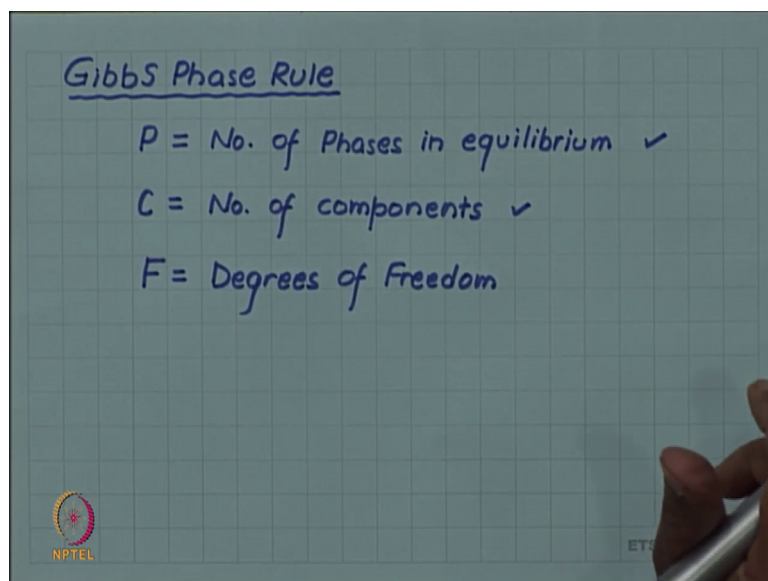


Introduction to Materials Science and Engineering
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Lecture – 76
Gibbs' phase rule

Let us now discuss an interesting rule known as Gibbs phase rule. This is an important rule, in the phase diagram and we will discuss this now.

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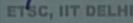
So, the Gibbs phase rule relates a relation between the number of phases, P is number of phases in equilibrium C is the number of components in the alloy system, which we are considering. And we will define a quantity F known as degrees of freedom. Already through the introduction of the phase diagram we understand; what are the number of phases and what is the meaning of number of components. The degrees of freedom require a bit of explanation and we will do that now. So, before we understand degrees of freedom.

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Thermodynamic Variables for Gibbs Phase Rule

- *Pressure and Temperature (if both are variables)*
If Pressure is fixed, then only temp is variable
- *Composition variables*
** Only phase compositions are considered as variables*

Overall alloy composition is not a variable, except when we have a single phase equilibrium when alloy composition is also the phase composition.

Let us may look at what is meant by the thermodynamic variables in this context, the thermodynamic variables for Gibbs phase rule. So, by thermodynamic variables we mean first 1 set of thermodynamic variables is pressure and temperature, pressure and temperature. If both are variables, in some cases like for example, the kind of diagram which we are considering binary diagram, we did not have the pressure as variable we only has had the temperature as variable.

So, in some cases pressure can be fixed. So, in those diagrams tacitly we assumed that the pressure was fixed at 1 atmosphere. So, if pressure is fixed and only temperature is variable. If pressure and temperature are not the only variable, then we have composition variables and for the application of Gibbs phase rule, the relevant composition variables are the phase compositions, only phase compositions are considered as variables. Overall alloy composition another composition which is relevant in the phase diagram as we have seen is the alloy composition so, but overall alloy composition is not considered as a variable, is not a variable except, except when we have single phase equilibrium, when alloy composition is also the phase composition.

So, this is important to keep in mind. So, only phase compositions should be considered as variables when we are applying the Gibbs phase rule. How many composition variables we will have?

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No. of composition variables.


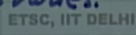
If there are C components then one need to specify $C-1$ compositions for each phase.

\therefore for P phases one needs $P(C-1)$ composition variables.

Total no. of variables

$V = P(C-1) + 2$ if Pressure and Temp are variables.

$V = P(C-1) + 1$ if P is constant only Temp varies.

Let us say number of composition variables. If there are C components, let me use capital C if there are C components, then one need to specify the composition of the phase, one need to specify C minus 1 compositions. So, if you give the ratio or the fraction of C minus 1 components, then the last component can always be found by 1 minus the sum of other compositions.

So, you only need 1 less than the number of components so, many composition variables to be specified for each phase. So, if there are C component then 1 needs to (Refer Time: 08:13) C minus 1 compositions for each phase therefore, for P phases one needs P into C minus 1 composition variables, thus the total number of variables, let me call that V will be P into C minus 1 plus 2, if pressure if pressure and temperature are variables, or V will be P into C minus 1 number of composition variables will remain same, but instead of 2 you will have 1 if pressure is kept constant, if P is constant and only temperature varies. We have so, many variables. Now we can talk of the degrees of freedom.

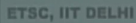

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Degrees of Freedom:

F = No. of thermodynamic variables which can be specified independently without changing the phases in equilibrium.

Since there is thermodynamic equilibrium, there are equilibrium relations between the thermodynamic variables. If we specify certain no. of variables, others are automatically fixed by these equilibrium relations.

$F \leq V$



So, there are certain thermodynamic relations between these V variables because, the phases are in equilibrium there are equilibrium conditions. So, those equilibrium conditions then define the degrees of freedom, let us define the degrees of freedom as number of thermodynamic variables, which can be specified independently number of thermodynamic variables, which can be specified independently without changing the phases in equilibrium.

Since there is thermodynamic equilibrium, there are equilibrium conditions, the equilibrium relations between the dynamic variables. So, that is why if we specify, if we specify certain number of variables, others are others are automatically fixed by these equilibrium relations, F will always be less than equal to the number of variables which you have the thermodynamic variables because, all the variables you may not be free to specify, as soon as you specify certain minimum number of variables others get decided by these equilibrium relation.

So, how many can you specify independently that is what is given by the degrees of freedom. Degrees of freedom number of variables which you can specify independently and, V is the total number of variables.


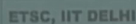
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GIBBS PHASE RULE:

$F = C - P + 2$ if both pressure and temperature are variables

$F = C - P + 1$ if only temperature is variable (Fixed Pressure)

Applicable for binary phase diagrams considered by us. (Pressure = 1 atm)

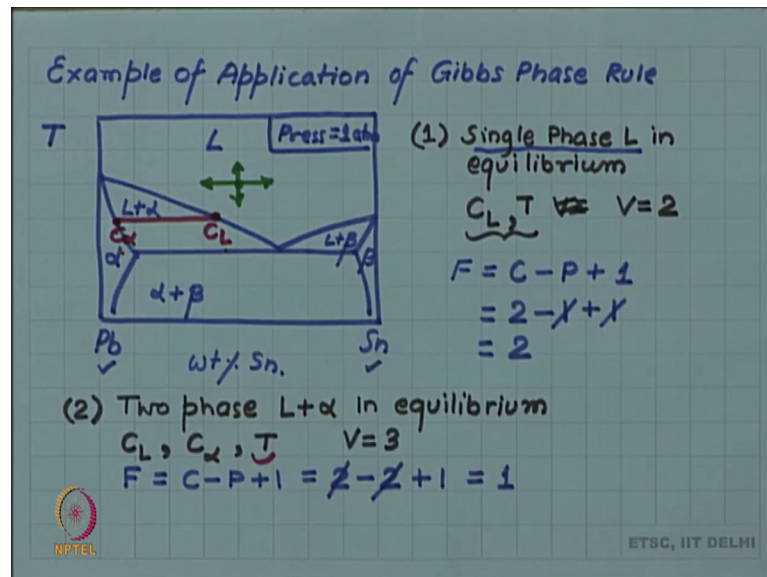



So, let us now give the rule itself, so rule is quite simple although we are not going into the derivation of the rule, we are only giving the rule. So, the rule is the degrees of freedom F is number of components minus the number of phases plus 2, this is if both pressure and temperature are variables. Another form of Gibbs phase rule so, this 2 this 2 actually comes from pressure and temperature, this 2 is from pressure and temperature is representing these 2 variables, but if pressure is fixed as in the diagrams which we have considered till now.

So, if pressure is fixed then this will become 1 if only temperature is variable fixed pressure so. In fact, this is the binary phase diagram, which we have considered this is the law applicable for applicable for phase diagrams, considered bias because although, we did not specify specifically in our diagrams pressure was tacitly assumed to be 1 atmosphere.

So, P can confuse with the number of phases. So, I am not writing that so, let us let me write pressure, pressure is equal to 1 atmosphere. So, let us look at the rule will become clearer, once we consider some example.

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So, let us look at the example of its application example of application of Gibbs phase rule. So, let us look at the diagram with which we are now very familiar the lead tin diagram. So, this is the lead tin diagram this is the liquid phase, alpha phase, beta phase, liquid plus alpha, liquid plus beta, alpha plus beta, this is the temperature axis and this is the composition axis.

Now, let us consider a situation of a single phase equilibrium. First example let us consider single phase liquid in equilibrium. So, what are our variables? Since only a single phase liquid is there, we have only one composition variable C_L and we have the temperature C_L and T are the variables. So, the total number of variables is 2, one phase composition single phase is in equilibrium and one temperature.

So, we have 2 variables the question is if I want to have liquid in equilibrium, which of these or how many of these variables I can vary. So, let us apply the phase rule. So, the phase rule gives us the degree of freedom F as the number of components minus number of phases in equilibrium plus 1 because, this is an isobaric let me write that pressure in one atmosphere.

So, I have the Gibbs phase rule in this form the number of components here, the components are lead and tin. So, the number of components is 2 minus the number of phases 1 plus 1. So, the degrees of freedom is 2. So, what is what is it telling us it is telling us that, if I want to have a single phase liquid in equilibrium I am free to specify both the liquid composition and the temperature. And you can see the single phase liquid

here can be obtained, if I want a single phase liquid in equilibrium, I can vary the liquid composition and I can vary the temperature and I can still have liquid in equilibrium.

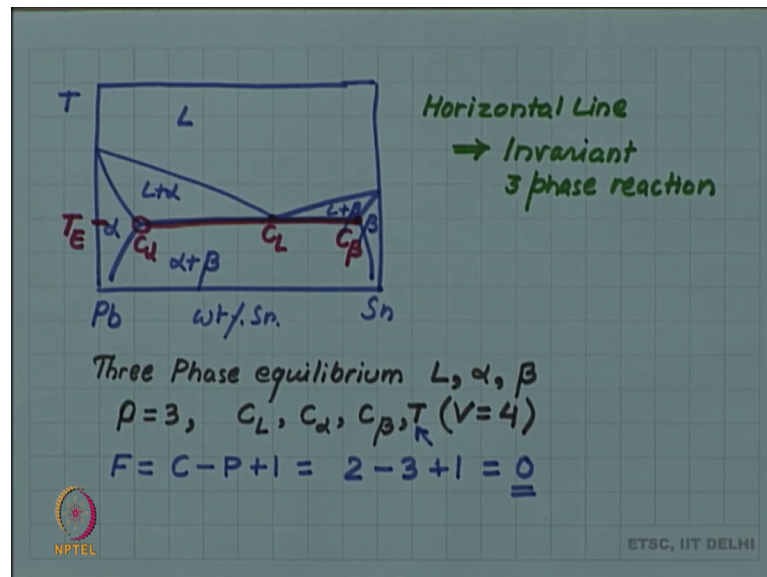
Now, let us let us consider the two phase equilibrium, two phase let us say liquid plus alpha, two phase liquid plus alpha in equilibrium. Now how many variables I have, I have since the 2 phases are there I need composition of both the phases. So, I have C L and I have C alpha and of course, I have T so the number of variables increases by 1 with respect to the previous case. Now I have 3 variables, but what has happened to our degree of freedom.

If I now apply the degree of freedom $C - P + 1$ the number of components is still 2, but the number of phases have also become 2 liquid and alpha. So, you find that although the number of variables increased the number of degrees of freedom actually decreased, we have only one degree of freedom. So, what the phase rule is telling that although you have 3 variables, you have composition of liquid, composition of alpha and temperature T only one of these you are free to specify. The other 2 will be determined by the equilibrium conditions.

How is that? So, let us look at that suppose we choose to specify T. Now if I specify at T, you can see and I want to be in the liquid alpha region. So, I have to be in the two phase field. So, at and for a given temperature the liquid and alpha in equilibrium are given by the tie line. The end points of the tie line the alpha end of the tie line gives me the composition of alpha. And the liquid end of the tie line gives me the composition of liquid.

So, as soon as I specify the temperature and I insist on a liquid plus alpha equilibrium, the alpha has to have the composition given by the tie line and the liquid has to have the composition again given by the tie line I am not free, I cannot ask for equilibrium of between liquid and alpha at this temperature, with alpha composition being something else or a liquid composition being something else. So, only one of these 3 variables I am able to specify.

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If I now continue with one more case; let me continue with one more case and that is a 3 phase equilibrium, suppose I insist on a 3 phase equilibrium, in this alloy system. If I insist on 3 phase equilibrium what will be the situation. So, I have. So, let us consider 3 phase equilibrium.

Let us insist that we have liquid, alpha, beta all 3 phases in equilibrium then of course, I have now 3 phases. So, P is equal to 3 and I will have 3 composition variables C liquid, C alpha, C beta, and a temperature variable. So, my number of variables has grown to 4. So, I have many variables, but what has happened to the degrees of freedom. So, if I apply F is equal to C minus P plus 1 this gives me number of components is 2 number of phases has become 3 and I have 1 there. So, you can see that you get 0 degrees of freedom.

What is it telling although we have 4 variables, we have liquid composition alpha composition beta composition and temperature, I have 4 variables, but if I insist on this 3 phase equilibrium, I am not free to vary any of these variables? So, I will have you if at all I will have this equilibrium at fixed composition of liquid alpha beta and a fixed temperature. And this is what the eutectic line gives you the eutectic line gives you that the alpha composition is this, the liquid composition is here in the middle and the beta composition is at the beta end.

And the temperature is fixed at the eutectic temperature. So, the 3 phase equilibrium is possible only at this temperature and the composition of each phases is specified. So, the

eutectic horizontal this eutectic horizontal is actually the line of 3 phase equilibrium. So, that is why this eutectic reaction where you have this 3 phase equilibrium is known as an invariant reaction, you cannot vary any of the variables the degrees of freedom is 0.

Also see that since temperature one of the variables, also is going to be fixed all these 3 phases will occur at that same temperature, that is why for any invariant reaction you will have a horizontal line, or the reverse of this is also true that whenever in a binary phase diagram, if you see an horizontal line horizontal line will always be indicative of an invariant reaction, invariant 3 phase reaction. Eutectic reaction is only one of the example, we are soon going to see other examples of invariant reactions.