Heat Treatment and Surface Hardening - II

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Lecture - 09
Formation of ideal solid or liquid solution and (G-X) diagrams for Ideal solutions (Part-I)

Welcome back. Let us get to the lecture number 9.

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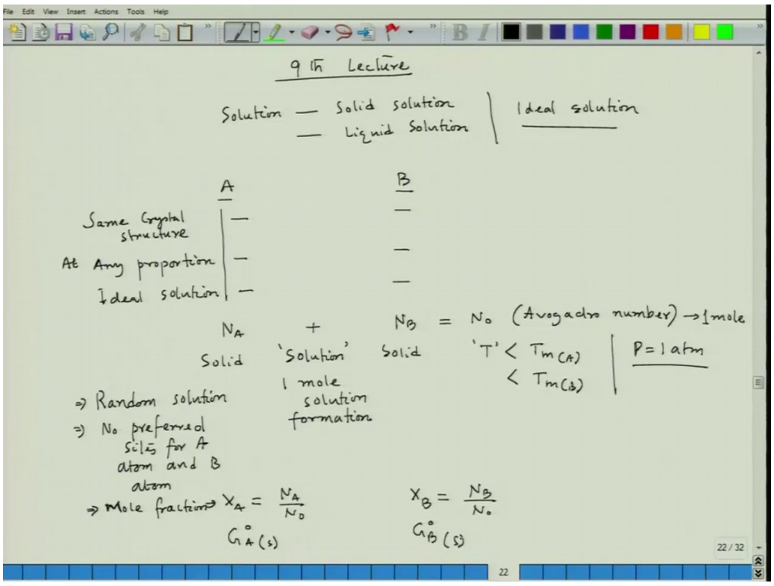

9th Lecture

Solution — Solid solution
— Liquid Solution | Ideal solution

A | B
Same Crystal structure | — | —
At Any proportion | — | —
Ideal solution | — | —

N_A + N_B = N_0 (Avogadro number) → 1 mole

Solid 'Solution' Solid

1 mole solution formation

'T' < $T_{m(A)}$
< $T_{m(B)}$ | P = 1 atm

⇒ Random solution

⇒ No preferred sites for A atom and B atom

⇒ Mole fraction $X_A = \frac{N_A}{N_0}$ $X_B = \frac{N_B}{N_0}$

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

Let us bring in solution formation, either solid solution or liquid solution. And we would concentrate on ideal solute solution formation, ideal solid solution or liquid solid solution.

Now, in the beginning we have considered two metal A and B, and we consider that both of them have same crystal structure, and we also assume that they can be mixed at any proportion. Means, we can vary the concentration from pure metal A to pure metal B. The entire range we can have solution, and we are also assuming that they would form ideal solid solution, whether its solid or liquid, it does not matter, but the entire concentration range will form ideal solution, which is a kind of crude assumption, which cannot be true, but since we are dealing with ideal solution, the simplicity aspect of it, we can assume that

Now, we say that these are the assumption for both. So, now, I say that in the beginning, I have N A number of A atoms and N B number of B atoms, and we are considering that both of them are solid. And both of them are solid means, the temperature at which we are considering the solution formation, must be less than T M of A and T M of B; that means, the melting point of A, and melting point of B at A pressure one atmosphere. We are fixing this pressure one atmosphere, whenever we mix them, it will form solid solution.

And here also, we are considering that they would form random solution, and also we would have a complete disorderedness in the system; that means, there will be no preferred sides for A atom and B atom in that solution. So, random solution and no preferred sites for A atom and B atom. And another thing we are considering is, when we add this N A number of A atoms and N B number of B atoms, they will be same as avogadro number. And whenever we consider avogadro number, it means this is one mole.

Now, if we consider that we are considering one mole solution formation, I can also calculate; what is the mole fraction of A and B in the solution? Simple I can consider X A and I consider X B, which is the mole fraction here. It is equal to N A by N 0. Here it is equal to N B by N 0. Since the total addition, total number of atoms would be N 0, this is mole fraction.

Now, once we have this picture, then we have to consider a free energy change. We have already seen that for any process, whether it is a solution formation or whether its a melting, we need to have a gradient and that gradient, the energy gradient should be negative, and that actually supplies the energy for the formation of solution, or the formation of different phases from another phase.

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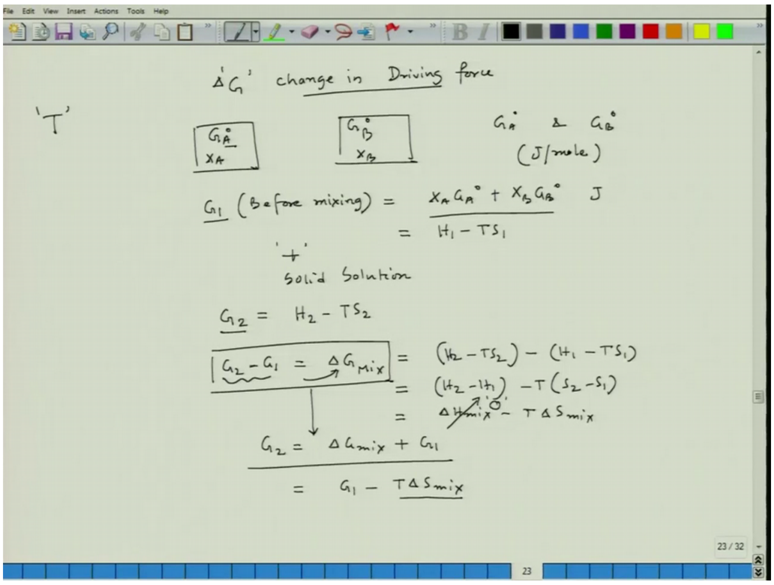

'ΔG' change in Driving force

'T'

G_A° x_A

G_B° x_B

G_A° & G_B° (J/mole)

G_1 (Before mixing) $= x_A G_A^\circ + x_B G_B^\circ$ J

$= H_1 - TS_1$

'+'

Solid Solution

$G_2 = H_2 - TS_2$

$$\boxed{G_2 - G_1 = \Delta G_{Mix}} = (H_2 - TS_2) - (H_1 - TS_1)$$

$$= (H_2 - H_1) - T(S_2 - S_1)$$

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

$$G_2 = \Delta G_{mix} + G_1$$

$$= G_1 - T\Delta S_{mix}$$

So, we have to see change in G, which is del G. Whenever we consider that, I can also take it back and I can also consider one more thing, that whenever I consider a pure metal, it is also having its inherent free energy, and I can take it as G A. And here I can take it as G B. And since the pressure is maintained at one atmosphere, I can consider it to be standard free energy in solid. So, I am not writing this particular term solid, but whenever we consider liquid solution that time we have to notify this, whether it is a solid standard free energy of pure metal or liquid standard free energy for pure metal. And we are here using standard, means we are specifying the pressure at one atmosphere pressure.

So, before mixing we have A with a free energy G A 0, and we have B with a free energy of Z B 0. This zero, superscript 0 means to the standard state, and here we have X A mole of A X B, mole of B, and if this G A 0 as well as G B 0 are termed as joule per mole, then before mixing I can count what is my total free energy, which is G 1. I can say before mixing is equal to X A G A 0 plus X B G B 0. And since the unit for both the standard free energy for pure A and pure B is joule per mole. So, these becomes my total free energy, and if we combine X A and X B, it would become one mole. So, that you can also say that, this is for one mole of total A and B

Now, after mixing; so now we are mixing them together, we are forming solid solution, it would once, it forms solution, it would go to a different free energy, and that time this would be. If this can be written as H 2 minus T S 2, and can we not also write it in the form H 1 T S 1. This is the H 1 is the enthalpy before mixing of the total A and B, but they are separately considered, and entropy of A and B separately, and the temperature as we have mentioned already, this is the temperature, where we are trying to mix them and mix up

Now, before mixing, this was my free energy which is G 1, and after mixing, this is the free energy of that particular solute solution is G 2, then what is the change in free energy for the formation of solid solution is G 2 minus G 1, which is equal to del G. And now since this particular difference is coming due to the solid solution formation, because of mixing I can simply mention it as del G mix, which will be equal to H 2 minus T S 2 minus H 1 minus T S 1. This can be simplified H 2 minus H 1 minus T S 2 minus S 1. And if this is written as del G mix, I can also write in this form del H mix minus T del S mix. Therefore, I have, I can also write G 2 as del G mix plus G 1.

So, now if I consider this part only, I can write this. And since we are dealing with ideal solution, what would be the value of del H mix. It would be 0. Therefore, I can write it as G 1 minus T del S mix. Now let us quantify, let us expand this del S mix. Let us see whether we can write in the form of mole fraction.

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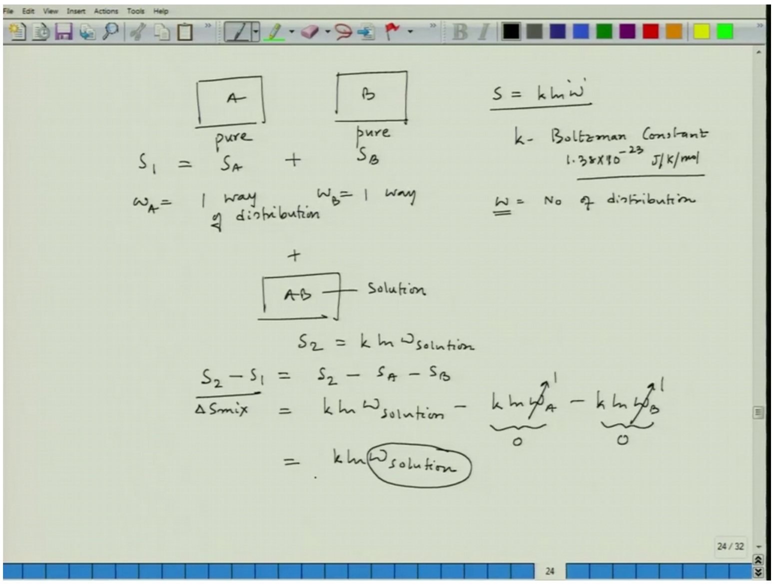

$S_1 = S_A + S_B$

$\omega_A =$ 1 way of distribution $\quad W_B =$ 1 way

+

$S_2 = k \ln \omega_{solution}$

$S_2 - S_1 = S_2 - S_A - S_B$

$\Delta S_{mix} = k \ln \omega_{solution} - \underbrace{k \ln \cancel{\omega_A}^{1}}_{0} - \underbrace{k \ln \cancel{\omega_B}^{1}}_{0}$

$= k \ln \boxed{\omega_{solution}}$

$S = k \ln W$

k - Boltzman Constant 1.38×10^{-23} J/K/mol

W = No of distribution

Now, whenever we are mixing A and B, these are pure A and B, and it has got a crystal structure, though they have same crystal structure. So, they would have their own entropy, and from Boltzmann consideration we can write entropy in this form K LN, omega K is the Boltzmann constant, which is 1.38 into 10 to the power minus 23 joule per Kelvin above.

Now, this omega is number of independent distributions, when we consider is A constant volume, and A constant internal energy. It is coming from statistical consideration of distribution. So, that time if it is a pure metal, and if there is no impurity. So, how many ways we can distribute the inital A atoms. There is only one way of distribution. Similarly here it is one way. So, omega is equal to 1 omega is equal to 1 in both the cases.

Now, if I try to mix them together, and get A B solution, it would attain an entropy which is 2. So, in the beginning the entropy was S 1 equal to S A plus A B and S 2; that means, if I consider S 2 minus S 1. So, it would also can be written in the form of L N omega solution. So, I can write it as S 2 minus S A minus S B. since this is L N K LN omega solution minus, this is 1, this is 1. So, this becomes 0, this becomes 0. So, it ends of, and this is what in the previous of. Just here we have seen that this is nothing but del S mix. So, this is del S mix. Now entire attention goes into this particular quantity omega solution.

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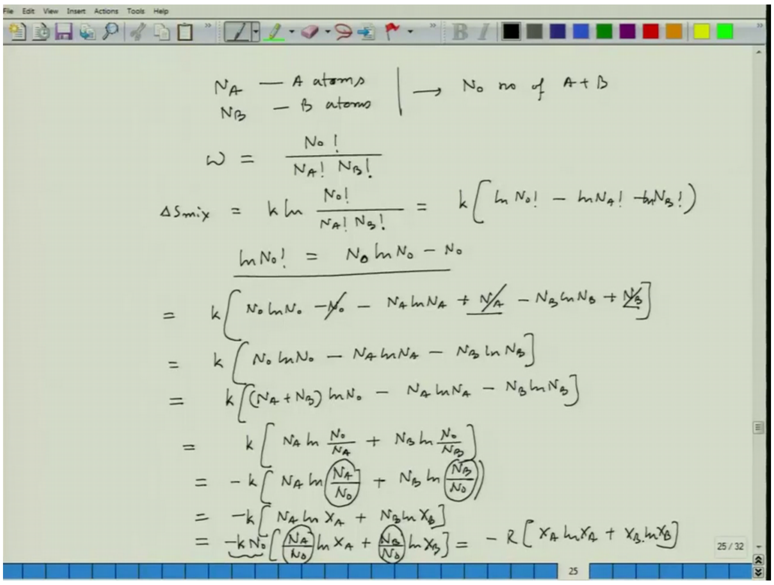

N_A — A atoms
N_B — B atoms $\longrightarrow$ N_0 no of A + B

$$\omega = \frac{N_0!}{N_A!\, N_B!}$$

$$\Delta S_{mix} = k \ln \frac{N_0!}{N_A!\, N_B!} = k\left[\ln N_0! - \ln N_A! - \ln N_B!\right)$$

$$\underline{\ln N_0! = N_0 \ln N_0 - N_0}$$

$$= k\left[N_0 \ln N_0 - \cancel{N_0} - N_A \ln N_A + \cancel{N_A} - N_B \ln N_B + \cancel{N_B}\right]$$

$$= k\left[N_0 \ln N_0 - N_A \ln N_A - N_B \ln N_B\right]$$

$$= k\left[(N_A + N_B) \ln N_0 - N_A \ln N_A - N_B \ln N_B\right]$$

$$= k\left[N_A \ln \frac{N_0}{N_A} + N_B \ln \frac{N_0}{N_B}\right]$$

$$= -k\left[N_A \ln \left(\frac{N_A}{N_0}\right) + N_B \ln \left(\frac{N_B}{N_0}\right)\right]$$

$$= -k\left[N_A \ln X_A + N_B \ln X_B\right]$$

$$= \underbrace{-kN_0}\left[\frac{N_A}{N_0} \ln X_A + \frac{N_B}{N_0} \ln X_B\right] = -R\left[X_A \ln X_A + X_B \ln X_B\right]$$

Now, we have N A number of A atom and N B number of B atoms in combination, they are forming N 0 number of A plus B. So, then I can write omega as N 0 factorial N A factorial N B. if I put it back, this can be written in this form. We can use stirling approximation, which is LN N 0 factorial. it can be written as N 0 LN N 0 minus N 0. like that we can also do it for LN N A factorial, and L N N B factorial, and this entire thing is coming from the mixing of two different species at a particular temperature, because we are fixing the temperature.

Now, we can write it as. Now we see that N A plus N B, they are consider, they are actually nothing but N 0. So, I can cancel out these three quantities, and then we are left with N B. now here K N 0. I can write in this form, I can write this. I can take the minus out, and then write, as we know that N A, this quantity is nothing but X A, and this quantity is nothing but X B, and then further I can take N 0, and form N A N 0, L N X A plus this is also X B, this is X B, this is X A. So, I can write, and what happens to this quantity. This is Boltzmann constant into avogadro number, which leads to universal gas constant, and then it becomes X A L N X A plus X B L N X B.

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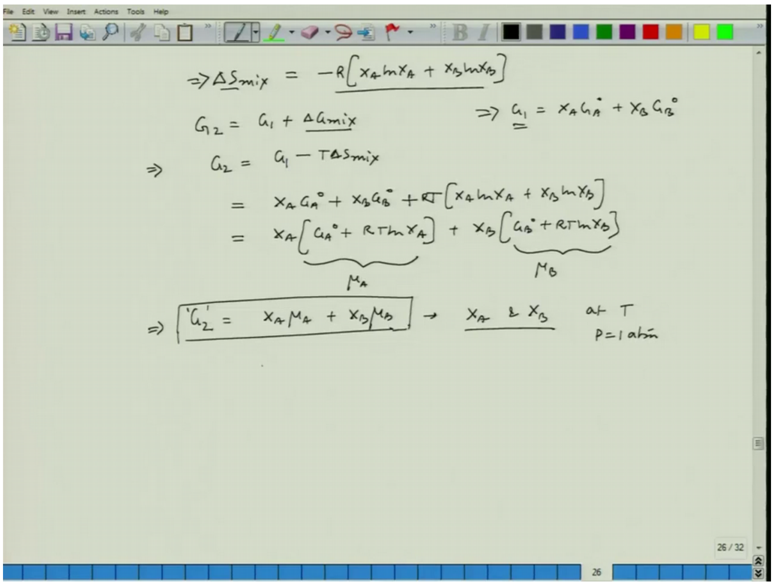

$$\Rightarrow \Delta S_{mix} = -R\left[\underline{x_A \ln x_A + x_B \ln x_B}\right]$$

$$G_2 = G_1 + \underline{\Delta G_{mix}} \qquad \Rightarrow \underline{\underline{G_1}} = x_A G_A^\circ + x_B G_B^\circ$$

$$\Rightarrow \quad G_2 = G_1 - T\Delta S_{mix}$$

$$= x_A G_A^\circ + x_B G_B^\circ + RT\left[x_A \ln x_A + x_B \ln x_B\right]$$

$$= x_A\underbrace{\left[G_A^\circ + RT\ln x_A\right]}_{\mu_A} + x_B\underbrace{\left[G_B^\circ + RT\ln x_B\right]}_{\mu_B}$$

$$\Rightarrow \boxed{G_2' = x_A\mu_A + x_B\mu_B} \rightarrow \underline{x_A \ \& \ x_B} \quad \text{at } T \quad P = 1 \text{ atm}$$

Finally, we can write del S mix equal to minus R X A ln X A plus X B L N X B. Now, I can go back to this original equation, this becomes G 2 equal to G 1. And since this is nothing but T del S mix. So, I replace G 1 and del S mix, and put this one for del S mix and. So, if I replace them X B. So, I just do little adjustment X A, this one is nothing but chemical potential of A in that solution, and this one is nothing but chemical potential of B in that solution; that means, in that solid solution of A and B

So, I can further write it as mu B. this is an important, very important equation, which tells what would be the free energy, if we mix X A and X B at a temperature T, when pressure equal to 1 atmosphere. So; that means, that is the point, that free energy point. We can also make out the physical aspect of aspect of G 2 physically. We have to understand; what is this G 2. We have to see the graphical representation of all this equations.

So, this equation we have to see the graphical expression. We have to see this, and we have to also see this. So, this is coming from S del S mix and this as well as this. From the graphical representation, we can also get to this, and that would give clear cut picture how physically this G, this G 2.

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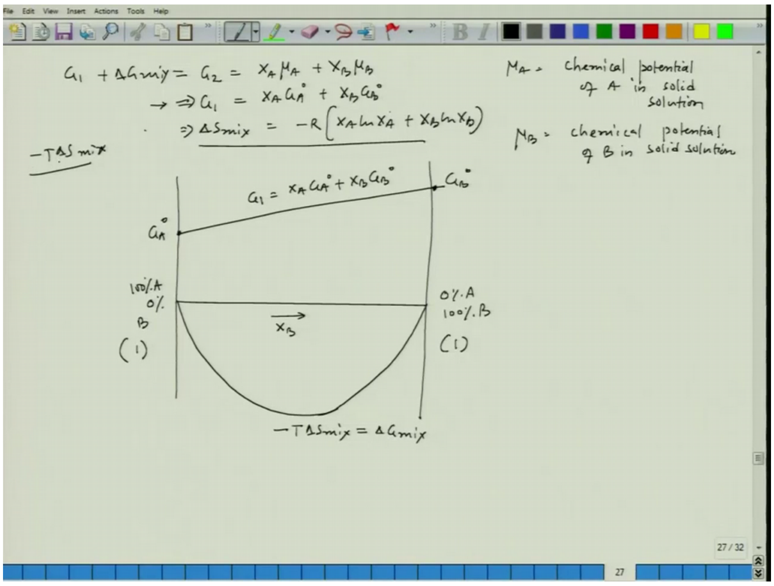

$G_1 + \Delta G_{mix} = G_2 = X_A \mu_A + X_B \mu_B$

$\rightarrow \Rightarrow G_1 = X_A G_A^\circ + X_B G_B^\circ$

$\Rightarrow \underline{\Delta S_{mix} = -R\left(X_A \ln X_A + X_B \ln X_B\right)}$

$\underline{-T\Delta S_{mix}}$

μ_A - chemical potential of A in solid solution

μ_B = chemical potential of B in solid solution

Now, if I try to see this, let me again rewrite those equation G 2 equal to X A mu A plus X B mu B G 1 equal to X A G A 0 plus X B G B 0, and del S mix equal to minus R X ln X A plus X B L N X B, and here mu A is basically the chemical potential of A in solid solution, and mu B is basically the chemical potential of B in solid solution.

Now, if I try to plot, let us see how the plot look like. Let us say this is 0 percent B 100 percent A, this is 0 percent A 100 percent B; that means, these two are pure end, if we try to see they are mole fraction, this is one, this is also one. Here the mole fraction of B is 1. Here the mole fraction of A is 1, and if I try to see the mole fraction of B varying in this way. So, gradually the mole fraction of B would increased from 0 to 1.

So, now here if I try to see G A is 0 position and G B is 0 position. So, then this two are two extreme points, when the mole fraction is 1 for A and mole fraction of B is 1, when its G be 0. Now if I try to see this equation, this equation is simply a straight line equation. Here this is G 1 equal to X A G A 0 plus X B G B 0.

Now, if I try to plot this one, then we will see that this plot would look like, and this is del S mix, and I can also write this G 2 as G 1 plus del G mix. Since its ideal solution, then I can also get the knowledge of Belgium X, which is nothing. This would become minus T del S mix, because del S mix, if I consider this particular thing these are fraction. So, it will be negative, and there is a negative term. So, it would become positive. So, del S mix is always positive, but if I multiply with the minus T del S mix.

So, it would become negative, and here since del S mix is 0, which is the enthalpy of mixing, because of the ideal solution, this becomes del G mix. So, now, we have drawn this equation as well as minus T del S mix we have plotted. We will take it up in our next lecture, and complete this entire picture, and then it will be clear the significance of G 2.

Let me stop here. We will take it up in the next lecture.

Thank you.