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Phase field modelling: the materials science, mathematics and computational aspects

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Module No. 1
Lecture No. 3
G vs X diagrams

Welcome so let us start as I said with the free energy of mixing expression.

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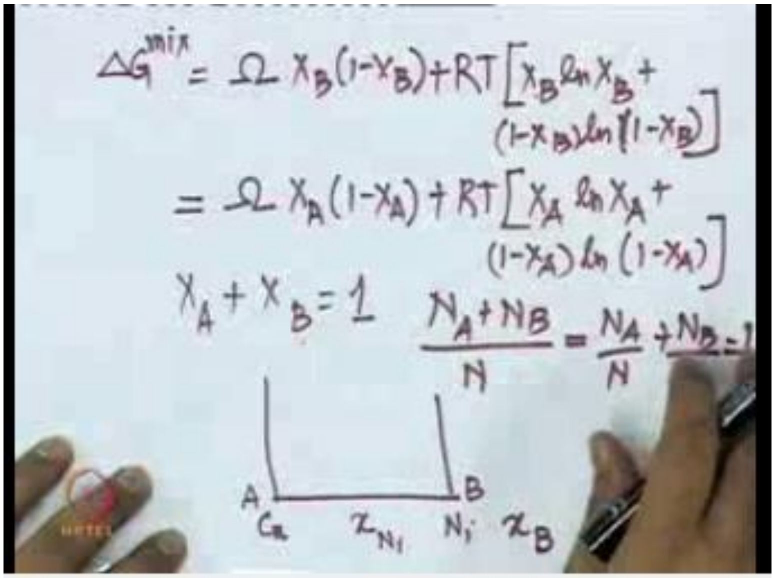

$$\Delta G^{mix} = \Omega X_B(1-X_B) + RT\left[X_B \ln X_B + (1-X_B)\ln(1-X_B)\right]$$

$$= \Omega X_A(1-X_A) + RT\left[X_A \ln X_A + (1-X_A)\ln(1-X_A)\right]$$

$X_A + X_B = 1$ $\quad \frac{N_A+N_B}{N} = \frac{N_A}{N} + N_B = 1$

That we discussed in the last section which was derived in the previous module so the free energy of mixing as you can see is written as $\Omega\ X_B(1 - X_B) + RT[X_B \ln X_B + (1 - X_B) \ln(1 - X_B)$ if you remember in the first module when I derived this expression I wrote this as $\Omega X_A(1 - X_A) +$ $RTX_A \log X_A + 1 - X_A \log(1 - X_A)$ as you can see these two expressions are the same this is because $X_A + X_B$ is equal to 1 that is because the total number of sites n is occupied by X_A and N_B atoms and $X_A + N_B$ adds up to 1.

So if you have $N_A + N_B$ which is equal to n divided by n that will be equal to 1 so N_A by N which we defined as $X_A + N_B$ by N which we defined as X_B is equal to 1 so thus we have this symmetry between X_A and X_B suppose if you want to write everything in terms of X_B you can write it is X_B $[1 - X_B] + RT[X_B \ln X_B + 1\ X_B \ln 1 - X_B]$ suppose if is tart replacing X_B is nothing but $1 - X_A$ $1 - X_B$ is nothing but $X_A +$ similarly X_B is $1 - X_A$ and $1 - X_B$ is X_A so you can write it so already you can see that this expression is a symmetric with respect to X_A X_B and typically the reason why I wrote it as X_B is as follows typical phase diagrams for example if you take copper nickel phase diagram.

so then you have pure copper here pure nickel here so the x axis of the phase diagram basically gives you the which is denoted typically x it is basically the composition of nickel okay, so and if you decide to call this kind of phase diagram by a generic A and B type of atoms then the composition axis is basically nothing but X_B so that is the reason why most of the times the expressions are written in terms of X_B but if they can equally well be written in terms of X_A in other words I mean copper nickel phase diagram you can start with the pure nickel and go to your copper or you can start in pure copper and you can go to be on nickel.

It does not make any difference okay so in the regular solution model on top of it the expressions themselves are also symmetric with respect to using X_A and X_B so they are interchangeable and you get the same expression so let us consider these terms or one by one. So let me take the free energy of mixing it consists of two parts the enthalpy of mixing and entropy of mixing if you look at these terms are individually.

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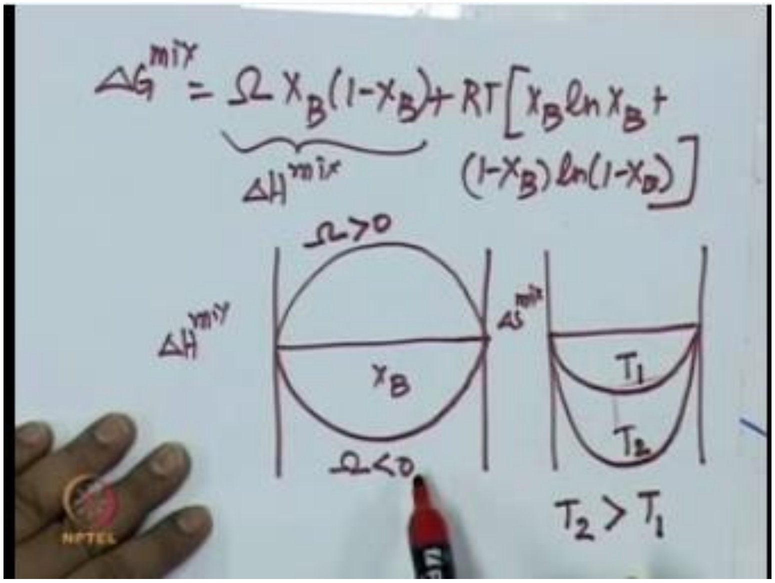

$$\Delta G^{mix} = \underbrace{\Omega X_B(1-X_B)}_{\Delta H^{mix}} + RT\left[X_B \ln X_B + (1-X_B)\ln(1-X_B)\right]$$

So let us take a look at it ΔG^{mix} is nothing but Ω X_B 1 - X_B + RT X_B log X_B + 1 - X_B log 1 - X_B by the way irrespective of whether I call it log or ln it is a logarithm to the base E and we typically do not use logarithm to the base 10 so I keep calling it sometimes as log sometimes as ln but it is the same okay so by default when I say logarithm I mean to the base E all right so let us take a look at this expression so this is nothing but Δ_H so if you try to plot this quantity then as a function of composition which is given by X_B .

So this is a parable and if $\Omega > 0$ so it is a parabola that looks like that if Ω is < 0 it is a parabola that looks like this in a similar fashion you can try to plot this quantity so this is ΔH^{mix} plot and I can also plot ΔS^{mix} remember like we discussed yesterday in the previous module X_B is < 1 so logarithm of X_B is going to be a negative quantity and the rest of the terms here or positive so this quantity is always negative which means depending on the temperature it will only tell you how deep this parabola is this is also looking like a parabola right.

This is also a curve which is symmetric about the central point and it looks like this so this is at some temperature T_1 this is at some temperature T_2 and you can see that T_2 is $< T_1$ so ΔH^{mix} always is going to give you negative quantities and only ΔH^{mix} can give you positive or negative depending on whether Ω is < 0 or Ω is > B now let us take a temperature T which is high so that you will see only the entropy of mixing term to be dominant okay so in terms of this plot how does it look like so it looks like this.

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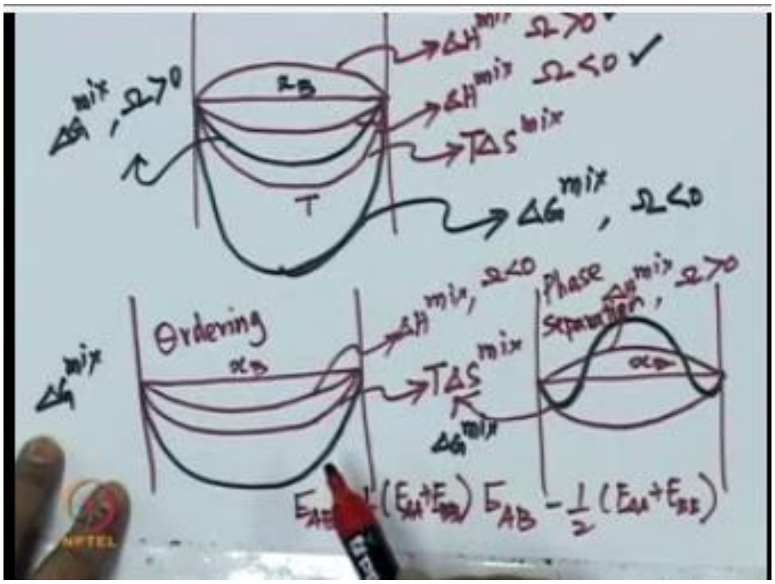

Okay so my ΔH^{mix} could be like this my ΔH^{mix} looks could be like this it does not matter my ΔS^{mix} like this okay so this is ΔS^{mix} makes this is ΔH^{mix} with $\Omega > 0$ this is ΔH^{mix} with Ω < zero now let us find out what happens if you add and you make the ΔG^{mix} because in this case both add up so you will get something that looks like that it should be symmetric so this is a ΔG^{mix} in the case Ω is > 0 and in the other case of course this much will be taken off so it will come something like this because this quantity is positive you are adding to this so it will go somewhere here so this is the case where you have ΔG^{mix} where Ω is < 0.

So in other words we are talking about a case this is $T\Delta S^{mix}$ by the way because T term is already late so we are talking about a temperature T which is large enough that the most important contribution is coming from the entropy of mixing okay so it does not matter whether your Ω is < 0 or Ω is > 0 because the temperature is very high that is the dominant term and you always get your free energy verses composition diagram something like this right this is B composition axis this is the X_B axis.

On the other hand let us consider a case where the temperature is not very high okay so I have a ΔS^{mix} and temperature such that it is something like this okay so this is at some $T\Delta S^{mix}$ okay now I am going to consider two cases one in which the ΔH^{mix} is also negative so this is ΔH^{mix} in the other case that I am going to consider remember this is the X_B axis so I have the X_B axis and I have $T\Delta S^{mix}$ again which is here at the same temperature but now my ΔH^{mix} is not negative but it is positive okay so this is my ΔH^{mix} because this $\Omega < 0$ whereas this $\Omega > 0$.

So as you can see in this case again we find that if you add ΔH^{mix} + RP ΔS^{mix} you are going to get something like this on the other hand when you have these two terms at the extreme ends where X_B is 0 or X_B is 1 the entropy term the term is still going to dominate because very small composition changes can give rise to huge changes in entropy you can imagine it like this suppose if you have one atom and you have about 10^{23} sites and this one atom can occupy about 10^{23} different sites so the total number of available configurations becomes.

So large that that becomes very dominant so at these extreme end either you have pure B in which you're putting very small A and or you have pure A in which you are putting very small B this is always dominant and so this will always dominate to add the lower compositions but somewhere in the middle because the ΔH^{mix} will start dominating it will become like this and again it will become like in other words in the case when $\Delta H^{mix} < 0$ we get to some interesting composition verses free energy curve.

Is remember the free energy that we are talking about is a free energy of mixing okay so we are only talking about free energy of mixing so in cases where the temperature is very high you always have this kind of shape in cases where temperature is not so high that ΔH^{mix} can still dominate then depending on the sign of ΔH^{mix} you might get a parabola or you might get a curve which has two minima and one maxima in a binary order.

So these kind of systems are known as phases separating systems and we will discuss his a little bit more detail later and this is phase separating system because remember $\Delta H^{mix} < 0$ meant this $\Omega < 0$ and Ω was nothing but E_{AB} -1/2 (E_{AA}+ E_{BB}) now this quantity is positive means that AB bonds are costlier as compared to on the average making A and B so if you have to AB bonds you will break them and you will make AA bonds and BB bonds out of it and in the process you will reduce the internal energy which will lead to intern reduction in free energy.

So it is always favorable in this case for the system to face separate that is become pure N_A and pure N_B separated on the other hand in this case when this Ω is negative that means EAB -1/2 (E_{AA}+ E_{BB}) is negative that means the E_{AB} bond energy is lesser than on the average AABB bond so if you have AABB bonds the system will break them and make one AB bond and this is the case that we discussed short very low temperature such systems I will go what is known as ordering.

So this is ordering remember that this is only at low temperature this is phase separation again only at low temperature at high temperature all the systems are dominated by entropy and so they will all become Randall solid search but at low temperatures the systems might become ordered or phase separated and they will become random solid solution only if Ω is 0 and may Ω is not zero there is always a temperature at which you will find that the system may that prefers to order or prefers to phase separate okay so we will discuss this case in a little bit more of detail with specific emphasis on phase separation in this module little while later thank you.

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