Phase Diagrams in Material Science Engineering
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Lecture – 03
Concept of Chemical Potential

So, you have already listened to my first two lectures, and got some idea about phase equilibrium, and also the free energy formulation. Today, we are going to do some recap of this, and then, move on to derive phase rule.

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Welcome to another glorious day of phase equilibria!!.

So, I just wanted to say you that I showed you this picture last time, that two seals are moving in a ice-water mixture, and they are trying to understand what are the factors which can be used to describe the two phase single component system. There is a single component system because its country contains water and there are two phases because you have ice and water, liquid water. So, therefore, can we describe this thing in terms of measurable thermodynamic parameters? The questions of these kinds of things will be answered in today's class. Before I do that just I want to recap you a few of the things.

You know thermodynamic in a system is defined to get equilibrium n. There are three equilibrium things are satisfied: one is mechanical equilibrium; second one is your chemical equilibrium; and third one is the thermal equilibrium. So, mechanical equilibrium analogy I have discussed you with match box concept. Thermal equilibrium means in the system there will no temperature gradient. Chemical equilibrium means the reaction rates of the forward and backward reactions will be same. So, there will be no net change of the reaction. So, when all of these three equilibrium - that is, mechanical chemical, and thermal are satisfied we call a system to be at thermodynamically equilibrium. And, as you know, all the phase diagrams are calculated based on thermodynamic equilibrium. So, therefore, we must learn the thermodynamics of equilibrium first.

So, in doing that, first we like to do thermodynamics of single component systems - like water, the one which is showed you just now. Water is a single component system with molecule containing two hydrogen atoms and one oxygen atom, with the formula of phase two, but you can have two or three phases, see if two phases coexist together or three phases like water, liquid water, ice, and vapour coexist together, how you can describe a system. So, let us do that first.

Well, to do that we have to first get back to free energy expression, that is the expression I have written at the top. Free energy is here - the Gibbs free energy, and Gibbs free energy is defined as G as a function of temperature equals to H as a function temperature minus T S T. So, H is nothing but enthalpy or the heat content, and S is the entropy of the system, and we know that by knowing the c p, we can calculate both the enthalpy and the entropy, just by integrating over c p in T, reference to T, we can get enthalpy, and by c p by T integrating over T reference to T to actually any temperature we can get entropy. So, by plugging in these two we can get an idea about the free energy.

And I showed you in the last class that the free energy curve for such a kind of system will look like this, we plot G versus temperature.

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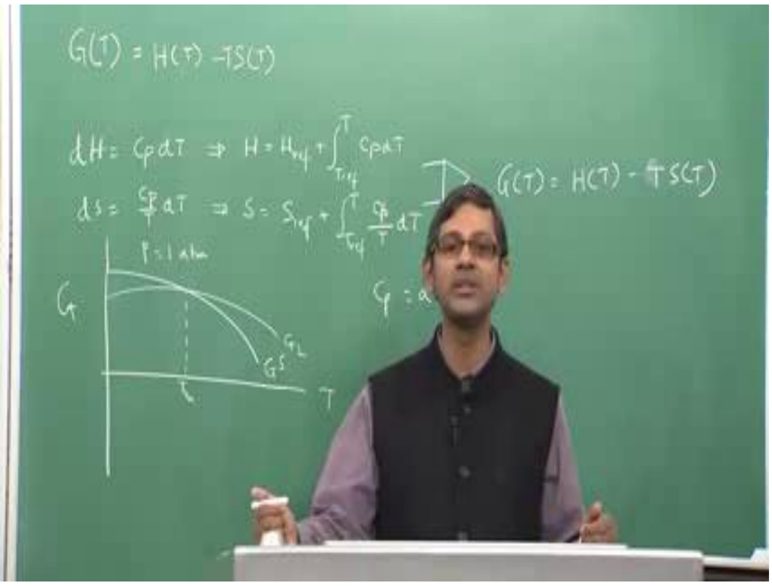

So, free energy of a solid will be looking like this - this is G S and free energy of liquid will looking like this G L, and the cross section of these two will be giving as the melting temperature; temperature at which both solid and liquid can coexist is defined by this point. Why does this curve (Refer Time: 03:29) kind of slope? This is because of entropy. If you clearly look at this is a negative slope. So, slope of this curve is a function of temperature is basically minus entropy, and entropy is a positive quantity; therefore, the slope of this curve is negative. And if we assume the simple equation of c p is equal to a plus b t, then we can actually find out - by using this mathematic analogy you can find out - what will be the g t, and I have done already to you

So, for a single component system this is the way to describe the equilibrium between solid and liquid or solid and vapour or vapour and liquid; anything, you can do that. We will utilise this diagram when we describe what are phase diagrams in maybe another one or two lectures after this. So, now, question is this - this is fine for a single component system because g is nothing but a function of temperature and pressure, and here we have assumed pressure to be constant, if we assume p to be one atmospheric pressure, then this is only function of temperature, but for an alloy, for anything which consisting of more than one element.

For the sake of understanding - suppose instead of pure water, you use water plus some amount of salt into it, which is the case in sea water, ocean water; in that case this analogy, these derivations will not work; we have to use something else. What is that we have use? We have to know that how g varies as a function of composition also; that is what we should do. And how we can do that? Let us see how it is possible to do that.

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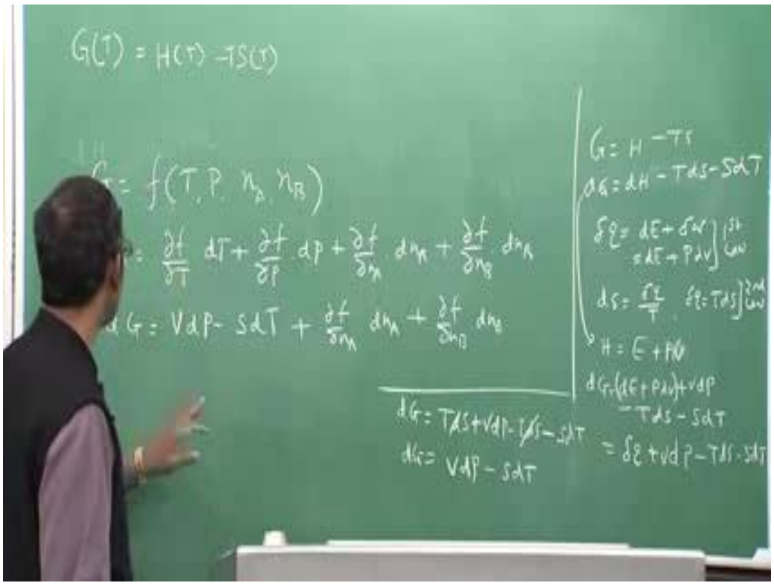

So, g will be a function of temperature, pressure, and composition of the element. That is what will happen if we consider of the free energy of any system consisting of more than one element. And there are, suppose there are, two elements. So, therefore, there will be two composition variables. Here T is the temperature, P is the pressure nA is the number of molecules of a, nB is the number of molecules of b. Like water and salt system nA is the molecules - number of moles of water; nB is the number of moles of salt.

For a steel containing iodine carbon, nA will be number of molecules of iron, nB is the number of molecules of carbon. So, that means, we have to now expand these things in terms of compositions. So, if I take a total differential of this - simple maths, but we get total differential of this dg is equal to simply df by dT, capital T, dT or this is the differential; similarly for pressure; similarly for composition. For a and for b, let me rub up this one also, so that you can be clear. So that means, total differential is differentiation of (Refer Time: 07:40) temperature, pressure, number of moles of a, number of moles of b, and you know that this can written like this (Refer Time: 07:50). I will derive it and show you how it is possible as a function of function of temperature and pressure. This is equal vdp minus sdT. I will just show you right now. And let me keep this one as these, the composition variable as is it is; well I will not change that right now.

So, how do I get this? That is very simple. Let us write down here: g is equal to H minus ts. So, if I take differential of that, then it becomes dH minus Tds minus sdT. I will just take in total differential. So, I will differential everything. So, now, I know from the first law of thermodynamics - what do I know? For the first law of thermodynamics, I know the total energy is conserved; so that means, that I can write down from the first law of thermodynamics, I can write down del q is equal to del e plus del w which is nothing but del e plus pdv or a gas system, right? This is from the first law, first law of thermodynamics.

And, what do I know from the second law of thermodynamics? This law of thermodynamics tells me the definition of entropy that is equal to ds equal to dq by T. Therefore, del q is nothing but Tds and this is second law of thermodynamics; very easy to deal with this kind of equations.

Now, if I plug in there those things, what will you get? I know H is equal to; I just get back here; H is equal to E plus pb, right? So, I can expand dG is equal to dE plus pdv plus vdp. I expand this one fully. dH is equal to dE pdv vdp. I can expand it very easily. So, that become minus Tds; Tds minus sdT. So, now, we can clearly see dE plus pdv is equal to del q. I can write down from first law dE plus pdv is equal to del q. So, this dE plus pdv become del q plus vdp minus Tds minus sdT. Is it clear? So, now, I just go up and write down these things because you cannot see from the pattern.

So, see if I just write down here, let me just do it here. I derive it of here; that is better. So, is it very clear dG is equal to del q plus vdp minus Tds minus sdT. So, dq is again Tds by second law. So, I can have Tds plus vdp minus Tds minus sdT; that means Tds Tds get cancelled. So, vdp minus sdT; this is the typical relationship between total differential of free energy as a function of pressure and temperature, because pressure and temperature are the variables. So, that is what I used in these derivations. So, I now rub it off. You probably have noted down how to derive this expression. I will… let me get back into the whole derivations of this.

So, I have seen that this is what is the expression. Now, for such a kind of things, where g is function of temperature, pressure, and the composition variables, I need to define these terms, but in chemical thermodynamics these terms are defined as chemical potentials. What are these? So, I define this one del f del f by del nA equal to mu A.

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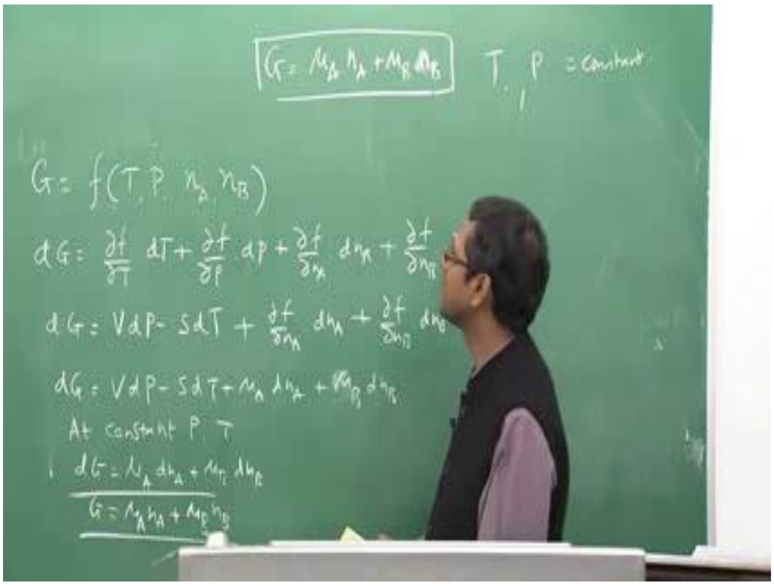

Similarly, del f by del nB equal to mu B. So, this means that this quantity defines the chemical potential of A; this quantity defines the chemical potential of B. I can write down also chemical potential of A. Similarly, this is chemical potential of B. You can clearly define this way these terms.

Now, what is the meaning of chemical potential? This is something which is very common in thermodynamics but never understood by the students. It always been told in the books that it means, if I add is very small amount of A into the solution - into the system - the change of G is what is known as the chemical potential of A, but this is a very big statement; very, very big statement. Nobody understands. This means that ability to do work. What does it mean? Let me explain. Suppose, if I say, you have the potential to become Prime Minister of this country; that means, that you have all the qualities to become the Prime Minister of the country. Similarly, chemical potential of A means it as all the qualities to become part of the solution, part of the system, and if they become part of the system, the change of the free energy because of that system is what is known as the chemical potential.

So, potential means ability to react. In basically thermodynamic sense ability to react in the environment that is what is known as potential. So, if I plug in this balance here - I hope you understood this. Now, if I plug in this balance, I get vdp minus sdT plus mu A dnA plus mu B, dnB; this is what I get, very simply. Now, at constant pressure and temperature, at constant pressure and temperature, I get dG is equal to muA dnA plus muB dnB and g is nothing but then integration of this. So, I hope you understood this part very clearly. I will write down again at the top, that you can see very clearly. I will erase this part. I erase this also.

So, I write down that G when is these composition variables are there, it can be written as muA nA plus muB nB. This is when the temperatures and pressure are constant. That means, if I know the composition of any system, then I can actually calculate the free energy system. Obviously, I can calculate free energy system for, you know, pressure and temperature; that I have shown you already - how this to be done. Why these quantities you need? You need cp; if you know cp as a function of temperature or pressures even calculate G of any pure component, any system there is no composition change, but when there is a compositional change, you must need to consider that you have to use this equation to change to measure the free energy change.

If you have to consider temperature and pressure effect, you have to add that part with this with these. So, then it will become a big equation with four different variables nA, nB, and temperature, and pressure; that is possible, right? So, you have an idea that how to basically incorporate effective compositions into the system of the thermodynamics to measure the effect of or changing the free energy of a system or gives free energy system.

Now, I just wanted to go into little deeper into that, so that you can understand it better way. So, let me just erase this part and keeping that equation at the top. So, what I can do is this like this. I know that in metallurgy or material science we never deal with number of moles of A and B. We always deal with the mole fractions of any component.

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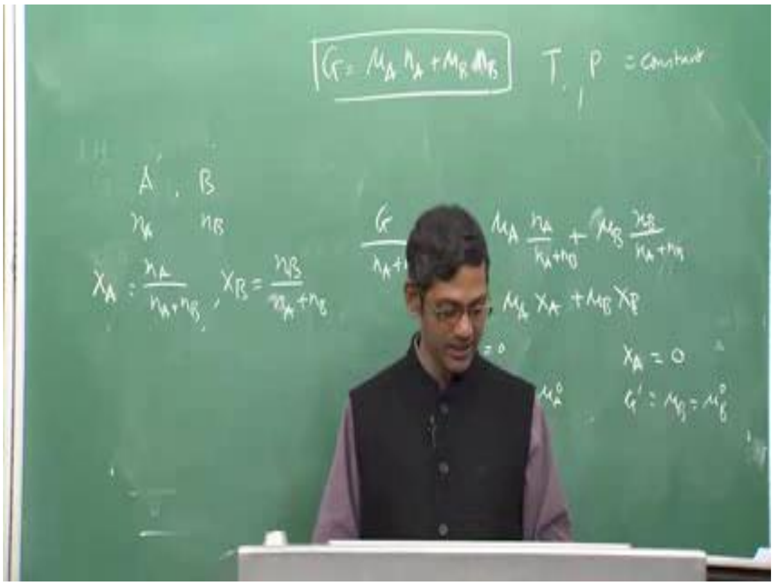

Suppose, I have two components A and B in a system; I know there are nA moles of A and nB moles of B, then I define the more fraction of xA is like this nA divided by nA plus nB; that means, the number of moles of A divided by total number of moles present; it does not matter have that two components present; if there are n numbers of components, well, you can do the same thing. So, basically, this is the way the mole fraction of A is defined.

Similarly, mole fraction of B is defined like this. Number of moles of B divided total number of moles. So, we can actually change this G expression, very simple, you can change that. So, if I divide by G nA by nB and call this as a G prime, that means, this is per mole basis; this is total free energy, if I divide by total number of moles this becomes per mole basis. The free energy per mole I put a prime because to differentiate that; that is equal to mu A nA divided by nA plus nB plus muB nB divided by nA plus nB. That means its equal to muA xA muB xB; clear? I hope it is understood. So, therefore, the free energy per mole can be given as muA - chemical potential of A - multiplied by the mole fraction of A plus chemical potential of B multiplied by the mole fraction of p.

This is the generalized expression of free energy change of any system containing two components. Why we discuss these things more frequently in metallurgy because, all our alloys are solutions. Consider steel; can say aluminium alloy, copper alloy; these are all solid solutions, because they are solutions that means, there are more than one component present. Solution is nothing but like you add sugar into water - a solution. So, this is also a solution, but they are solid solution not liquid; that is why this kind of analogy must be used. So, now it is very clear.

So, for any pure component, suppose you have only A. So, therefore, xB is 0; if v is not present, then nB is 0; nB 0 means xB 0; then G prime is becoming x muA because mu xA is one. This is known as muA 0, right? Thermodynamics we defined. Similarly, if there is no xA in the system; xA becomes 0. So, G prime become muB and we write down that as muB 0; is it clear? So, this is what is the way the chemical potential is defined.

So, whenever you want to talk about chemical potential of pure component we say we put a 0 here, whenever you want to discuss pure component we always write, put a superscript 0, but whenever we think it is a chemical potential, where component which contains more than one component it comprises of any individual component in a solution like that, we always put muA; we do not put any superscript. We always put superscript 0 when there is a pure component in a solution, and this can be possible because when you draw the diagrams it will be clear to you much easily. I have shown already to you in the last class, but I am just defining you this way. Now this is very clear. So, just I go back, go to the next few slides and show you what are the diagrams I was doing and time to do that.

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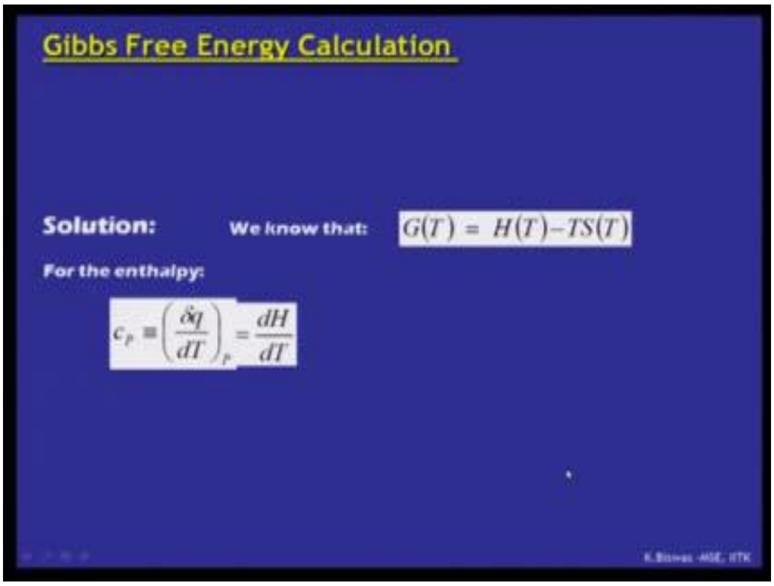

Gibbs Free Energy Calculation

Solution: We know that: $G(T) = H(T) - TS(T)$

For the enthalpy:

$$c_p \equiv \left(\frac{\delta q}{dT}\right)_P = \frac{dH}{dT}$$

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Let me just go back over there.

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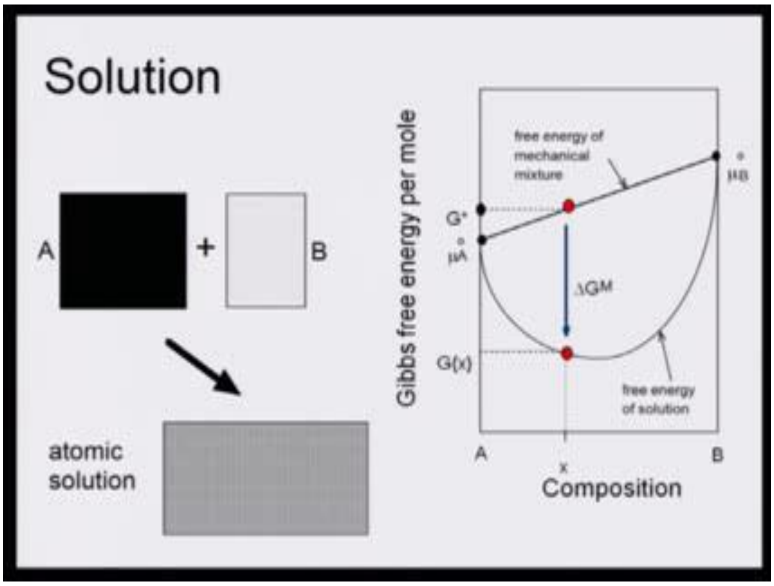

Solution

Yes, here, correct? I will just tell you that the free energy of a solution is defined by this curve, defined by this curve; free energy solution is defined by this curve. So, now, in this curve we have plotted free energy per mole same as G prime as a function of x; x is nothing but composition you can write an xB.

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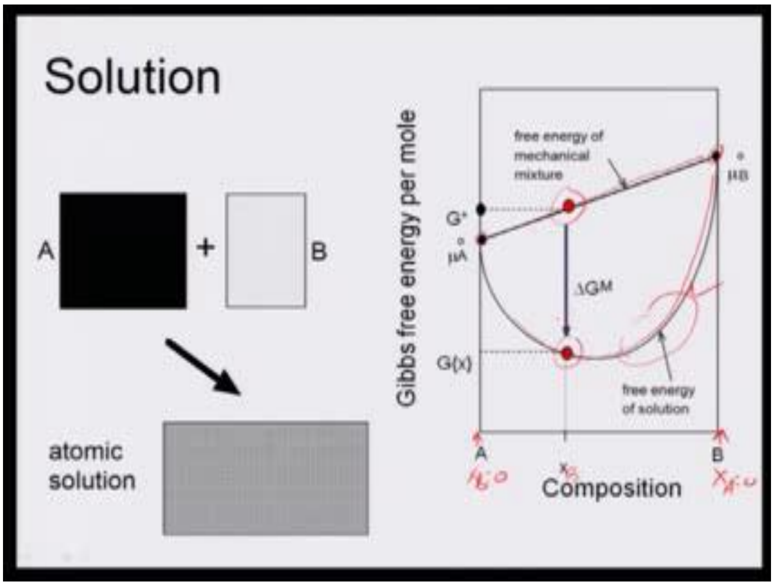

Solution

Let us suppose the xB; xB is the mole fraction of B and you know the xA plus xB is equal to 1 (Refer Time: 20:48) system xA plus xB is equal to 1; very easily you can see , that if we find xA, I can know xB also, very easily, one of the components are required.

So, now question is this - when I plot this at the pure end, like A when the A is here, B is here. So, for this component xB is 0; for this component, this part, xA equal to 0, I get chemical potential of pure A, chemical potential of pure B, and you see, I marked muA superscript 0, muB superscript 0. This is the definition of that. This is what is explained to you right now.

So, you got an idea of how actually to deal with different kinds of solutions, and now, in this diagram again I want to tell you, taking from the last class that this particular curve is basically free energy of the solution, but this line is free energy of physical mixture; physical mixture means they are not mixed atomistically together. So, that you can see the nature of the curves are different; for a physical mixture you get a straight line and for a solution we get a parabola.

Why do we get it we will explain very soon, but you have must see that in comparison to the pure physical mixture, solution is stable much easily or analytically – why? Because solution has a low energy than the physical mixture if you consider same composition that is why the solid solutions are most. So, alloys are easy to make, this is the main reason. So, if you add salt into water it form easily solution; that is why if you add sugar into water or coffee into milk it gets mix very easily; this is the main reason; thermodynamically this is the reason we always keep. Thermodynamically if we have solid solution as compared to physical mixture because of free energy change, it gets stabilised.

So, now I get back to the, I will get back to the derivations of this free energy curves in the next class. So, in a nut shell, I just want to tell you that if you are not able to get ideas very clear you can either get in touch with the TS, they will explain you or you can actually read those books I have given you as a reference in the first class, so where actually basic thermodynamically things are discussed. I will not be able to go into details of this thermodynamic derivations in this class, because I assume you have already have fair amount of idea what basic thermodynamics - metallurgical thermodynamics - very clear idea; otherwise you will not be able to follow many of this stuff.

So, if you are still not well conversed with this concepts, I suggest you that you also read those two books which I have given to you or look at literature available in the internet, so that you can understand very clearly. If these concepts are not clear to you, future lectures will not be also very clear to you, because many of this phase diagrams derivations are based on the thermodynamic calculations. So, the thermodynamics is basically backbone of phase diagrams; that is why this is prerequisite for this course.

In next class actually I will show you how this curve actually evolves and how can I use this curve to derive equilibrium.