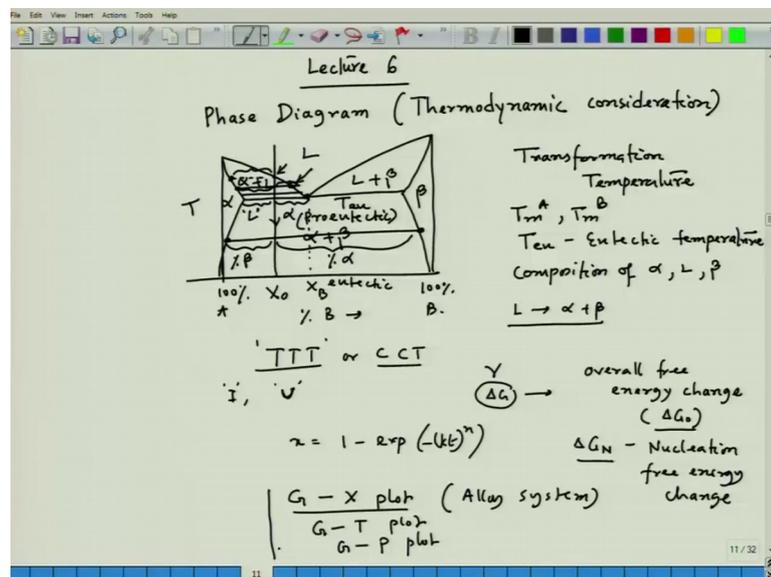**Heat Treatment and Surface Hardening - II**
Prof. Kallol Mondal
Prof. Sandeep Sangal
Department of Material Science & Engineering
Indian Institute of Technology, Kanpur

Lecture - 06
Determination of Phase Diagram (Thermodynamically)

Hello everyone. Let us get back to lecture number 6.

(Refer Slide Time: 00:21)

And today we will get to the phase diagram from the point of thermodynamic consideration plus two lectures. We talked about drawing phase diagram from cooling curve, and actually we have drawn and eutectic phase diagram, where this is my T eutectic, and this composition is X B eutectic, and this is 100 percent, A and this is 100 percent B, and this is temperature axis, this is percentage of B.

So, this was drawn further with the use of cooling curve, and that time saw the informations are obtained. For example, transformation temperatures like TM A TM B, which are the melting point of pure A and pure B, and also T eutectic. The eutectic temperature and also we can get the information of compositions of alpha liquid, and beta at different positions. Different positions means as per the temperature and composition. For example, if I try to take this composition, which is X 0, then at this point first solid would appear, and that solid would have composition, which is here and

then the solid amount would be very small, but the liquid amount would be decided by the lever rule, which is this much amount of liquid would be there.

Now, as we go down, and then we will see that at different points, we get different fraction of alpha phase, as well as its composition and correspondingly the liquid fraction and composition are also changing. For example, if we consider this particular tie line. I could see that alpha would have composition at this point, and the liquid would have composition at this point, but the liquid fraction would be this much, and solid fraction would be this much. So, like that way, will have, will reach to the point of eutectic temperature, where the remaining liquid, this much liquid will convert into alpha and beta as per the eutectic reaction liquid, converting alpha plus beta, and this much amount would be alpha, and that alpha would have a name called pro eutectic alpha.

So, this amount would be alpha pro eutectic, and this much liquid will get to this particular transformation. Now once I reach here, I will also find out what will be the composition of alpha and beta, and here the composition of beta would be this much, and the amount of beta would be this. This is the fraction of percentage of beta, and of course, this is basically coming from wet fraction, and then this is my alpha percent. And since tie line is based on mass conservation. So, these are basically weight fractions and beta would have composition, this amount and alpha would have composition this.

So, like that way at different points I could get to know what are the phases coming up, and at the same time, what are the composition as well as fraction of those transformation products, but during heat treatment, we need to know TTT diagram. So, that would decide my time temperature. Means, how long I would like to continue heat treatment, and at what temperature we need to do the heat treatment, depending on what sort of properties we would like to get from the final product.

So, that will be decided by TTT or CCT, but in both the cases I need to know, I as well as U or V, which are my nucleation rate, as well as growth rate respectively. Now in order to know I and V, we also need to know few other things; one is interfacial energy, which is gamma, then free energy change which is driving force for the transformation, and when we consider the free energy change, I need to have two more information; one is overall free energy change; that means, for overall transformation kinetics, which is decided by Jk ma, equation X equal to 1 minus exponential minus K T to the power N.

So, that time we need to know the overall free energy change, and it should be negative to have the transformation possible, and another term which is there, which is termed as delta G 0 another term which is there, which is called delta G N, which is the nucleation driving force or nucleation free energy change.

Now, these two quantity we cannot get from this diagram if we have this diagram from cooling curve. So, for that reason we need to get to thermodynamics, and we need to know free energy versus X plot for alloy system, and in case of pure metal system, or pure system that time we need to know G versus T plot, or G versus P plot which is the pressure.

So, now in order to know these things, we need to also get to the basic data thermodynamic data in one case .For example, in this case we need to know C P of that metal, as well as in this case, we need to know the molar volume change with pressure, and in this case, we need to know the chemical potential change with temperature and that time we keep pressure, constant if it is a conduit system. Now since, we will be handling with conduit system for our A treatment purpose. So, would be looking into the chemical potential data, then C P data as well as molar volume data of the metals.

(Refer Slide Time: 09:58)
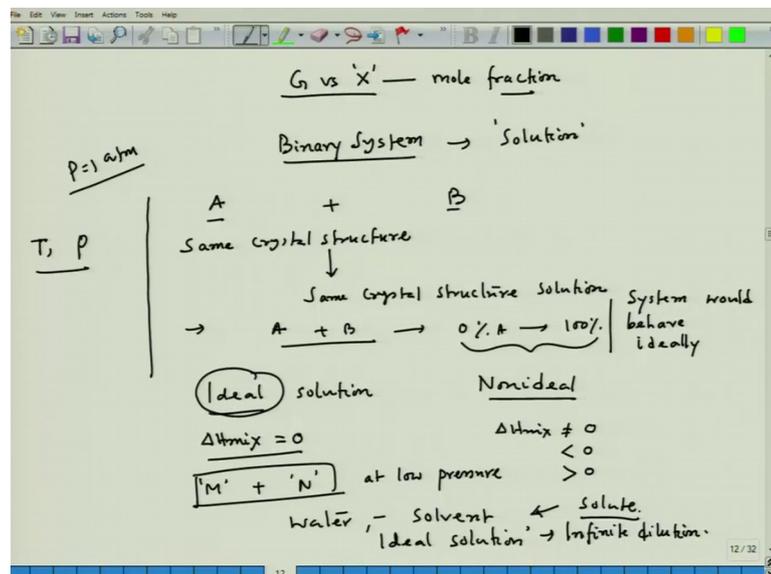
Now coming to this G versus X, and X means mole fraction; now we understand that in order to know this free energy change for nucleation, which is part of nucleation rate and overall free energy change, which is part of overall transformation kinetics. We need to

have idea how to get to this particular G versus X plot, and whenever we get to the mole fraction. Now we are considering the binary system, because if we go to the ternary system things will get complex.

So, let us confine to a simple system, which is binary. And in case of binary system we can, and whenever we talk about binary system, we generally consider solution in the beginning. There could be formation of compounds, but let us keep it aside for the time being. We will just consider solution, and that time would consider that solution means, it could be liquid solution, it could be solid solution of two elements. Let us consider element A and element B, and they appear in the beginning, before they mix and form solution. And we are assuming in the beginning, that they have same crystal structure, same crystal structure V and when the mix, they form the same crystal structure again.

So, these are some of the assumptions. The another assumptions we take that A and B can be mixed over the entire composition range; that means, the solution could vary from 0 percent A to 100 percent a. So, entire range we can constitute a solution, either it could be liquid solution or solid solution. Now when we consider this, we consider that these are condensed system. We are not looking into the solution formed by gases, because we will be treating steel as well as aluminium alloys, which are condensed a solid state, as well as sometimes we have to also get into the liquid state; for example, casting.

Now when we do that, when we trick this solution; again there could be possibility of two types of solution; one could be ideal, another could be non ideal. Generally in case of ideal system, if we put it in terms of thermodynamic quantity or thermodynamic variables, we say that del H mix equal to 0, this is a kind of thermodynamic statement we can say, and here we say that del H mix can have nonzero values, which could be less than 0 or greater than 0, depending on the interaction between the atoms of element A and B. These elements can attract each other, A atom can attract B atom, or A atom can repel B atom. So, depending on the situation, we can have values of del h mix, which could be negative, and which could be positive two. So, will get to that particular part again later, because handling non ideal solution is little tricky.

So, first let us get into this much simpler situation, which is ideal solution, and that time we say that del h mix can to 0. Now we have to also physically visualize; what is this ideal solution, what do you mean by del h mix. So, del h mix 0 means the interaction

between the atoms of opposite character, means A and B two different elements, they are atoms, they do not like to interact each other, but at the same time they would like to form solution, means that they do not have any attractive or repulsive nature. So, in order to visualize this, let us again, let us also take example from gas, and then will get back to the solution.

Now, if we consider a gaseous mixture, if A and B let us say two different gases, let us say one gas is m and other gas is N. these two gases are there, let us say they are mono atomic gases. Now if we mix them at a low pressure, very low pressure, how do we attain low pressure? Let us say we fix the compare mass, let us say the amount of that gases, if we fix them one way to, and also if we fix the temperature one way to achieve low pressure is. If we can increase the volume, and if we increase the volume then amount of; that means, it is a control volume, the amount of metal as this gas atoms are fixed already.

Now, if we expand those gases, because you are increasing the volume, the gases will expand, and it will try to occupy the entire volume. So, its pressure is going down, now if the pressure goes down that interaction this atom, atom interact is becoming very minimal, and that we can consider as an ideal solution. Similarly in case of a liquid solution, let us say if we have a glass of water, and then if we mix some second solute, if we have water, which is as a solvent. And if we add some solute, and that case is the amount of solute is. So, low infinitesimally small, then also we can say the interaction between solute atom or molecule as well as water molecule, with the minimal and we can consider that condition to be negligible interaction.

We can say that its ideal solution and that time its infinite dilution. This is also possible in case of solid and later with the help of thermodynamic expression. We can also prove it that, yes if the composition goes to infinite dilution, we can get to the ideality, and we will prove that later on.

Now, interestingly here what we are considering that we are saying, that it can be mixed in the entire region. So; that means, we are going away from ideality, ins ideality means it has to have a very low dilution, but that is also an assumption, that we consider that the entire region, the system would behave like an ideal solution, this is an assumption. So,

system would behave ideally for entire composition regime. So, we are considering into that, we are getting into the ideal system.

Now, whenever we talk about ideal system, and we consider that it could be either liquid solution or solid solution, and liquid solution and solid solution means when the solution form is liquid, as well as the solid solution means the solution form is solid. Now when you do that, we have to also continue to more external parameters; one is temperature another one is pressure. Now liquid and solid both are condensed phase. Now it is very minimal effect from pressure on those conduction spaces. for example, in order to change little volume of our solid iron, you need to go to very high pressure

So, that the solid iron pressure can be, volume can be reduced. So, that is why even if we change around one or two atmosphere pressure, there will be hardly any effect on solid iron in terms of volume change. So, that is what we generally keep the pressure constant equal to one atmosphere, and then we consider that we are mixing them at different temperature. So; that means, we have A atom B atom, and we fix at a temperature and that temperature could be anywhere. It could be either that temperature could be above the melting point of both A and B, or it the temperature could be; such that the temperature is less than the melting point of A or more than the melting point of B, or we can choose a temperature where that temperature is less than the melting points of both A and B.

So, then we will fix the temperature, and form the solution, and then in order to get the temperature effect will change the temperature. Again the same way we will form the solution. So, that is the treatment purpose, that is the treatment sequence, but when you are fixing pressure. Now you must be wondering that if we fix pressure then people talk about vacuum treatment, people talk about high pressure A treatment. So, why those things are coming in? So, now it is important to talk little bit on the pressure effect

So, in order to understand why you need low vacuum in case of highly oxidizing prone metals, why you need little positive pressure while treating brass or steel containing manganese copper chromium. So, we need to know the philosophy behind it. So, in order to know philosophy behind it, let us get to the effect of pressure.

(Refer Slide Time: 22:02)

So, I feel that this is important in order to know that particular concept, that when we need vacuum treatment, when we need high pressure treatment although stuff, though normally in case of condenser stem heat treatment pressure effect is a minimal.

For example in case of steel, if you are fortunate enough to see a rolling plant, you do not, you will not find that it is done in vacuum, it is always done in normal atmosphere, because that entire plant, entire line the rolling plant could be almost about close to 200 meters long. So, maintaining vacuum in order to avoid oxidation of steel is economically not bad. So, that time we always operate at normal atmosphere pressure, but there are situations, where we do need to worry about pressure.

Now, let us get back to the effect operation. So, now, when I talk about effect of pressure, then we have to take help from one particular thermodynamic equation. If you have seen this, I think you have seen this equation, which is one of the famous equations of thermodynamics, basically from this Maxwell equations can be derived, and these equations are basically based on the equilibrium concept. Now I can have, I can consider solid and liquid, these two phases, and if I try to see what are the, what is the equation. This equation form in case of solid, I simply write D G solid equal to V solid DP minus S solid D T, and where S is the entropy, and V is the molar volume.

Similarly, in case of liquid Dg liquid equal to V liquid dp minus s liquid dt. Now if there is a there is an equilibrium between solid and liquid at some temperature, and pressure

then these two quantities for infinite decimal changes. This two quantities will be same, since if they have reached equilibrium previously, we have seen that if we try to see the effect of temperature pressure is constant, we have seen that the curve look like this, and at this point this is G solid, this is G liquid, and this is T melting point, and at this point I see G S equal to G M, that is the equilibrium concept.

Now, these particular things can be written in the form of infinite decimal change. Once we do this, then we can write it as V H D P minus Ss D T equal to V L D P minus S L D T, we can write it. Now if we take the pressure term our on side, and the temperature term at term on other side, we can write it as V S minus V L D P equal to. Now again I can write, now here you see in case of thermodynamics, what we have, what we experienced that final state minus initial. So, this is the transformation when some transformation is taking place. So, we say that the quantity at final state, and the quantity of the initial state that difference is counted, because two state functions like G S H, we cannot get the absolute quantity. So, we get the relative the change.

So, whenever we write that; that means, the transformation is taking place like this initial equal to final. Since it is written S S minus S L; that means, transformation is taking place from liquid to solid. So, this is my initial condition, and this is my final condition. So, then I can write it as liquid to solid, and where these quantities solid.

So, now this equation is valid in at equilibrium. Now we will get to this particular equation after awhile. Now first consider these two equations.
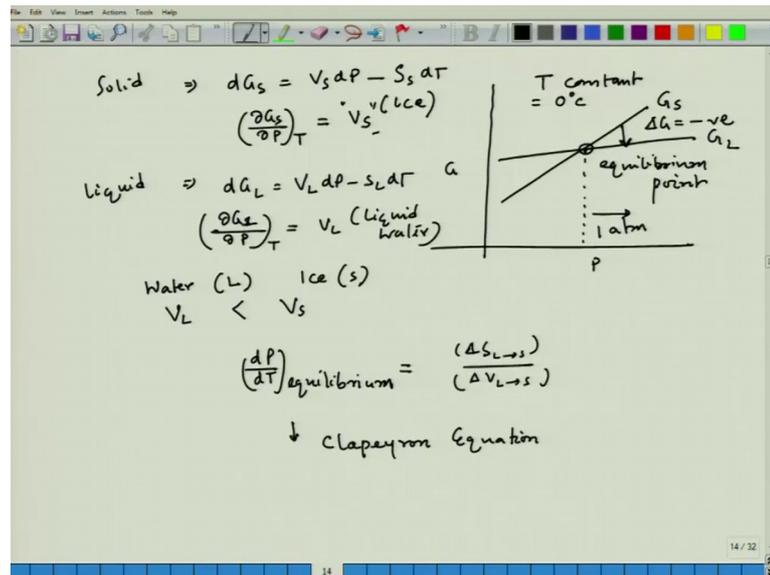
So, now D G S equal to V S D P minus at now if I try to see the slope at constant temperature, then it would become V S. Can we get negative volume; never. So; that means, this volume is a positive quantity. So, if it is a positive quantity, if I try to measure, try to see the variation of free energy with pressure at a constant temperature, it would always have a positive slope. So, if I try to plot that variation with pressure I will get a plot like this, which is G of solid. And now in case of liquid this is solid, in case of liquid I will see D G liquid equal to V L D. P minus S L D T. Then D G S L D P T equal to V L V L is also a positive quantity all the time.

Now, it would also have a positive slope; that means free energy change with pressure at a constant temperature. So; that means, T is a constant. Now in case of water, if we consider liquid as well as solid; that means, ice. Now if we see the molar volume of water and ice; that means, the liquid water and ice at 0 degree Celsius, when the pressure is 1 atmosphere, water has got molar volume of liquid, water is less than molar volume of solid water.

So, now if I compare, this is, if you say ice and if we say this is liquid water, this one would have lower value compared to V S. So; that means, V L is lower than the V S. So, the slope of that free energy change of liquid with pressure would also be long. So, then I can say that this is G L for water in case of water. So, now, that time we are considering,

if we consider this is as 1 atmosphere, and if we put it as 0 degree Celsius, then they will match at 1 atmosphere pressure. So; that means, this is the equilibrium point.

So, hence if I increase the pressure at 0 degree Celsius, then I should melt, so; that means, if I increase the pressure this way I see that ice is melting why, because the free energy of solid is more than the free energy of liquid, that is why ice melting is easy, because free energy change goes to negative.

Now, coming back to this particular equation, if we treat it further we would get to see an interesting phenomena and that phenomena relates to the fact that why ice melts, if we increase the pressure and why if I release it, then again it solidifies. That means we are getting into the terrain of Clapeyron equation.

So, we will stop here. So, we will continue in our next lecture, where we will talk about Clapeyron equation as well as Clausius-Clapeyron equation.

Thank you.