Advanced Metallurgical Thermodynamics

Prof. B. S. Murty

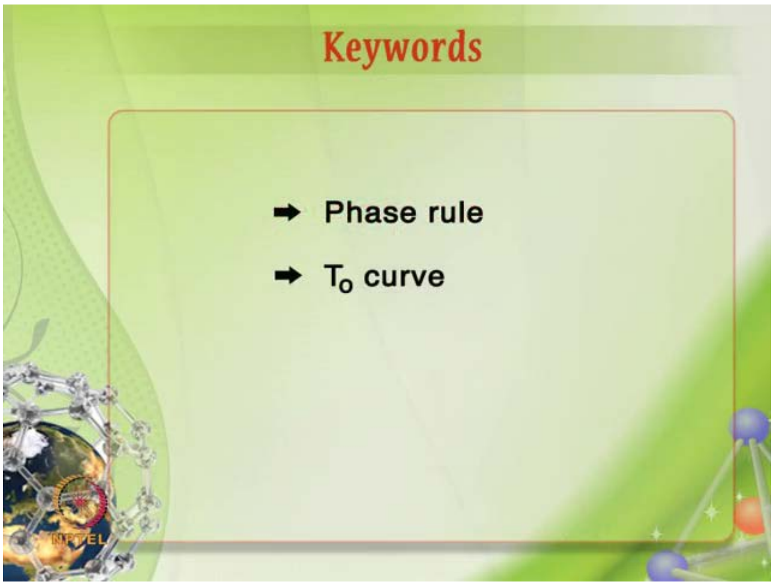
Department of Metallurgical and Materials Engineering

Indian Institute of Technology, Madras

Lecture # 06

Phase rule, Free energy-composition diagrams and Phase diagrams

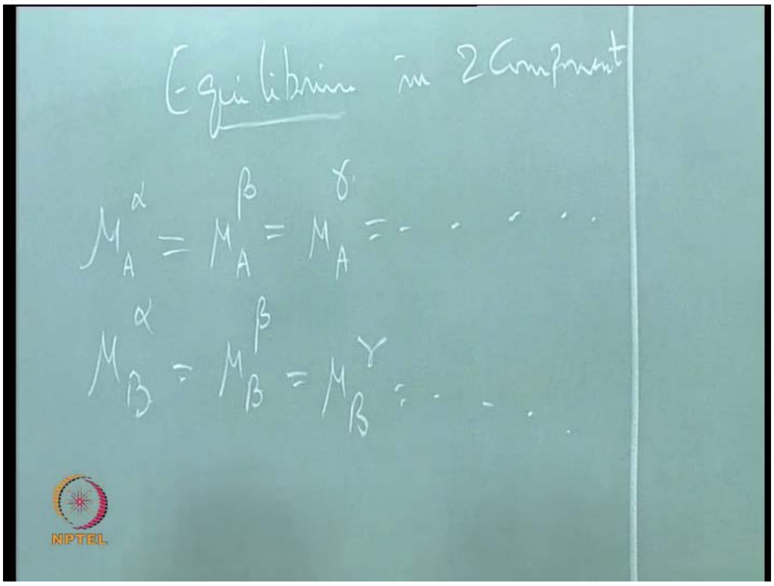
(Refer Slide Time: 00:08)



Keywords

- Phase rule
- T_0 curve

(Refer Slide Time: 00:16)



Equilibrium in 2 Component

$$\mu_A^\alpha = \mu_A^\beta = \mu_A^\gamma = \ldots$$

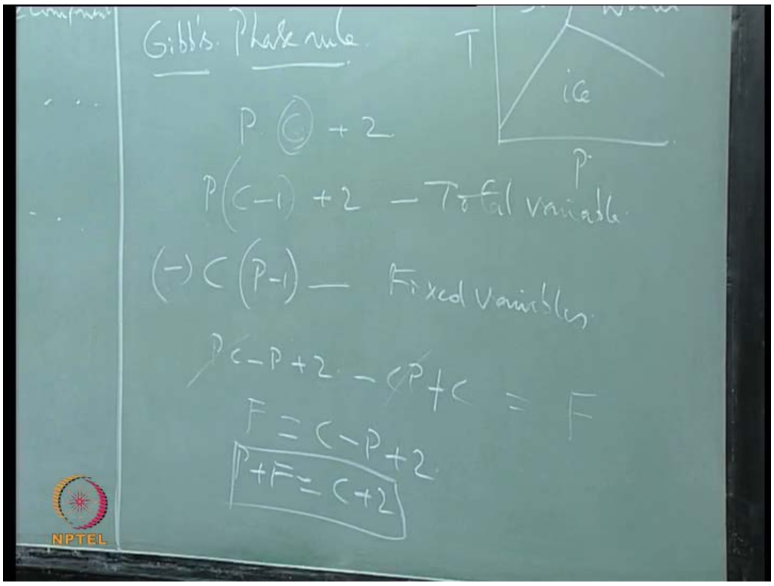
$$\mu_B^\alpha = \mu_B^\beta = \mu_B^\gamma = \ldots$$

Yeah, last class we kind of defined the equilibrium concept in two component systems and I said, in principle, we can extend this to any number of components. And the definition there was, that the chemical potential of a particular element A in a phase, let us call it as alpha, should be equal to the chemical potential of the same element in another phase, then we can say, the two phases are in equilibrium at that particular temperature and pressure. So, this is the definition.

And in principle, if you want to extend it to more number of phases, you can even say, chemical potential of A in gamma, for example, when we say, an eutectic reaction, a liquid giving alpha plus beta. And when I say, all the three phases are in equilibrium, it means this, the chemical potential of one of the elements, let us say A, is equal in the liquid, in the alpha, in the beta, that is the meaning of eutectic when I say a liquid is giving you alpha plus beta and all the three are in equilibrium.

And similarly, we can also extend this to another component and say chemical potential of B in alpha should be equal to chemical potential of B in beta and should be equivalent to chemical potential of B in gamma and so on and so forth, depending on whatever number of phases that is present. And this can be written to all the components that are present in the system. In a binary system we have only two components, in a ternary you can extend it to a 3rd component, in a quaternary four components and so on and so forth.

(Refer Slide Time: 02:11)



And this actually brings us to a concept called phase rule, which Gibbs talks about, this is, that is why we call it as Gibb's phase rule, which is again related to this. In fact, when we talked about this phase diagram, which is the temperature-pressure diagram for the solid, which is ice, the water and the steam, we drew this diagram if you remember. And there, you had a doubt about this triple point, how do we talk about it and once you understand this phase rule, then understanding that become very easy.

So, what is this phase rule? Phase rule talks about what are the degrees of freedom that are available for any system, independent variables that are available for any system at any given condition of temperature and pressure. If I look at, that any system when I talk about it, the total number of variables in a system are always related to the number of components. For example, if I say I have a phase here, I want to describe this phase. When I want to describe this phase, I describe it like the way we describe a human being in terms of his emotions.

So, we talk about the, this particular phase in terms of the number of components present in it and additional variables are the pressure and the temperature. So, this phase is present at this pressure and at this temperature and this has so many components. So, for each phase, I can actually define a certain number of components, which we can call it as, let us say, call the components as C and call the phase as P. The total number of components and the total number of variables are always P into C plus 2; this will be the actual total number of components.

But one thing, that you have to remember is, whenever I am talking about a phase, I need not have to talk about all the components present in the phase. For example, if I am talking of a binary alloy, let us say steel, iron-carbon alloy and I am referring to what is the composition of a alpha ferrite, let us say, if I talk about how much of iron is there in it or how much of carbon is there in it, automatically I need not have to tell about the 2nd element.

So, that means, whenever a certain number of components are present in any phase, I need to talk about only the components minus 1 as the independent variables, one of them becomes automatically a dependent variable. If it is a three component system, if I talk about how much of a, how much of B is there, I need not have to say how much of C is there, automatically it is 100 minus this plus that. So, as a result, in principle, I need not have to describe all the components present in a phase. So, that is why, we define it as P into C minus 1 plus 2 as the total number of variables to describe a system. If I have P number of phases, each phase has C components, for each phase I need to define how much. For example, you think of a eutectic reaction, a eutectic reaction, where a liquid is giving you alpha plus beta. If I want to describe this liquid, I need to describe what is its composition, how much of A is there, how much of B is there in this, but if I tell how much of A is there, automatically I am telling how much of B is there.

Similarly, I need to tell, what is the composition of alpha? Composition of alpha is not same as composition of liquid; similarly, composition of beta is not same as that. So, for each of the phase, I need to define how much of A is there, how much of B is there. And because this is a binary system, if I tell about how much of A is there, that is enough or if I tell about how much of B is there, that is enough.

So, that means, for each of the phase I need to define what is this the, the number of components, that are independent variables. And at the same time, because this is a eutectic, all of the phases are at the same temperature; they are going to come to it, why it should be at the same temperature. It turns out from the phase rule that it has to be, all the three have to be at the same temperature, otherwise eutectic reaction will not take place. So, they are all at the same temperature and of course, because I am doing this whole transformation at atmospheric pressure, they are also at the same pressure.

So, in principle, pressure and temperature are constant for this reaction, but it need not be the case for all the cases. For any reaction, that is happening, you need not have to have temperature and pressure of both the, all the phases being at the same. So, considering, that we in principle talk about, whenever we talk about the total number of variables to define the whole system containing P number of phases is this way, that each phase, I need to define C minus 1 components and all this phases are at a particular temperature and pressure. So, I need to define what is that temperature, what is that pressure is? So, I need to have two additional variables for temperature and pressure and if I have P number of phases, P into C minus 1 will tell me that.

And if I say, that all these phases are at equilibrium or in equilibrium with each other, then equilibrium demands, that certain variables become automatically constant. What is that equilibrium tells me, that for each component if I define, for example, one chemical potential for pure A mu A alpha, I need not have to define mu A beta and mu A gamma and so on. Once I define this they are all fixed. That means, for each component P minus 1 gets fixed once I define the chemical potential. So, for every component, I need to basically define only one chemical potential. For the remaining P minus one phases, I need not have to define, they are all automatically fixed. Once I define chemical potential of A in alpha and similarly, chemical potential of B in alpha and similarly, chemical potential of C in alpha. Once I tell these three, I need not have to tell all these because this is equal to this, this is equal to this, this is equal to this. That means, for each component I need to define a chemical potential in any one of the phases; if I define in any one of the phases, the remaining phases I need not have to define.

So, that means, for each component, P minus 1 variable gets fixed once I define the chemical potential, so that means, this becomes kind of fixed variables. For each component P minus 1, I need not have to define and once I do that, this minus this would give me what is the number of variables that need to be defined for a given system. This is a total number of variables, out of them some gets fixed because of the concept of free equilibrium and once I subtract this 2, you would see, that this is actually P C minus P plus 2 minus C P minus C. This turns out to be, you will see, that this is, this goes off and this is what we call it as degrees of freedom, which is called F.

The number of variables, that need to be defined for a system is what we call it as number of degrees of freedom, that are available for this system and that is F and that turns out to be basically, ok, yes F, somewhere did we make, something, this is a minus, so this has to be plus. So, C minus P plus 2, am I right, there is a minus here, so this is actually plus C; this is minus C into minus 1, plus C. So, C minus P plus 2 or we also usually define it as P plus F equal to C plus 2. This is what we call it as the Phase rule P plus F equal to C plus 2. We used to remember, when we were students of your stage, police force is constables plus 2, something like that. So, it is, so it is easier to define, remember.

So, anyway, what is important is, this is a general phase rule and from this general phase rule we get, what is also called, a condensed phase rule, where we, we keep, one of these two is the pressure constant because most of our system, most of our processes occur at atmospheric pressure. I need not have to define pressure, pressure is fixed and once I fix up the pressure, this becomes P plus F equal to C plus 1, that is what is called condensed phase rule.

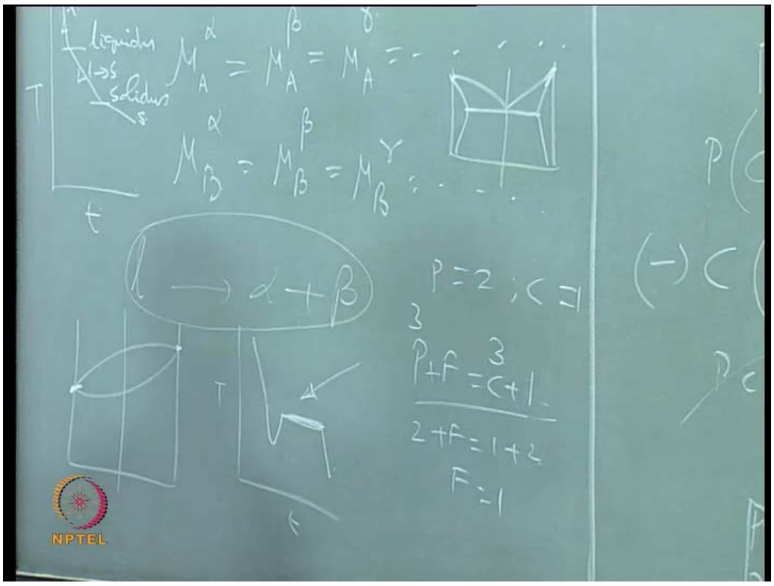
And if I look at this phase rule P plus F equal to C plus 2 and then look at this phase diagram, now it becomes clear to me, why do this, the melting point for example, ice to water melting point, should change as a function of pressure. For example, you look at this, whenever an ice is becoming water, how many phases are involved in the process? There are two phases, one is changing into other; so, there are two phases. And how many components are there? Here, there is one component, so P is 2 and C is 1, you put that into this happens F equal to, F equal to 1.

So, that means, there 1 degree of variable, there is 1 degree of freedom for the system because if I put P equal to 2 and plus 2 plus F equal to 1 plus 2, so F equal to 1. So, there is one degree of freedom for the system. That means if I fix up, that particular degree of freedom, then everything else gets fixed. That means, if I fix up the pressure, then the temperature at which ice transforms to water gets fixed because that is the only degree of freedom that I have. Once I fix up that degree of freedom, then I do not have any degrees of freedom in my hand, there are no more variables that are possible. The system has to be, everything has to be fixed, there are no more variables possible and that is how we define this as this.

And similarly, if I fix up the temperature, the pressure at which the ice transforms to water again gets fixed. So, that is how we look at it and any, any of this lines you can talk from that point of view. And now, if you come to this point, where the three phases are in equilibrium, you put P as 3 and C as 1, you would see F becomes 0. That is where we say, there are no degrees of freedom for this.

If at all you want all the three phases to co-exist, they can co-exist only at a fixed temperature and pressure and that is not in your hands. You cannot make all the three phases co-exist at your wish, that at any temperature and pressure of my choice, no and that is fixed by the, by the thermodynamics, that they all three can be together only at a fixed and this is what you see in all phase diagram.

(Refer Slide Time: 14:45)



For example, if I draw a phase diagram, what is this phase diagram? Isomorphous; so, in this isomorphous phase diagram, what are these two points? Melting points of A and B. And if I look at the melting points of A and B and apply my phase rule there at that temperature at that point, what is happening at this point? What is happening? Solid is becoming liquid or liquid is becoming solid depending on which direction I am looking at. And when solid is becoming liquid or liquid becoming solid, how many phases we have? We have two. And how many components we have? We have one. And then, how many degrees of freedom we have? One; that is where the problem is.

When we are talking about isomorphous diagram of metals, melting or solidifying, we always keep the pressure as constant and once we keep the pressure as constant, because this diagram has come only when you have fixed the pressure, this is at atmospheric pressure, if I vary the pressure, then this diagram changes. So, all the melting and solidification that we come across in our day to day life, we all do at atmospheric pressure.

So, as a result, we do not use this phase rule, the generalized phase rule, but we use a condensed phase rule. And once I use the condensed phase rule because P plus F equals C plus 1, then you see, that F equal to 0 there and that is the reason why the, the melting and solidification occurs at a fixed temperature.

If you remember this cooling curve temperature versus time, why does this solidification occur at a fixed temperature for a pure metal? It is because of this, the Gibb’s phase rule tells, that the melting and solidification has to occur at a fixed temperature. Thermodynamically it is not possible, that melting can occur over a range of temperature, but if I take an alloy of this composition, let us say, there I am not having components as one, now components is two, when I consider C as 2, in the same equation P as 2 and C as 2, then F equal to 1.

So, when, when I see F equal to 1, that means melting can occur over a range of temperature and that is what you see. That is why, we call liquidus and solidus; for a pure metal, liquidus and solidus are equal, there is no separate liquidus and solidus for a pure metal. So, that is why you see, that both the liquidus and solidus merge into each other when you come to one end of the phase diagram or the other end of the phase diagram because phase rule says, that they have to have the same melting point and that is why, if I draw a, what is called, a cooling curve for an alloy T versus t, you would see this kind of a curve and this is what we call it as liquidus, this is what we call it as solidus; liquidus and solidus. And here it is liquid, here liquid is changing to solid, here it is solid.

And because there is an enthalpy change, there is an enthalpy release when a liquid becomes solid, that is why you see the slope changes that take place. Why should the slope change? The moment you reach the liquidus is because the moment you reach the liquidus, solid is coming out of it and when solid is out of it, solid cannot take all the heat that is there inside the liquid. So, this excess heat, which is their inside the liquid, has to be given out. When it is given out, this excess heat also has to be extracted by the mould into which you have poured this liquid and as a result, because the, heating rate is, cooling rate is fixed, you have an excess heat, that is available. So, automatically, the cooling rate, that dT versus dt is nothing, but the cooling rate. The slope of this tells you the cooling rate, this is a higher cooling rate and the moment solid starts coming because excess heat is available, the cooling rate suddenly stops and that is the reason why, you see this change.

And once the solidification is over, again it starts cooling by the normal Newtonian cooling in a, any single phase material. When it cools, what is the rate at which it cools? Anybody knows rate is proportional to what?

(( ))

4th power of temperature; is not it. So, that is why you see and that is why this slope has to be higher than this slope because the temperature is already low here. So, because the cooling rate is 4th power of temperature, so in the liquid state, the material cools faster in the solid state it cools slower and that is how we can find out, whereas in a pure metal it is like this.

And now, if I look at a eutectic alloy again, you see, the thing will be exactly like this, why? Because I have three phases there, liquid giving alpha plus beta; there are three phases that are involved. And how many components? Two components; it is a binary alloy.

So, you imagine this eutectic diagram you would see, that again, whenever you are drawing, be careful, that these two have to meet each other at that because that is the melting point of pure B, this is the melting point of pure A. And so, this horizontal that we are talking about and that horizontal, if you take an alloy of this composition and do a cooling curve analysis, you will exactly get this kind of a thing excepting, that you sometimes get something different, what is that?

You, actually you do not see this all the time, you see an under cooling. Whenever the solidification is difficult, whenever you do not have, what is called, heterogeneous nucleation sites available, you see for a homogeneous nucleation, you see this. You see the same thing for a pure metal, you see the same thing for the eutectic alloy because if here, because there are three phases are in equilibrium, liquid is giving alpha plus beta, there are 2 components, put P equal to 3 and C equal 2 and use condensed phase rule and you would see, that F becomes, for example, if this is 3 and this, this is 2, F has to be equal to one equal to 0.

So, that is how you have to see in a eutectic, that F becomes 0 and once F becomes 0, then solidification occurs at a fixed temperature and that is the reason why, we call this as invariant reaction, whereas this is a univariant reaction. Solidification in a, in a binary alloy, in an isomorphous binary alloy is a univariant reaction, whereas solidification of a eutectic alloy is a invariant reaction. But again, you have to remember, it is not always eutectics are all invariant reactions.

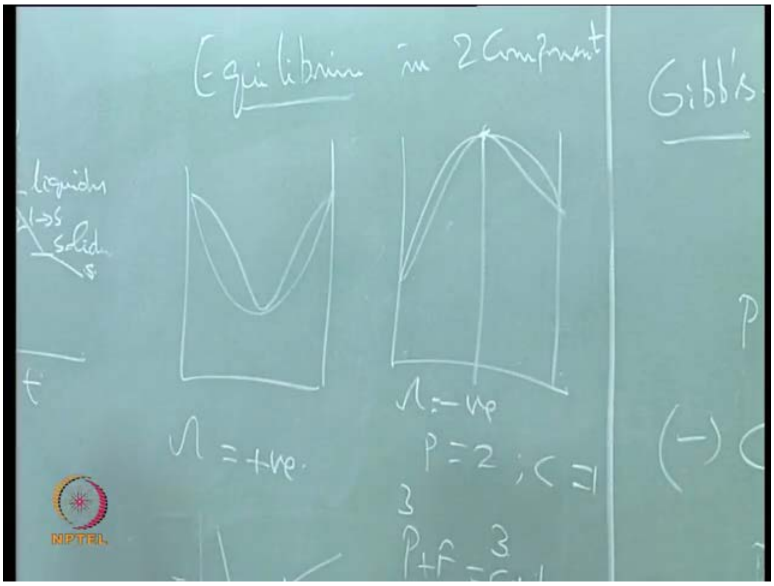
The moment I go to a ternary system, there are also a number of ternary systems and if I take the same eutectic reaction liquid giving alpha plus beta in a ternary alloy, let us say you have a cast iron, let us say, iron-carbon-silicon alloy and in a iron-carbon-silicon cast iron, if the same eutectic reaction is taking place, where, what is the eutectic reaction in iron carbon system? Austenite plus cementite plus liquid gives ledeburite let us say.

That reaction if it is taking place, instead of iron-carbon alloy, if it is taking place in an iron-carbon-silicon alloy, same reaction that, would never be an invariant reaction, why? Because in this reaction, in the C plus 1, condensed phase rule, I have to put P as 3 and C as 3, then you will see F equal to 1. So, that means, the same horizontal, that you see at 1130 degree centigrade, am I right, whatever it is, 1120, 1130, 1140, depending on which book you see, that temperature that you see as a horizontal in a iron-carbon diagram, it will be an inclined line, it will not be a horizontal in a ternary.

So, that is why, you know, there is a standard way of asking people, ask binary, eutectic in a ternary system is univariant, but at the same time, you can have other type of eutectics, where liquid gives 3 phases in many ternary systems. Such kind of eutectics do exist, where one liquid gives alpha plus beta plus gamma and the moment you have such a reaction, that reaction will be definitely invariant reaction in a ternary system because there P will be 4, C will be 3, then you will see F will be again 0.

So, one has to be careful in which system, that you are talking about; what kind of a reaction, that you are talking about; whether it is a binary or a ternary or a quaternary, accordingly this reactions will be either invariant or univariant or bivarient, whatever it is. And so, phase rule can really give us a lot of idea. Then, there are also interesting things, interesting phase diagrams; I will just show you one such phase diagram if you have ever seen it.

(Refer Slide Time: 25:01)



Have you ever seen a phase diagram like this? It is called as pseudo-eutectic phase diagram. You might also have seen another phase diagram something like this; that is a phase diagram. These two have a lot of meaning in terms of thermodynamics; we are going to see how phase diagrams evolve.

And based on this kind of concepts, whenever you see this kind of a phase diagram, it means, solid is trying to be stable up to higher temperatures. Here, it means solid stability is much lower when compared to liquid; solid is not stable. This happens when the two elements do not attract each other, they do not have a strong attraction. So, that means, if omega is close to 0, but positive, then you see this kind of a situation; when the omega is negative, you see this kind of a phase diagram.

That means, there is an attraction between A and B, the, and B bonds are stronger and they do not want to break at low temperatures. So, they retain their bonds even at higher temperature. So, as a result, the melting point of the alloy is higher than the two individual pure metals and you see, in all such diagrams, there is a tendency for formation of inter-metallic compounds.

Is the Cu 3 Au, I mean, copper-gold system, if you look at it, you will see something similar. If you see nickel-aluminum system, you see a suddenly an inter-metallic compound at the center of the phase diagram like that. So, this is what is called congruent melting system and whereas, this is what is called as pseudo-eutectic. But if I look at both these cases, how do I explain this, here this alloy is melting at a fixed temperature, am I right; it is melting at a fixed temperature.

If it is melting at a fixed temperature, means, degrees of freedom is 0 and whenever melting is taking place, there is a liquid and a solid. P, number of phases is 2 and if I take number of phases are 2, number of phases as 2 and if degrees of freedom has to be 0, then C has to be 1. Whereas, I am saying, that I am talking about a binary alloy, how do I reconcile with this? That is why, I said sometime back to you that you get into problems like this, how do I visualize this? Now, that is where we treat this as a, as a, as a simple component system with, which is nothing, but a cluster, which is a strongly bonded cluster.

So, I cannot, it is like treating H 2 O. When H 2 O is melting or solidifying, we do not treat H 2 O as two components, we treat H 2 O as one single component. Similarly, we treat this also as one single component in all such cases. So, otherwise, you will not be able to explain this. So, these are the things that you need to remember as you go along.

(Refer Slide Time: 29:01)

Now, let us come out of this phase rule, we have had enough of it and try to understand, how to use free energy composition diagrams in various phase diagrams. Let us look at a typical phase diagram, such as an isomorphous diagram. Whenever I am drawing an isomorphous diagram and what is this diagram, it is an equilibrium diagram, am I right?

When I say an equilibrium diagram, that means, all the phases, that are present there are all equilibrium phases at that particular temperature and that particular pressure.

And that the concept, that we have defined just a little while ago where we are talking about equality of chemical potential, that is also an equilibrium concept, so anything, that we see and where did it come from? For example, if you remember, we have drawn, let us say, two free energy curves and then drawn a common tangent, and we say, that alpha of this composition is in equilibrium with beta of this composition, if this is beta. So, alpha of this composition is in equilibrium with beta of this composition at that particular temperature and pressure. We will not talk about pressure because we assume that pressure is already constant, but it is at that temperature.

So, that means, if I draw a line, a constant temperature line like a, what we call such lines in phase diagrams? They are called tie lines; tie lines. So, if I draw a tie line there and then, this particular composition and this particular composition that you see, there should be, if I draw for example, what are the phases here? Liquid and alpha and this is liquid plus alpha. So, that means, if I have a liquid here and I have an alpha here, in principle, if this is a schematic free energy composition diagram for this system, then this particular composition should represent this composition and this particular composition should represent this composition. There has to be a one-to-one correspondence between the free energy composition diagram and the phase diagram and this is the simple concept, which people use when they try to calculate this phase diagram based on this.

For example, what I can simply do is, at each temperature I can find out, how the free energy of alpha and free energy of liquid are changing. For example, if I draw free energy curves at this temperature, at that temperature what is stable? Liquid, so how should the free energy curves should look like? Yes, liquid should be below that of solid. So, if I draw G versus X, I should see liquid curves, should be like this and the solid curves should be something like this. Anything more than this, that we can get information?

Yes, yes, these differences are also important; why they are important? For example, look at this side on the pure A side and a pure B side. If I look at pure A side, the melting point is very low; pure B point, the melting point is high. That means, on the pure A side at this temperature because that is much higher than the melting point, the liquid is much more stable than the solid.

So, the difference in the free energy of the liquid and solid for the pure A should be larger when compared to the difference in the free energy of liquid and solid on the pure B side because here, the temperature of our consideration and the melting point are closer to each other. As a result, when I draw this and of course, schematically only I am drawing, but in principle, if I calculate it, it turns out to be like that. You would see, that this difference is larger, this difference will be smaller, this is alpha, this is liquid.

If you calculate using whatever formula, that we have given, G equal to X A G A plus X B G B plus R T X A ln A and X A, that formula plus omega X A X B. If you put the whole thing and what you need in this whole formula is you need to know, that T for temperature I am calculating, I need to know what is omega, what else I need to know in that equation? Molar fractions is, actually when I am calculating free energy I am calculating as a function of composition, so there is nothing to know about molar fractions. I calculate G of alpha as a function of X B, fixing the temperature this is what and I try to plot. So, you need to know, what is the temperature; you need to know, what is the omega and anything else you need to know? The G A and G B.

And also, keeping in mind about, in, in systems, which are not isomorphous, in case of isomorphous there is no problem for me because A and B have the same crystal structure. If A and B do not have same crystal structure, I need to go into that lattice stability criterion and find out the free energy of one phase with respect to the free energy of the stable phase of that particular pure metal, and in this case, that problem does not arise. So, this is what I need to know.

Once I have this and this G A and G B at that temperature, I need to find out G A and G B at that temperature. That means, G is H minus T S. I need to calculate H at that temperature, S at that temperature and then get this, then I can say I have the G of alpha or G of liquid as a function of composition. This is how we calculate. And if I calculate it at a fixed temperature like that, this is how it will look like.

Now, if I come to lower temperature like that, what would happen to the free energy curves? Close; so, what is happening? I mean, are the free energy curves going up or free energy curves are coming down, what is happening? Alpha will come down and liquid will go up?

(( ))

He is right; as the temperature comes down, both will go up, why? Remember our 1st class, where we said, that dG by dT is minus of entropy. So, free energy decreases as the temperature increases; free energy increases as the temperature decreases. So, if I am decreasing the temperature from T 1 to T 2, then the free energy should increase. So, what happens, the free energy of liquid and free energy of alpha, both of them will increase.

The only question is what is the rate at which they increase? The rate at which they increase, because liquid has a higher entropy, the rate at which liquid curve will go up is going to be faster than the rate at which alpha curve is going to go up. So, slowly it is like catching game, two fellows are running, the other fellow is running faster, tries to catch up with the other fellow.

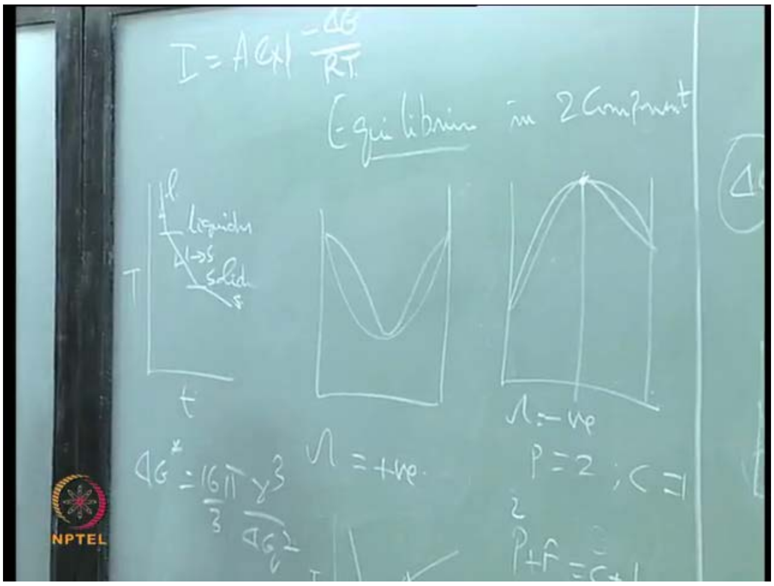
And exactly, that is what happens. So, liquid is trying to go up and alpha is also going up, but alpha is going at, at a slower phase and liquid is going up at a higher phase. And as a result, if I now draw a T 2, I would see a situation, that this is, if, if this is at T 1 and if I am drawing at T 2, you would see a situation, this would be, this would be the situation, liquid and alpha.

You would see, that this difference comes down, both the differences come down, but these two come down closer, much closer, because this temperature is very close to the melting point. And the moment you chose, now another temperature T 3, which is exactly the melting point, then you would see, that these two will merge with each other. So, you will see a situation, where this curve, something like this you would see a situation. So, both of them will meet each other at this point indicating, what does it indicate? That means, at that particular composition of B alpha and liquid have the same free energy, that means, alpha and liquid are in equilibrium.

Remember, for a pure component, equilibrium is defined in terms of equality of free energy. In a multi-component system, equilibrium is not defined in terms of equality of free energy; it is defined in terms of equality of chemical potential. So, you can see, that

that means, that is the, the moment you see at pure B, that these two come together and become equal, that temperature, whatever, if I keep on varying the temperature by every 1 degree and do the same calculation. In fact, large number of people have done, in fact, in one of the thermodynamics class like this, we have at least generated 10 phase diagrams, simply calculating it and proving, that what you see in a. in a (( )) hand book, let us say, is what you actually can calculate.

(Refer Slide Time: 39:47)



And if you vary the temperature every 1 degree and start calculating, you will see, exactly when you reach that melting point, these two will meet there and now, if you come to a lower temperature like this, then you start seeing situation becomes… So, the liquid is now going up with respect to the alpha and as a result, you would see, a situation may be, I will draw it once again, you will see a situation where a liquid curve will intersect the alpha curve and when it intersects the alpha curve, when I draw the common tangent here, these two compositions, this is the liquid curve, this is the alpha curve and what does it tell you, what are these two points? This is the free energy of liquid B, this is the free energy of alpha B and you can see, here the alpha has a lower free energy than the B than the liquid on this side.

You see, the liquid has a lower free energy than the alpha, why? Because on this side it is still liquid, but stable. On this side, once I come to this temperature, it is already alpha. So, if I call this as a T 3 temperature, let us say, I call this as T 3 temperature, that T3, this side pure A, pure B side I am already below the melting point. And because I am already below the melting point, the solid should have a lower free energy than that of the liquid. On the other side, you will see the reverse and wherever these are intersecting and if you draw a common tangent to these two free energy curves, you get these two points. And those 2 points are nothing, but these 2 points.

And if I keep doing it at various temperatures, at each temperature I can generate these 2 points, which I will call it as a liquidus point and a solidus point. And if I keep on joining all these points, that I get, I can generate a phase diagram and in fact, in an experimentally, how are we doing? We are doing this, we are doing this for each composition there. We are not considering temperature, we are choosing, let us say, A to B, every 1 percent. Let us say, I make an alloy, 100 alloys I make, for each alloy I do this, I will be able to generate liquidus and solidus points for each alloy and join all those liquidus points, join all those solidus points, you will get a phase diagram like this.

Instead of doing those laborious experiments, I can actually do this calculation and do it at various temperatures, just one single equation and just only thing is, put it into a do loop and ask it to calculate at every 1 degree of increment of temperature or 1 degree of decrement of temperature, whatever you want. Simply, the program can calculate and at each of that temperature, you ask it to find out, which are the two points, find out where are the common tangents. So, draw the tangents, ask it to draw the tangents and find out where the slopes are equal or find out that and that is how we can actually do it and get this whole thing.

And in this process, you would also come across one point, which is here. There is an intersection point, what is that intersection point, tell us? Both free energies are equal, what is the significance of this, that is not equilibrium, equilibrium is this; equilibrium is this. For example, where is that particular point? That point is somewhere between these two, am I right, it has to be between these two and so that means, at a given temperature T 3, when I look for this point, that point falls somewhere here, somewhere between these two compositions. That point will be there, where, which is the intersection point, where you are calling it as, where G alpha is equal to G liquid.

So, that means, there is a particular composition where the alpha having that composition will have the same free energy as the liquid having the same composition, and this is what we call it as a point, where the equi-free energy point. And if I do this exercise for various temperatures, at each temperature, whenever I see a common tangent, whenever I see two compositions corresponding to equilibrium alpha and equilibrium liquid compositions, you will also find out an intersection point and all the intersection points will always be between the two equilibrium compositions of liquid and solid.

And so, that means, you will get the points like this, which if I join, you would get a curve like this, which goes like this and on the two pure metal ends, this point will join with the melting point because the two pure metals, the definition of melting point itself is the free energy of alpha, is equal to free energy of liquid. So, as a result, our, this point is also nothing, but locus of all those compositions, which have the same free energy, where the alpha and liquid have the same space. That means, this tells you at what, for example, if I choose an alloy of this composition, if I choose an alloy of this composition, at this composition, what is the temperature at which free energy of alpha of that composition is equal to free energy of liquid of that composition? And that particular point is this.

And this line is called T naught curve, and what is the significance of this T naught curve? We will see as we go along, it is a very profound concept and this is the one, which brings you into what are called metastable phase diagrams, and we will see as we go along.

So, this is how we can, in principle, calculate phase diagrams and the more complicated it is, that means, if you have more, for example, if it is a eutectic, you have to add one more phase, liquid giving alpha plus beta. So, that means, in principle, I should calculate the free energy of liquid, free energy of alpha and free energy of beta and in principle, for example, you may say, that Sir, at this temperature why should I calculate the free energy of alpha, it does not exists there?

But at any temperature, at any pressure, whether the phase exists or not, you can always calculate the free energy, excepting, that you will be able to show that it is definitely having a higher free energy than the stable phase. The only question, that comes is, how I calculate it? For example, there are problems, for example, I take this pure metal, bring it to this temperature. I have talked about this difference, what is this difference?

I call this as delta G. The delta G is nothing but, let us say. G of solid minus G of liquid. If I want to find out this delta G, what do I do? I need to find out the G of solid, G of liquid, am I right? You may say, Sir, why should I find out this delta G? It is this delta G, which is the driving force for solidification when a liquid is and this driving force in our nucleation equation. If you remember delta G star, where does this driving force come in the activation barrier? Anyone remembers nucleation kinetics? Delta G star is, yeah, correct, from that equation you come to what is called an activation barrier delta G star. What is the expression for delta G star? Delta G star is 16 pi by 3 into gamma cube by delta G V square. And this delta G V is this delta G that you see here, because that is the volume free energy change. And so, as a result, if I know this, I would know this, of course, I also need to know gamma.

So, this influence has the activation energy. So, the higher the driving forces, the smaller the activation energy. If I take the liquid, bring it to below the melting point, to very much below the melting point because it is much below the melting point, there is a large driving force for the solid to come out. And because there is a large driving force, the activation barrier will be very small and if the activation barrier is very small, if you remember your I, nucleation rate, anybody knows how do we define nucleation rate? This is what it is, nucleation rate is some pre-exponential term into exponential minus delta G star by R T. So, the, the smaller the delta G star, because this is negative and it is exponential, you would see the larger the nucleation rate.

So, that means, if I take a liquid, bring it to below the melting point, to a larger extent I am providing a large driving force because of which I am giving you, I need only a smaller activation barrier and because of which I am, have a higher nucleation rate. And what is the use of it? When I have a higher nucleation rate, I will get fine grain structure.

This is exactly what you see when you take a liquid metal, pour it into a metallic mould and take the same liquid metal pour it into a sand mould. When I pour it into a metallic mould, because of the cooling rate being higher, the liquid does not solidify at the melting point, but gets under cooled to lower temperature and get solidified at below the melting point.

And because of that you see all this happening, and all this if I have to calculate, what is the nucleation rate? And then, without doing an experiment and finding out, getting a micro structure, polishing it, putting it under microscope and measuring the grain size. If I want to really calculate the grain size without doing an experiment, what I need is this. If I have this and if I have this, I can calculate. We will talk about it later.

Thank you.