Materials Science and Engineering
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Lecture – 13
Phase Diagram Part I

Hello friends, we will start with a new topic and this is a very important topic in materials engineering and this is called phase diagram. And we will try to learn few things in this particular lecture and there will be at least a 4 or 5 more lectures which will be dealing with this particular topic only ok. So to start with we will see few terms and a few concepts, in which will be related to phase diagrams ok. For example, we will start with Gibbs free energy, that what do we mean by Gibbs free energy ok. Then we will come to another concept called equilibrium ok.

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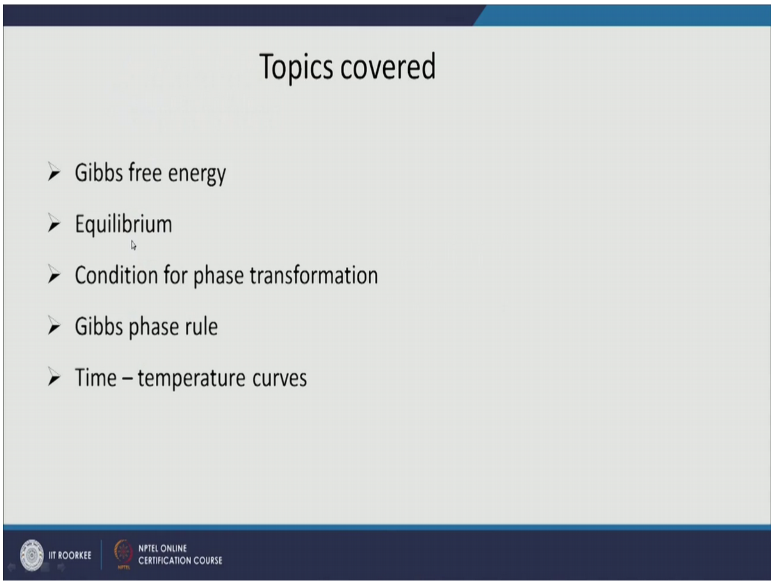

Topics covered

- Gibbs free energy
- Equilibrium
- Condition for phase transformation
- Gibbs phase rule
- Time – temperature curves

That what do we mean by equilibrium ok, condition for phase transformation ok. What do we mean or what is Gibbs phase rule and some time temperature curves for a different type of phase transformation ok.

And from there actually the whole concept of phase diagram also comes ok, that how you plot phase diagram. One of the method is to find out that as a function of time, how the temperature is varying in a system, which is going through a phase transformation ok. So, we will see these concepts which will be later on will be used in phase diagram ok. So, the Gibbs free energy is basically given by an expression like this ok.

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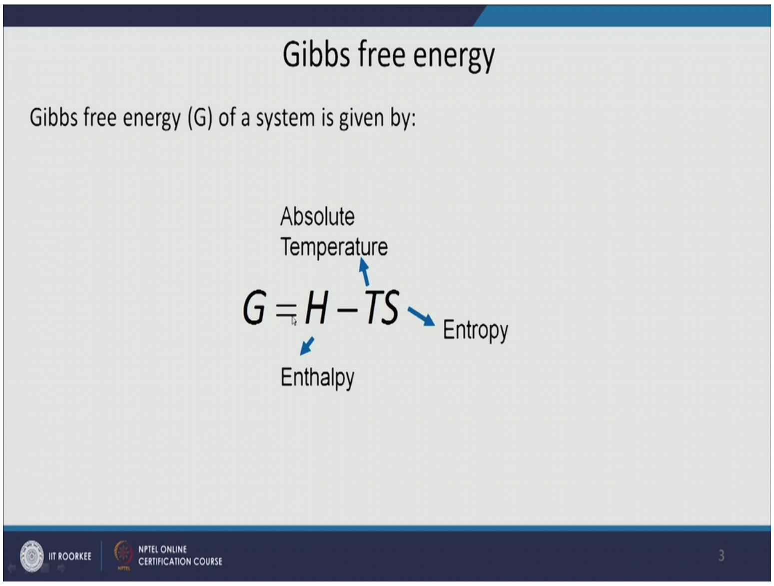

Gibbs free energy

Gibbs free energy (G) of a system is given by:

$$G = H - TS$$

So, for any system I can define a Gibbs free energy by knowing it is enthalpy and it is entropy and there is a relationship, where you have to subtract the entropy term which is multiplied by temperature from enthalpy to get the Gibbs free energy ok.

So, you can understand that the system will be, actually the system will always be a stable system if it is Gibbs free energy is small ok. So, for having a smaller Gibbs free energy either enthalpy has to be low or entropy has to be more ok, because there is a negative term in front of entropy. Now to understand this concept of Gibbs free energy I have I like this particular slide which I made ok, that what how I can explain the this 3 terms of Gibbs free energy enthalpy and entropy. And I, take this analogy of a one a very popular novel called ‘Godfather’ ok. There was there was a movie also a big a very successful movie on that.

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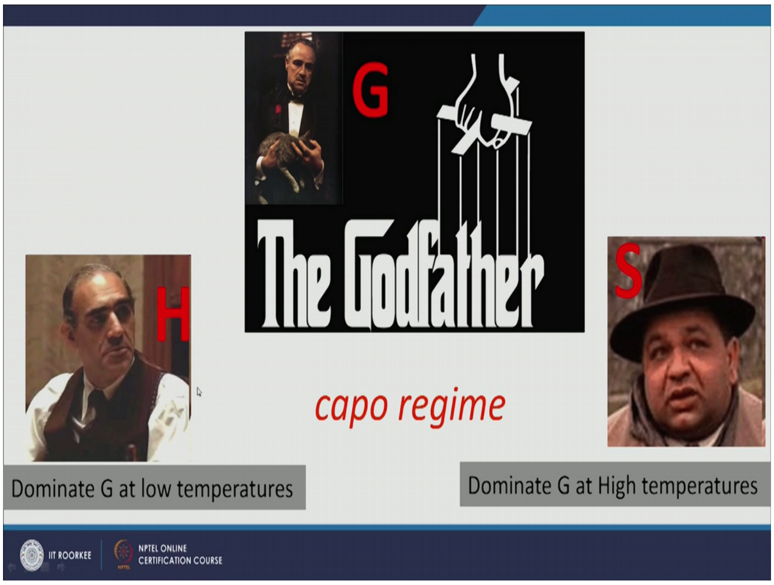

capo regime

Dominate G at low temperatures

Dominate G at High temperatures

And I say that the Godfather which is G which is also relates with the Godfather the he is he is the G the godfather. And this is a very famous actor who portrayed this particular role in the movie. And he is a kind of playing with the system and to help him in playing with this system there are two agents ok.

So, one agent is which is in their term in Italian it is called capo regime and these two are enthalpy and another one is entropy ok. So, these two are helping him the Godfather to play with the system. And there instead of we usually we say when any industry is there or any form is there that they are more devious to make profit ok; here we can say in terms of Gibbs free energy that there motivates to bring down the losses ok. So, these 2 guys will help to bring down the G ok, so they have fewer losses. And both of these guys these two there is main guys they have a region of a where they operate ok.

So, for example enthalpy will be dominating the free energy at low temperature. So, at lower temperature enthalpy term is more important ok; that means, it is his region of a where he will play ok, way where he will operate, because you can understand a Godfather has large number of people who are helping him there he want to give them separate area so that they do not interact with each other. And the entropy will dominate the free energy at high temperatures ok, so they have their own areas ok. So, high temperature whenever you come with the system which is at high temperatures you always remember that entropy should be the term which is going to dominate the free energy and when you are at a low temperature you should always remember that enthalpy is the term which is going to dominate the free energy.

I am not explaining here the enthalpy and entropy parts because, I assume in your mechanical engineering course it will be done in the thermodynamics course ok. So, I am not going into details of enthalpy and entropy, but there is a term called free energy which depends on enthalpy and entropy that is what we are interested in. And this free energy is also going to define whether my system is going to be in equilibrium or not ok.

So, as a system is in equilibrium will be in equilibrium when it is in the most stable state ok, what do we mean by that? When I will say it is it is a most stable state, that it shows no desire to change add infinite term means it will not change you keep that system for any length of time and it is not going to change then it is a stable. So, you are stable when you do not want to change ok. If there is any unstability there has to be some change in the system ok. So, the most stable state means I do not want to change.

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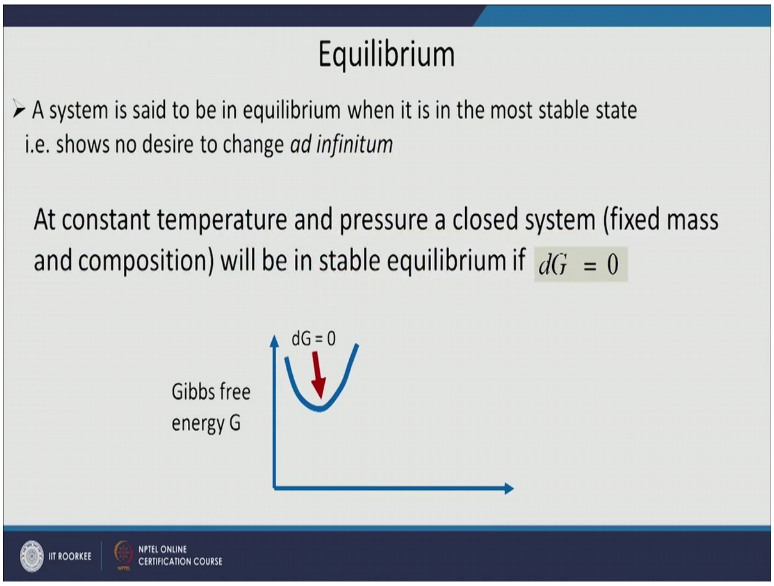

Equilibrium

- A system is said to be in equilibrium when it is in the most stable state i.e. shows no desire to change *ad infinitum*

At constant temperature and pressure a closed system (fixed mass and composition) will be in stable equilibrium if $dG = 0$

So, at a constant temperature and pressure in a closed system; a closed system means it will have fixed mass and composition, so there is no change in mass and composition there is no change in temperature and pressure ok. For different states you can draw a Gibbs free energy curve as shown in the slide. You can see that a Gibbs free energy calculi basically you keep changing the states ok; at different state what will be the Gibbs free energy you will get a curve something like this ok.

So, a stable state for this particular system which is showing a Gibbs free energy curve like this is when it has a minimum energy ok, as we said that when Gibbs free energy is minimum that is going to be the stable state ok. So, when it is going to be minimum? When the slope of this particular curve if I draw a slope at different points the slope of this curve will be 0; that means, the dG is going to be 0 ok. So, when you have this particular condition that is the condition for a stable equilibrium for any system ok. In this state it is not going to change, it is most stable ok.

So, dG is equal to 0 should be the condition ok. But now you will see that there are more scenarios ok, in which this condition will be met and if all those condition are not the stable condition ok. So, we have to kind of define more that what do we mean by this stable condition, and that is this ok.

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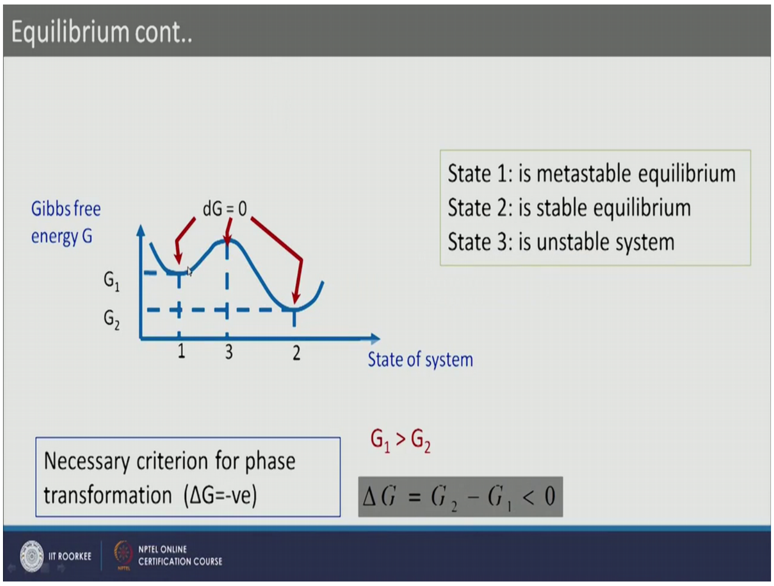

Equilibrium cont..

State 1: is metastable equilibrium
State 2: is stable equilibrium
State 3: is unstable system

$G_1 > G_2$

Necessary criterion for phase transformation (ΔG=-ve)

$\Delta G = G_2 - G_1 < 0$

So, as you can see a Gibbs free energy curve is shown here and you can see the dG is equal to 0 at 3 location. So, slope will be 0 at this state which is we are calling as a state 1, the slope will be 0 at this state which we are calling a state 3 and then the slope will be 0 at this particular condition also which is we are calling as a condition 2.

Now, you can argue that why these different states will be there for a system ok, so to explain that I will take an example of carbon ok. For example, carbon exist in free as a free carbon or it exists as graphite or it exist as diamond ok. So, it has 3 electro morphs 3 different crystal structures are there. And these, diamond are not the stable state for carbon at normal temperature and pressure condition. So, if I put diamond right now here that is not a stable condition for diamond at this a room temperature and pressure for example normal pressure ok. That means, it is not a stable means it should change to the stable state which is basically free carbon ok.

But it is not going to change the reason is that it has a another condition which is called a metastable state ok, it is not exactly unstable it is not exactly stable it is in between that with which is called metastable state ok. So, diamond can exist in a condition where it is not stable and you can understand people buying expensive diamonds and they must be knowing that it is going to stay like that forever ok; that means, that it is not going to change into carbon. If I buy and keep it in my drawer and after few days if I see that and if it is change into free carbon, then we will have a problem ok. So, it is not going to change, it is in a metastable equilibrium and we will see that why it is not going to change into free carbon ok. But before that, another way to explain these 3 conditions these 3 states at which dG is equal to 0 ok. So, state 1 we are calling as metastable equilibrium, a state 2 we are calling as stable equilibrium and a state 3 we are calling as a unstable in a unstable condition ok. Two kind of a bring out this idea more let me give you another analogy ok.

Suppose you have a box of this shape and these points are shown that where there is the center of gravity of this particular object is lying ok. This is 1 state, obviously, it will be more or less a stable state if I put a box like this here, it is going to be like that it is not going to change ok. I can keep box in this position also, so it is lying down now ok. The center of gravity has come down and there is a another condition which is in which I am keeping this box in a tilted condition like this ok. Now you can understand that in the first condition where I am keeping box like this it will remain more or less stable if I keep it keep it lying down it will be very stable condition ok, but if I keep it in tilted on the edge that it is going to come to this position or it will go and lie down ok. So, from this if you just see from the center of gravity point of view, this is the most stable state for this box ok. This is also a stable state but it is a metastable state in the sense if I push it, if I give a nudge maybe it will fall down and come into this lying position.

From lying position if I give it a nudge it is not going to change ok. So, it is more stable state a small change is not going to change it is status or state. Whereas, in this particular condition the tilted condition it is all always either going to fall in the metastable condition or a stable condition? Metastable condition can be there, if I push it maybe it will go to the lying position or if I do not apply any external stimuli it will remain like that ok.

So, that is how we are defining the equilibrium here, this is the metastable equilibrium; that means, it can it if any small push is given it may like to go to the stable position and that small push is basically this uphill which here it has to cross.

So, it has to go just; the system has to go from this state to this state and then will come down to the stable state. So, that much energy is required. For unstable system you do not require to do anything any small perturbation will bring it down to either metastable state or stable state ok.

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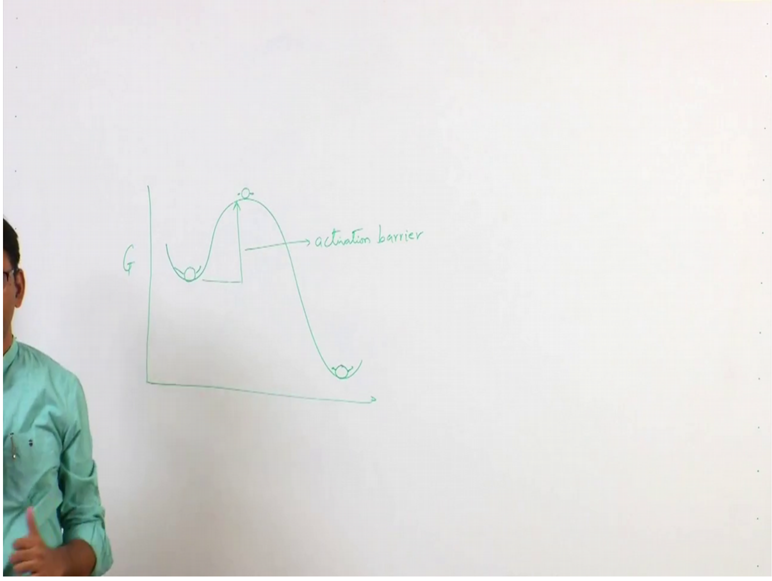

So, you can think of this particular thing as a it is like this, let us say suppose I keep a ball here and try to take in this 2 direction it will again come back to the bottom position if I keep a ball here and if I just do give a small push it will either roll down here or roll down here and I have another ball here, in this case I am also going to if I change the state ok; it will try to come back to the position where it has minimum potential ok.

So, any change you can see that it is going to change the increase the free energy any change here, it is going to increase the free energy on both the side only at this position any change is going to bring down the free energy of the system. So, this is the unstable state this is a metastable state, if in from this metastable state if I give it this much energy to the system I will be able to bring it to unstable condition and then it will go to the stable condition. So, from metastable to stable I need to have this much energy and actually this is what is called activation energy also we saw earlier, the activation barrier which has to be crossed by supplying this much activation energy to bring it to the stable state ok.

So, for the diamond to go to the free carbon state this activation barrier is very high; that means, you will require very high activation energy to take it from the state of diamond and in the state of carbon from diamond to free carbon and that is why it is not going to change in normal pressure a temperature condition, though it is not a stable state of carbon ok, so that is the reason. So, for any system to have a phase transformation for example, a necessary criterion for phase transformation is that the change in the free energy between the 2 states should be negative ok; that means, if I want to subtract G 2 minus from G 1 if it is less than 0; that means, it is negative then my system would like to go from this metastable condition to the stable condition, so there should be a phase transformation when this condition exists ok.

Now we will understand few terms before we go forward ok, for example 1 term which I think you heard earlier also when we were discussing microstructure is called phase ok. So, what do we mean by phase?.

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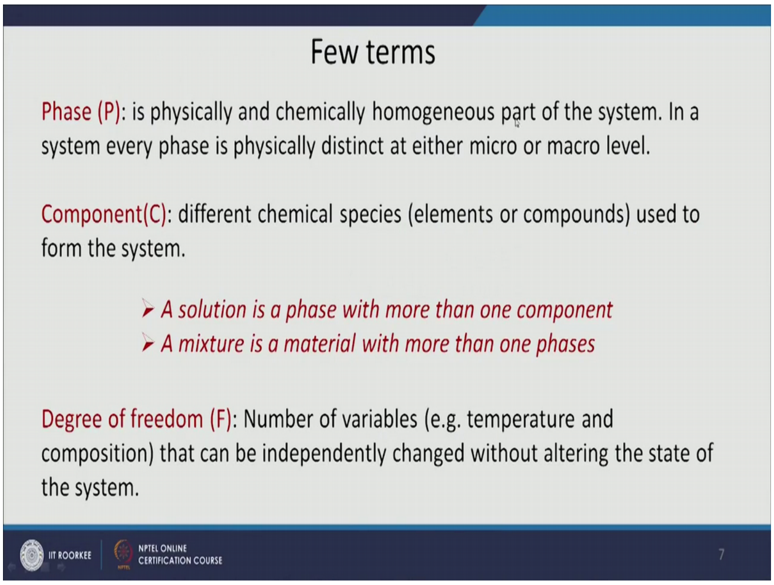

Few terms

Phase (P): is physically and chemically homogeneous part of the system. In a system every phase is physically distinct at either micro or macro level.

Component(C): different chemical species (elements or compounds) used to form the system.

- *A solution is a phase with more than one component*
- *A mixture is a material with more than one phases*

Degree of freedom (F): Number of variables (e.g. temperature and composition) that can be independently changed without altering the state of the system.

Phase is the physically and chemically homogeneous part of the system ok. So, for example, if I take water it is 1 phase of a H2O if I put ice in that then that is another phase ok. So, it is it should be physically in that case chemical chemically it is same both are H2O but physically it is different ok, 1 is in liquid form another 1 is solid form ok.

So, when we want to call it a particular phase only water in liquid form it is one phase water in solid, solid form as a ice another phase; if I put ice in water then they these are two phases chemistry same. So, physically and chemically all also should be homogeneous part of the system ok, in a system every phase is physically distinct at either micro or macro level ok; physically distinct it should be then only we will call it as phase ok. For example, I can add sugar in water ok, so when I have just added sugar is there in solid form water is there in liquid form, physically they are in solid and liquid two different forms chemically also it is this is water that is sugar two different chemical species, so these are two phases ok.

Now, suppose I mix it now after some time you would not see where is sugar has gone ok. So, now, the water is only one phase water having sugar, sugar you can think it as a solution now ok, but chemically and physically it is a homogeneous mixture ok. I cannot see where the sugar particle has gone or where the water particle is there. So, microscopically if I see I do not see any difference between the two and I will see it as a homogeneous distribution of sugar in water ok, physically also it will be all liquid chemically also if you see microscopically it is going to be homogeneous, so it is one single phase now ok.

What do you mean by component? component means different chemical species elements or compound used to form the system ok. So, when I added a ice into water chemically component wise both have one component only ok, phase are 2 different phases when I added sugar in water there were 2 different phases components also one H2O, 1 is sugar molecule; when I mix them now there is only 1 phase, but still there are 2 components 1 is water molecule another is sugar molecule ok.

So, a solution if you want to understand what do we mean by solution is a phase with more than 1 component, as I told you sugar dissolved in water it is a solution of sugar in water. So, it is a single phase, but having more than 1 component a mixture is a material with more than 1 phases. If you have 2 different phases then we will call it as mixture ok, there is another term called degree of freedom which is basically the number of variables that can be independently changed without altering the state of the system ok; variables can be temperature composition and so on ok.

So, I can independently change them and still I have the same state of the system ok. So, that is the degree of freedom I have, solid solution basically it consists of atoms of at least 2 different type where solute atoms occupy either substitution or interstitial positions.

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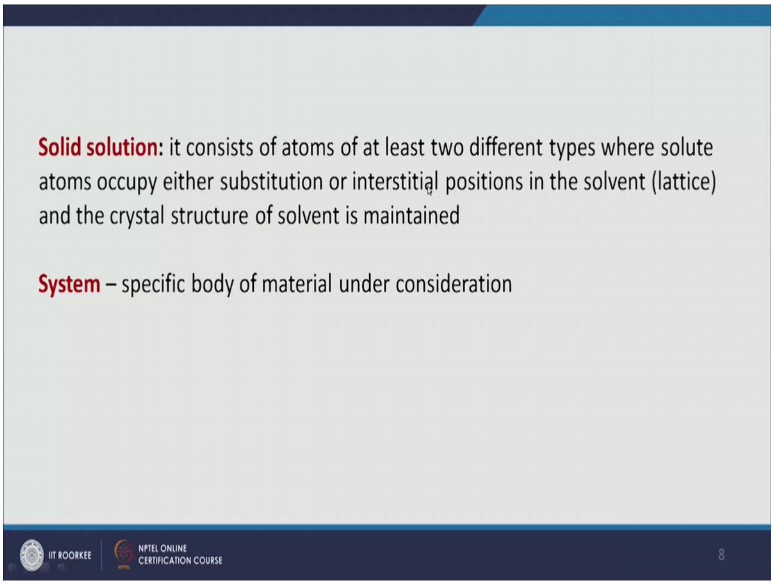

Solid solution: it consists of atoms of at least two different types where solute atoms occupy either substitution or interstitial positions in the solvent (lattice) and the crystal structure of solvent is maintained

System – specific body of material under consideration

We have discussed this in defects that an atom can occupy a substitution position or interstitial position ok. So, these are called solute solution. So, it can be either substitution solid solution or interstitial solid solution; depending upon the atom is occupying a substitution position or interstitial position in the solvent which is the host lattice having the host atoms and the crystal structure of solvent is maintained.

The most important thing here is that whatever is the crystal structure of the solvent ok. So, when I add carbon in iron to make steal, my crystal structure of iron which is bcc at room temperature is not going to change ok. So, my crystal structure of solvent should not change when I am adding any atom or any I am adding any solute atom. A system is basically a specific body of material under consideration. So, in thermodynamics also you must have seen that you can define system in different ways ok. So, that is what you the given material which you are considering that can be called as system.

Now, coming to Gibbs phase rule a very important relationship to understand the phase diagram there are different type of variables of a system.

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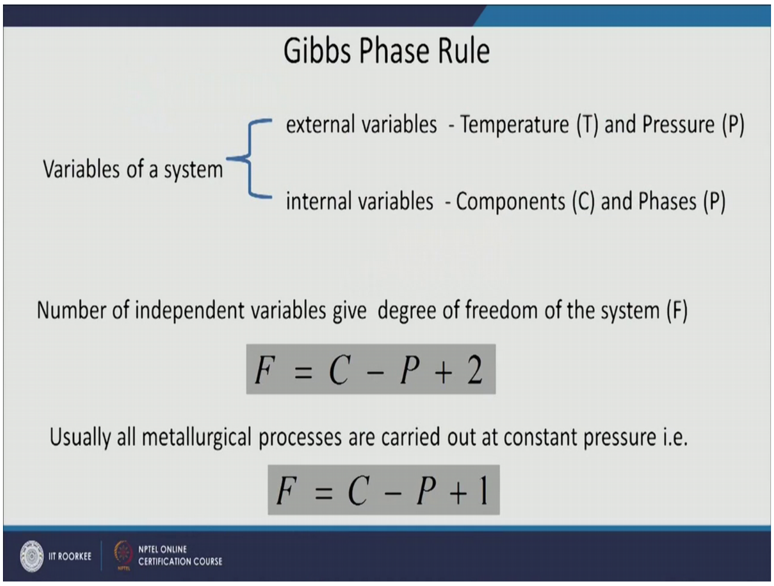

Gibbs Phase Rule

Variables of a system
- external variables - Temperature (T) and Pressure (P)
- internal variables - Components (C) and Phases (P)

Number of independent variables give degree of freedom of the system (F)

$$\boxed{F = C - P + 2}$$

Usually all metallurgical processes are carried out at constant pressure i.e.

$$\boxed{F = C - P + 1}$$

Some are external variable like temperature and pressure some are internal variables like components and phases. So, the number of independent Gibbs free a Gibbs phase rule, actually gives the relationship between the num degree of freedom a system has and the variables which are there in a system. So, C will be one variable phase will be one variable and there is one constant added to here that is to take care of temperature and pressure ok, so plus 2 means one is for temperature one is for pressure.

So, how many variables are there that will give me a independent variable that will give me the degree of freedom a system have. So, usually because all metallurgical process are carried out at constant pressure because, we do not change whatever is the normal atmospheric pressure is there in that we do all the heat treatment or solidification or melting or whatever we will take out the pressure from this equation. So, now instead of 2 we will only have 1 here. So, now, my degree of freedom will be calculated from what is the number of components in the system, what are the number of phases in the system and one for the temperature ok.

. So, this is the Gibbs phase rule I have not gone into the derivation of that, but we do not have to worry about that right now. Now let me just use this particular Gibbs phase rule in one a particular condition.

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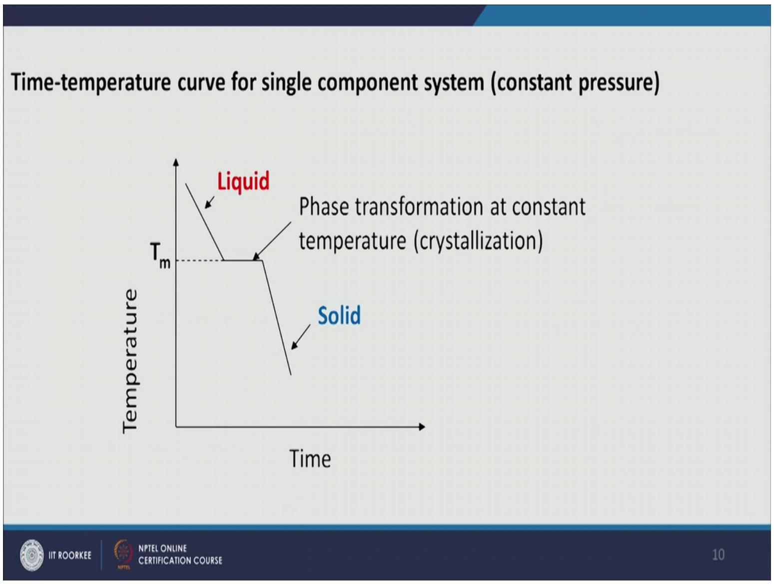

Time-temperature curve for single component system (constant pressure)

For example the second one is that the slide shows you a time temperature curve for single component system; that means, if I do a solidification or let us take water from liquid state it is going into solid state ok. So, we have taken water we are continuously decreasing the temperature of the system by some external means and we are measuring that how the temperature is varying we have put a thermocouple there. So, temperature is coming down in the liquid state ok.

At some point where the transformation starts from liquid to solid ok, that we know that the whole phase transformation from liquid to solid will happen at a constant temperature which is we can call as melting point or solidification point. So, we are we are saying that it is T m ok. So, phase transformation at constant temperature is happening here crystallization and after complete solidification, now the temperature is coming down in the solid ok. Now this is a one component system we have taken one liquid let us say water pure water and for that we have done this experiment ok. When it was a liquid if you apply a Gibbs phase rule which was if you remember.

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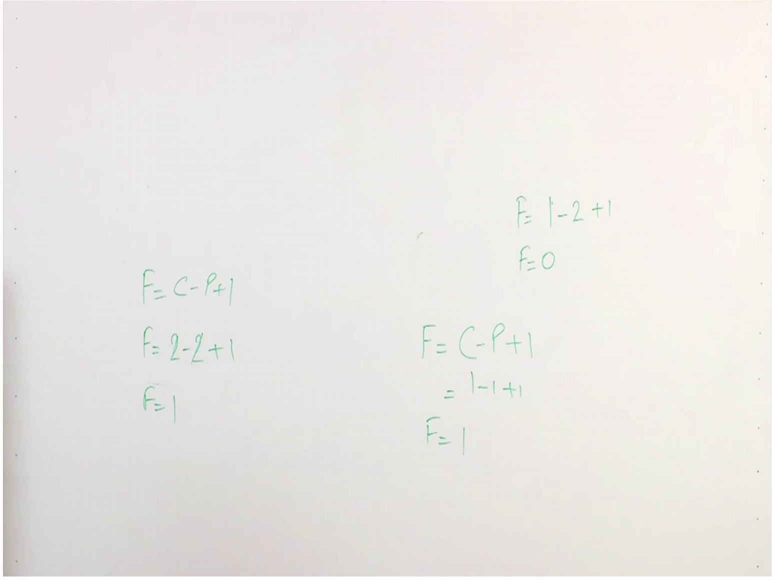

$F = C - P + 1$

$F = 2 - 2 + 1$

$F = 1$

$F = 1 - 2 + 1$

$F = 0$

$F = C - P + 1$

$= 1 - 1 + 1$

$F = 1$

F equal to C minus P plus 1 ok, now when what we when it was in liquid state you had 1 phase 1 liquid phase you had 1 component which is the water ok. So, 1 minus 1 plus 1 will give you F equal to 1 ok. So, there was one degree of freedom when it was in liquid state; when it was in solid state again you can do the same analysis it is 1 solid 1 water molecule 1 phase that is solid phase plus 1 again you will get the degree of freedom as 1.

What happens when it is doing the transformation ok? So, we know that at the transformation the solid and liquid are in equilibrium ok; that means, now you have 2 phases. So, if I again do the same analysis for degree of freedom component is same it is all water, whether it is in solid phase or liquid phase; phase you have 2 sorry I will write 1 because it is 2 phases in equilibrium and plus 1, this is 1 minus 2 will be minus 1 minus 1 plus 1 will be 0. So, this is the degree of freedom is 0. So, now, you understand that because degree of freedom is 0 that is why the transformation is happening at a constant temperature, I cannot change the temperature now.

So, for this particular case when the transformation is taking place it is going to take place at a constant temperature, because my degree of freedom of the system is 0, I cannot change anything there are no independent variables. So, all the variables are fixed and that is why the temperature is also fixed and I cannot have any variation in the temperature, the transformation has to take place as a constant temperature ok.

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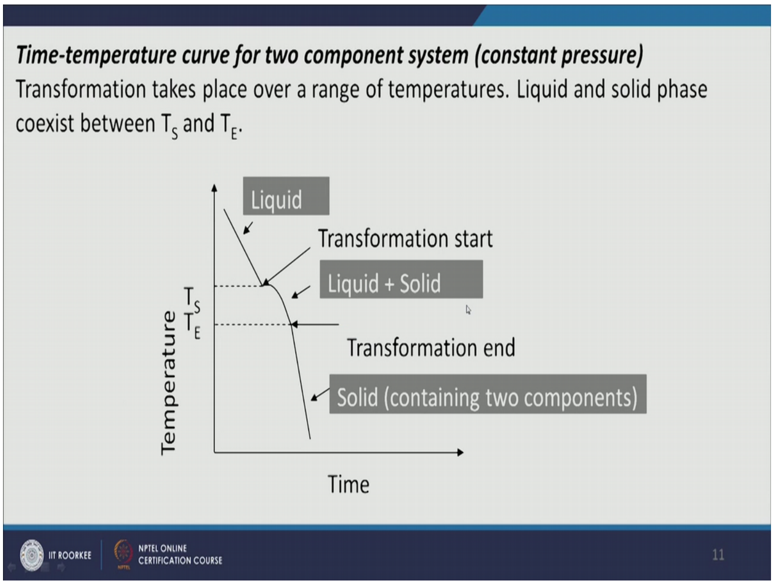

Time-temperature curve for two component system (constant pressure)

Transformation takes place over a range of temperatures. Liquid and solid phase coexist between T_S and T_E.

Liquid

Transformation start

Liquid + Solid

Transformation end

Solid (containing two components)

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This is a another case time temperature curve for two component system at a constant pressure, again I can use the same equation.

So, transformation take place over a range of temperature liquid and solid phase coexist between Ts and T E ok. Now you see in comparison to the previous slide here the transformation is taking place at a over a temperature range ok, in the previous case the transformation took place at a constant temperature why that is so? So if you see this is a 2 component system this is a 2 component system. Again I can use the same equation F is equal to C minus P plus 1 ok. So, components are 2, where the transformation is taking place 2 phases are in equilibrium ok.

So, now if I put 2 components are there my this is my 2 component system, 2 phases are in equilibrium when the phase transformation is taking place and one these 2 cancel, so you have degree of freedom is 1. So, now, as opposed to the previous one case I have 1 degree of freedom left in the system and that is why the transformation is taking place over a temperature range, there is in single component system the transformation from liquid to solid was taking place at a constant temperature ok.

So, this is how the time temperature curve vary between single component to component system and how degree of freedom can explain that why the transformation taking place at different temperatures. And this idea then we will use that I can do these kind of experiments, to find out the phase diagram of any system that we will do in the next lecture ok.

Thank you.