see this particular equation number 1.

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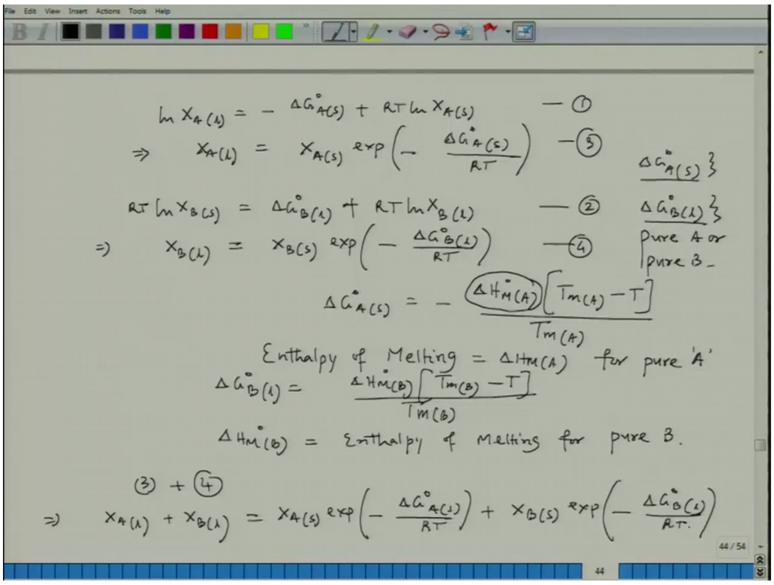

$$\ln X_{A(l)} = -\Delta G^{\circ}_{A(s)} + RT\ln X_{A(s)} \quad — ①$$

$$\Rightarrow X_{A(l)} = X_{A(s)} \exp\left(-\frac{\Delta G^{\circ}_{A(s)}}{RT}\right) \quad — ③$$

$$RT\ln X_{B(s)} = \Delta G^{\circ}_{B(l)} + RT\ln X_{B(l)} \quad — ②$$

$$\Rightarrow X_{B(l)} = X_{B(s)} \exp\left(-\frac{\Delta G^{\circ}_{B(l)}}{RT}\right) \quad — ④$$

$\underline{\Delta G^{\circ}_{A(s)}}\}$

$\underline{\Delta G^{\circ}_{B(l)}}\}$

pure A or
pure B.

$$\Delta G^{\circ}_{A(s)} = -\frac{\Delta H^{\circ}_{M(A)}\left[T_{m(A)} - T\right]}{T_{m(A)}}$$

Enthalpy of Melting $= \Delta H_{M(A)}$ for pure 'A'

$$\Delta G^{\circ}_{B(l)} = \frac{\Delta H^{\circ}_{M(B)}\left[T_{m(B)} - T\right]}{T_{m(B)}}$$

$\Delta H^{\circ}_{M(B)} =$ Enthalpy of Melting for pure B.

③ + ④

$$\Rightarrow X_{A(l)} + X_{B(l)} = X_{A(s)} \exp\left(-\frac{\Delta G^{\circ}_{A(s)}}{RT}\right) + X_{B(s)} \exp\left(-\frac{\Delta G^{\circ}_{B(l)}}{RT}\right)$$

Which is ln X A l equal to minus delta G 0 a solid plus RT ln X A solid which can be written in the form of this is equation 1; X A liquid equal to X A solid exponential minus delta 0, A is by RT this is equation 3 and then the another equation was ln RT ln X B s equal to delta G 0 B of liquid plus RT ln X B liquid. So, this is equation 2, I can write this one as X B liquid equal to X B solid exponential minus delta G 0 B liquid RT this is equation 4.

Now remember that this notation delta G 0 A s; this indicates that this s indicates that this we are considering with reference to solid solution and when you are considering delta G 0 B liquid this is with reference to the liquid solution, but in both the cases these two term are indicating pure A or pure B. So, this one is for pure a and the one is for pure B and remember in our previous lectures we have considered that everything should be with reference to the melting

Now, that is what this I can write delta G 0 A s equal to minus delta H M A TM melting point of metal pure metal A divided by melting point of pure metal A. So, this minus is coming because this term is basically the enthalpy of melting for pure A. Similarly delta G 0 B liquid equal to delta B TM B minus T divided by TM B and where delta H M B I can put A 0 sign here, because everything we are considering with reference to the standard because the pressure was kept one atmosphere. So, this would be equal to enthalpy of melting for pure B.

Now, if we add up equation 3 and four if we add them. So, we come to XA l plus X B l equal to XA s exponential minus delta z 0 a s by RT plus X B s exponential minus p liquid by RT. Now from our previous from our this particular expression which is XB, this equation as well as this equation if we see that this term leads to one Equal to X A s exponential minus delta z 0 s RT plus exponential minus delta z 0 B liquid RT minus X A s exponential minus delta z 0 B l by RT, because X A s plus X B s equal to 1 that indicates X B s equal to 1 minus X A s.

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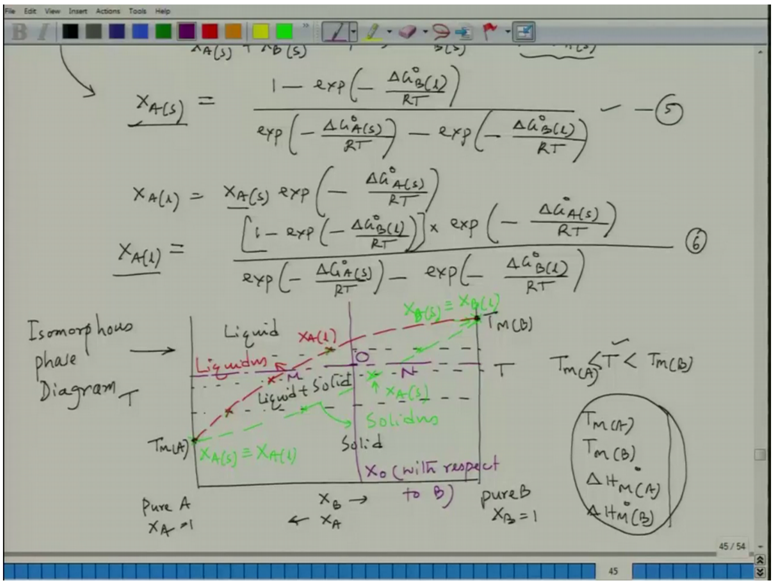

$$X_{A(s)} = \frac{1 - \exp\left(-\frac{\Delta G^{\circ}_{B(l)}}{RT}\right)}{\exp\left(-\frac{\Delta G^{\circ}_{A(s)}}{RT}\right) - \exp\left(-\frac{\Delta G^{\circ}_{B(l)}}{RT}\right)} \quad ⑤$$

$$X_{A(l)} = X_{A(s)} \exp\left(-\frac{\Delta G^{\circ}_{A(s)}}{RT}\right)$$

$$X_{A(l)} = \frac{\left[1 - \exp\left(-\frac{\Delta G^{\circ}_{B(l)}}{RT}\right)\right] \times \exp\left(-\frac{\Delta G^{\circ}_{A(s)}}{RT}\right)}{\exp\left(-\frac{\Delta G^{\circ}_{A(s)}}{RT}\right) - \exp\left(-\frac{\Delta G^{\circ}_{B(l)}}{RT}\right)} \quad ⑥$$

So, I am just replacing X B s with this term and that is what you are getting this equation and then from this from this I can get 2 X A s equal to 1 minus exponential minus delta z 0 B l by RT divided by exponential minus delta z 0 A s by RT minus exponential minus delta z 0 B l by RT.

So, this is solution for this is one solution I can put it as equation 5. Now if I know X A s, since we know this particular equation X A l equal to XA s exponential minus delta z 0 A s by RT if we see go back and see that particular expression this is the expression I can replace XA s with that this particular expression. So, then I replace it this XA I can replace. So, I can replace it as 1 minus exponential minus delta z 0 B l by RT into exponential minus RT divided by exponential minus d delta G 0 s by RT minus exponential RT. So, this is XA l.

Now, if we go back to this particular plot these 2 points, actually we have solved these 2 points, the composition of these 2 points composition of this point. That means, the point on liquid G 2 line and point on solid G 2 line these two compositions can be denoted either by X B l or X B s or it can be denoted as X al or XA; sorry, this should be X A XA s.

So, actually we have solved this particular composition and these particular compositions that indicates that actually we have solved we have found out two points in the composition in the temperature composition diagram which is actually a phase diagram .

So, now, if I get the expression for this as well as this; that means, the composition for solid solution and liquid solution; who are in equilibrium. So, then if I try to plot it on a temperature versus X B or X A plot this is pure b; that means, X B equal to 1 this is pure a; that means, X equal to 1 and our temperature is T which is less than T M B; that means, if consider this is as TM B melting point of pure B and more than melting point of a.

So, at this temperature if I consider pure a side then it will be all liquid because T less than T M B greater than TM A. So, at this temperature pure B would be in solid condition, but pure a would be in liquid condition. So, if we have pure a and pure B those points on the phase diagram would be this point as well as this point. So, now, I can put it in green color. So, this is for pure B melting point and this is for pure a melting point.

Now, in between we have resolved we have solved X A s and X A liquid; that means, the solid and liquid solution compositions who are an equilibrium. So, those two points I can plot these 2 points. Now gradually if I try to see another temperature line below this temperature as well as above this temperature and if we resolve this particular compositions of solid and liquid solution at that temperature following the exact the method what we have described till night till now we will see that those compositions will be lying here and here and in this case it would be here and it will be.

So, now these lines if I try to give a different notation these line are all X A liquid line and this line are all X A solid line . So, now, if we and at this point. So, X B solid is merging with X be liquid and here X A solid is merging with X A liquid.

Now, if we connect the composition X liquid compositions. So, I can connect those liquid compositions and I can also connect the solid compositions what I am seeing I am seeing a phase diagram where these portion would be entirely liquid and these portion will be entirely solid and here liquid plus solid. And these phase diagram has been calculated from only four basic data one is TM A another one is TM B, then delta H M A 0 delta H M B 0.

And this is possible because we are considering ideal solutions. So, these 4 basic data are used to find out the compositions which are in equilibrium for example, if I consider; let us say this particular we put it as a computer equation 6. So, this 5 and six if we see we are actually using this for composition through this for basic data and we are getting the entire phase diagram and these phase diagram we call it as isomorphous; isomorphous phase diagram.

Now, in this isomorphous phase diagram what we have also seen from our earlier discussion which was based on experimental cooling curve method. So, that time this line is called as liquidus and this line; we call it as solidus and at any compositions if we take any compositions any composition. And if we reach to this particular temperature we can also find out the fraction of liquid and solid solutions which will be in equilibrium as well as their compositions.

So now, for that reason we have to use make use of lever rule and if I consider this point it has M this point is at N and this composition is X 0 with respect to B.

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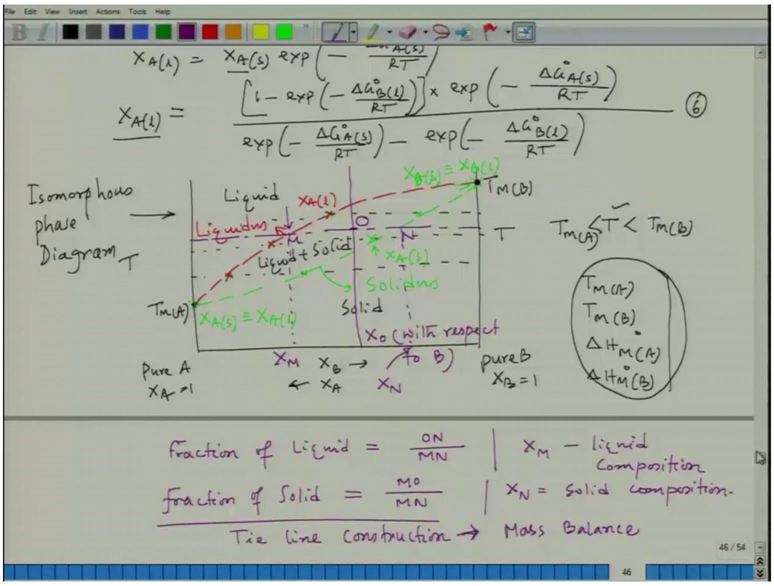

$$X_{A(l)} = X_{A(s)} \exp\left(-\frac{\Delta G_{A(s)}}{RT}\right)$$

$$X_{A(l)} = \frac{\left[1-\exp\left(-\frac{\Delta G^\circ_{B(l)}}{RT}\right)\right] \times \exp\left(-\frac{\Delta G^\circ_{A(s)}}{RT}\right)}{\exp\left(-\frac{\Delta G^\circ_{A(s)}}{RT}\right) - \exp\left(-\frac{\Delta G^\circ_{B(l)}}{RT}\right)} \quad ⑥$$

$T_{m(A)} < T < T_{m(B)}$

Fraction of Liquid $= \frac{ON}{MN}$ | X_M – liquid composition

Fraction of Solid $= \frac{MO}{MN}$ | X_N = Solid composition.

Tie line construction → Mass Balance

B then if I put it this point as O, then the fraction of liquid would be equal to ON divided by M N and that time the composition of liquid phase would be this one composition would be X M with reference to B that is liquid composition liquid composition. And similarly fraction of solid would be equal to MO by M N where X N equal to solid composition and remember these fractions are coming from tie line construction and that to the basis is mass balance.

So, now, from this entire discussion what we have seen that composition free energy diagram is actually leaving us to draw a phase diagram for the entire compositions range.

And we have done it for ideal solution for solid and liquid phases and in case of binary system.

So, now we can also see that these particular phase diagram has been drawn from the concept of chemical equilibrium that is the chemical potential of a particular component in a phase is equal to the chemical potential of that very component in other phase and that is the crux of getting to the solution of the compositions of pure compositions of liquid A la liquid solution and solid solution which are in equilibrium.

Let us stop it here. We will continue in our next lecture where we would be able to see that if I take any compositions between pure A and pure B and we can also predict that which phase would come out of what compositions if we know if we have an idea of free energy composition diagram.

Thank you.