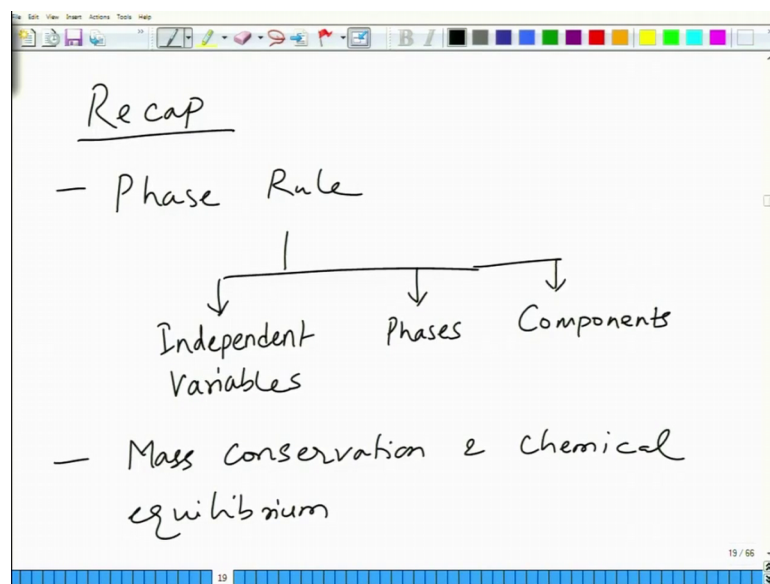


Phase Equilibria in Materials (Nature and Phase Properties of Materials - II)
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Lecture – 18
Gibbs Phase Rule: Unary and Binary System

So, we start a new lecture again. So, this is lecture number 20. So, what we started in the previous lecture was so, let me just give you a recap.

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So, we discuss we started our discussion on what we called as Phase rule. And phase rule is basically equation that will come up with which relates the number of phases in a system number of components in a system with the total number of independent variables that you can have to predict the phase equilibrium. So, we began this by considering a multi component system. So, in that total number of variables are temperature pressure and the all the components. So, you have let us say C number of components.

So, total number of C , C number of components make up P number of phases. Let us say in a given system as a function of various conditions. So, total number of possible variables is nothing, but C into P plus 2. Now, how do we now limit them how do we find out what is the total number of independent variables in these out of this $C P$ plus 2 number of total number of variables. This requires us to consider 2 things. First the

concept of mass conservation in a given system, second is the concept of chemical equilibrium in a given system.

So, this is going to be determined by so, basically we are going to determine we are going to relate independent variables phases and components. And this is going to be based on conditions of mass conservation and chemical equilibrium.

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total no. of variables = $CP + 2$

(i) Mass Conservation \rightarrow P equations for C Components

no. of equations = P equations

(ii) Chemical Equilibrium

So, we saw that total number of variables was equal to $CP + 2$. And then from mass conservation it follows, it is not conservation it is conservation it follows that number of constraints. So, we have if we have C components and we have P phases and we have so, $CP + 2$ is the first one and then we had P equations for C components and basically was and this gives rise to total number of independent total number of equations.

So, if you know $P - 1$ equations you would obviously, know P th equation for C component. So, this will make it C into $P - 1$ from this. Then we looked at chemical equilibrium. So, this is the number of variables $CP + 2$ total number of equations which is nothing, but you can say number of constraints C into $P - 1$ from the mass conservation.

So, this is the first condition, the second condition is chemical equilibrium which we started to do. So, basically what we were considering is we have 2 phases phase y phase i

and phase k. The J th component a small amount of J th component is transferred from i th phase to J th phase.

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$$\delta G_i = \frac{\partial G_i}{\partial N_J^i} \cdot \delta N_J^i$$

$$\delta G_i = \mu_J^i \cdot \delta N_J^i$$

$$\delta G_k = \mu_J^k \cdot \delta N_J^k$$

$$\delta N_J^i = -\delta N_J^k$$

$$\delta G_k = -\mu_J^k \cdot \delta N_J^i$$

So, what we did was, we have for the i th phase we wrote delta of G i is equal to del G i divided by del N J i into delta of N J i. This is equal to delta of G i into mu J i into del N J i. Similarly, for k th phase so, if this component J goes from i to k the incremental free energy change for k th phases del G k is equal to mu J k into del N J k. So, this is, but we also know for mass conservation that del N J i is equal to del N J k minus of, because the amount of solute which leaves J th phase i th phase is same as the amount of solute which enters the k th phase. So, if that is true we can write del G k to be equal to mu J k minus of mu G k into del of N J i.

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The image shows a whiteboard with handwritten mathematical equations. At the top, it says "Total change in Free Energy, $dG = 0$ ". Below that, it shows $dG = \delta G_i + \delta G_k = 0$. The next line is $\mu_J^i \cdot \delta N_J^i - \mu_J^k \cdot \delta N_J^i = 0$. Finally, an arrow points to a red-bordered box containing the equation $\mu_J^i = \mu_J^k$. The whiteboard has a toolbar at the top and a status bar at the bottom showing "22 / 66".

$$\text{Total change in Free Energy, } dG = 0$$
$$dG = \delta G_i + \delta G_k = 0$$
$$\mu_J^i \cdot \delta N_J^i - \mu_J^k \cdot \delta N_J^i = 0$$
$$\Rightarrow \mu_J^i = \mu_J^k$$

So, if the total now, for system to be in equilibrium the total change in free energy which means dG must be equal to 0 so that means, δG_i plus δG_k must be equal to 0. So, this is dG is equal to 0. So, what it means is that substitute the so, this is μ_J^i multiplied by δN_J^i minus of μ_J^k into δN_J^i ; this is equal to 0. Basically what it means is that μ_J^i is equal to μ_J^k .

And that is what we said earlier the so, this is basically the proof of what we said earlier when we drew the common tangent; that in the first instance we saw it graphically now we see it mathematically. That for a 2 phase equilibrium or for a multi-phase equilibrium the chemical potential of J th element in i th phase must be equal to that in the k th phase. So, that is chemical potential of a component in various phases in equilibrium must be the same.

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For 'C' components in 'P' phases

$$\mu_1^I = \mu_1^{II} = \mu_1^{III} = \dots = \mu_1^{P-1} = \mu_1^P$$

...

$$\mu_C^I = \mu_C^{II} = \dots = \mu_C^P$$

Total no. of equations = $C \cdot (P-1)$

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So, if you generalize so, for now for C number of components in P number of phases. So, how do you write this? So, let us say this is μ_1 phase I, let us say I plus μ_1 II plus μ_1 III plus μ_1 P equal sorry not what am I just doing this is not plus, equal to my apologies so, this is equal to. So, chemical potential of a component in first phase, second phase or third phase is equal. And they are all equal from first to P th phase in all the phases.

So, if you now extend it for C th component. So, μ_C 1 is equal to μ_C 2 and this is equal to μ_C P. So, basically what we are saying is that this is the transfer of C components in P phases for all those transfers and multi-phase equilibrium all these equations are there. So, we saw that number of equations that you have here is so, total number of equations.

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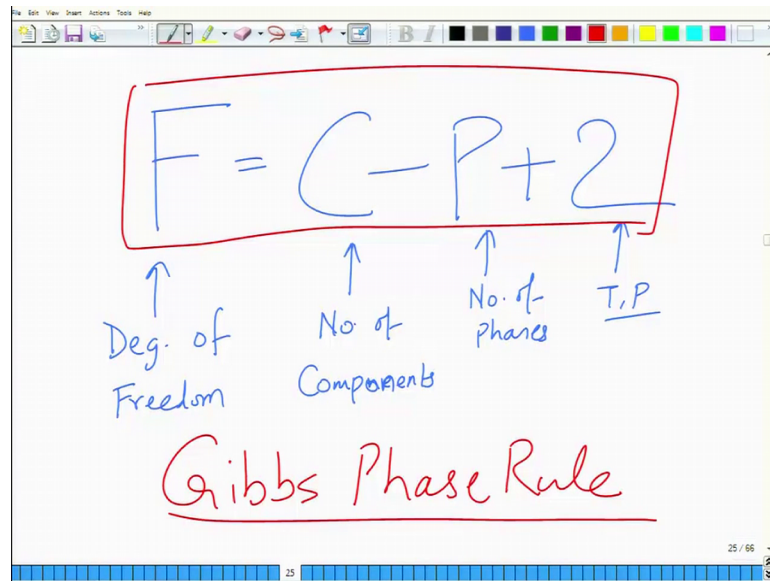
$$\begin{aligned} \text{Total no. of equations (N)} &= C(P-1) + P \\ &\quad \uparrow \quad \quad \quad \uparrow \\ &\quad \text{Chemical} \quad \quad \text{Mass Conservation} \\ &\quad \text{potential equality.} \\ \text{Total no. of independent variables} &= M - N \\ &= CP + 2 - C(P-1) - P \\ F &= C - P + 2 \\ &\hookrightarrow \text{Degree of Freedom} \end{aligned}$$

In the first case we saw total number of equations is C into P minus 1 and then we have total of P number of phases ok. So, if you from this condition if you know; so, you see that if μ_1 is same across all the phases then it has to be true for all the P phases. If you know that this condition is true for so, we have total number of equations as P equations. So, here I wrote sorry I wrote here P minus C into P minus 1 equations I should say P equations. And, from this since we are writing for C components in P phases there are the conditions are μ_1 is equal to μ_1 P and this is for all the C components, the total number of equations are is equal to number of components.

So, you have number of components C multiplied by P minus 1 because by equality if you know up to μ_1 P minus 1 obviously, P th known ok. So, this is C into P minus 1. So, total number of equations that you have is, P number of equations from mass conservation and C into P and minus 1 number of equations from chemical equilibrium chemical potential let us say quality.

So, what is the total number of variables? So, total number of independent variables; so, this is nothing, but N and the CP plus 2 will be equal to M . So, we are saying this is basically M minus N . So, M is CP plus 2 and N is C into P minus 1 minus P . So, if you now just do the math this is basically C minus P plus 2, C minus P plus 2 and this total number of very independent variables is called as F for a given system it is called as degree of freedom.

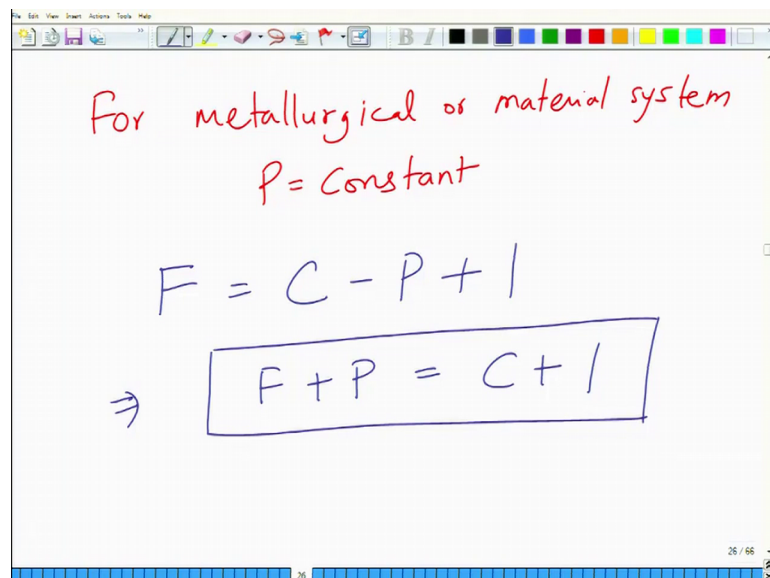
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The image shows a handwritten equation $F = C - P + 2$ enclosed in a red box. Below the equation, four arrows point upwards to the terms: F is labeled "Deg. of Freedom", C is labeled "No. of Components", P is labeled "No. of phases", and 2 is labeled "T, P". Below the equation, the text "Gibbs Phase Rule" is written in red and underlined. The slide number "25" is visible in the bottom right corner.

So, Gibbs Phase Rule is given as F is equal to C minus P plus 2. This is degree of freedom which means number of independent variables number of components, this is number of phases and this is temperature and pressure 2 extra variables. So, this equation is called as Gibbs phase rule; Gibbs phase rule which correlates the number of component number of phases with the degree of freedom and a given set of plus temperature and pressure being two other variables.

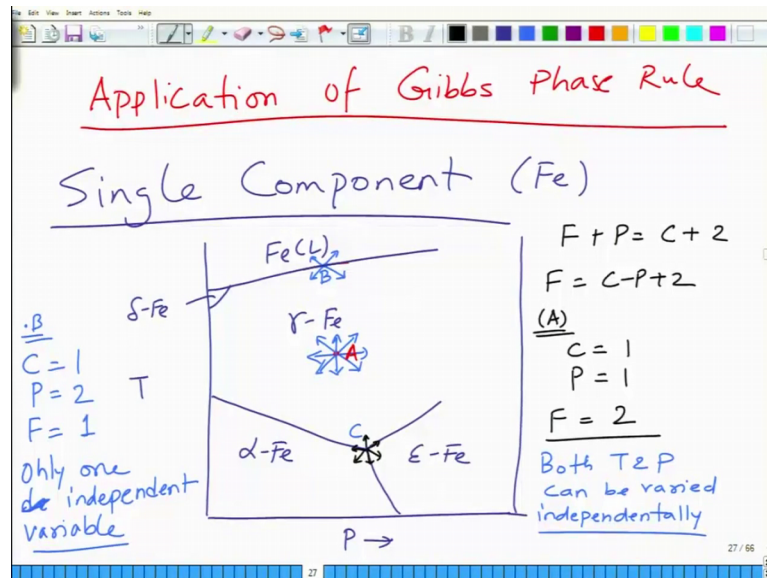
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The image shows handwritten text in red: "For metallurgical or material system" and " $P = \text{Constant}$ ". Below this, the equation $F = C - P + 1$ is written. An arrow points to the equation $F + P = C + 1$, which is enclosed in a blue box. The slide number "26" is visible in the bottom right corner.

So, generally for metallurgical systems or even materials systems pressure is constant. And, hence F is equal to C minus P plus; you can write this equation in a reform you can write this as F plus P is equal to C plus 1. So, F plus P you can say you know family planning and [laugh] C plus 1 is like 1 child. So, it is easy to remember. So, F plus P is equal to C plus 1 is the Gibbs Phase Rule.

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Now, let us see how this Gibbs phase rule applies to different phase systems in materials. So, now let us see how we apply this let us say application of here Single Component system. So, for the Single Component system we will begin with the iron system to begin with. So, here we draw the phase diagram as a function of temperature and pressure. So, this is temperature this is pressure. So, with phase diagram is something like this alright. So, this is $F e$ in liquid state this is δ $F e$ this is γ $F e$ this is α $F e$ and this is ϵ $F e$. So, this is pure $F e$.

So, now let us see what happens at different places. So, when you choose a particular point in this region let us say this region this point A. So, you can see that at this point A. So, the phase equation was F plus P was equal to C plus 2 in this case pressure is not constant. So, it is F plus P is equal to C plus 2. So, F is equal to C minus P plus 2; number of components in this system is equal to so, let us apply for point A. So, number of components is equal to 1, it is pure iron how many are a number of phases at point a we have only 1 phase.

So, P is also equal to 1. So, F turns out to be 2. So, we have two independent variables. So, what it means is that whether you change temperature whether you change pressure you can change both of them independently and it is still you can retain single phase equilibrium. So, both temperature and pressure can be varied independently while maintaining a single phase equilibrium ok.

Now, if you go to this line for instance, this line is the region on which you have this is point B on point B what we have is we have two phase coexistence. So, γ F e liquid and γ for example, both of them coexist; at point B it is again a single component system C is equal to 1 P is equal to 2. So, F turns out to be equal to 1 which means you have only 1 degree of freedom. So, what it means is that so, if you look at B.

So, for example, the moment you go you if you vary both print pressure and temperature let us say in this direction you immediately jump into single phase equilibrium. In order to be on this line the moment you change that temperature pressure is automatically fixed. So, when you want to be on this line the change in one variable leads to fixing of another variable. So, if you change temperature the pressure is fixed to maintain that 2 phase equilibrium or if you change the pressure the temperatures automatically adjusted to maintain the 2 phase equilibrium.

So, you can say that only and say only one independent variable, you vary temperature pressure is adjusted automatically to maintain 2 phase equilibrium because you have to be on this line. Similarly if you vary pressure that temperature is adjusted accord accordingly to maintain the 2 phase equilibrium. So, in a single component system these are the two scenarios you have, at some point you can have triple phase 3 phase equilibrium.

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Point C

$$P = 3, C = 1$$
$$F = 0$$

↓

No independent variable

↓

Point

↓

Invariant

So, for example, pressure point like C this is C point at the point number C at the point C number of phases equal to 3 and C is equal to 1. So, F is equal to 0 which means there is no degree of freedom. And, you can see that if you move away from this point anywhere whether you go here, whether you go here, whether you go here, whether you go here or here or along this line you lose 3 phase equilibrium.

So, from 3 phase equilibrium you move into 2 phase equilibrium or single phase equilibrium if you vary either temperature or pressure which means what it means is that no independent variable. So, this is like a point so, this is called as a invariant point. Invariant means nothing can be varied there is no change in any thermodynamic parameter that can be maintained to maintain to have a 3 phase equilibrium.

So, 2 phase equilibrium is possible in a unary component system only when only at a point, at a given point where three phases exist with each other and there is no change in parameter that can be made.

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Invariant point $\rightarrow F = 0 \rightarrow$ point
 $F = 1 \rightarrow$ Line
 $F = 2 \rightarrow$ 2-D or area

So, you can see that for a unary system. So, invariant point invariant point means F is equal to 0. It is basically a point when F is equal to 1 it is basically you can say a line you move along a line ok. So, you adjust 1 parameter second is adjusted automatically and F is equal to 2 means it is a 2 D or area based variation. So, you can both vary temperature and pressure independently to get a phase equilibrium single. So, basically in a unary system it will make, it will mean a single phase equilibrium. You can apply the same logic to binary systems.

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Binary System ($P = \text{Constant}$)
 $\underline{\underline{A}}$ $C = 2$
 $P = 1$
 $F = C - P + 1$
 $= 2 - 1 + 1$
 $= 2$
 $\begin{matrix} \swarrow & \searrow \\ T & X \end{matrix}$

Phase diagram showing temperature (T) vs composition (X_B) with regions L, S, and L+S. A horizontal line is drawn at constant pressure P through the L+S region.

Point B $P = 2, C = 2$ $F = 1 \rightarrow$ only one independent variable

So, we can see in case of Binary systems. So, you have a phase diagram like this temperature composition. So, you have liquid liquid plus solid solid. If you look at point A here so, we look at point A point B and point C. So, we only look at point A and B because a C is same as A. So, which is same as A in terms of applying the phase rule.

So, at point A so, in this case C is equal to 2 you have 2 components A and B number of phases at point A is equal to 1. In this case pressure is constant. So, F is equal to C minus P plus 1. So, 2 minus 1 plus 1 that is equal to 2 . So, you have 2 degrees of freedom. So, for point A for single phase equilibrium the pressure and pressure and so, in this case it means temperature and composition both temperature and composition can be varied independently for point A; that is when the degree of freedom is equal to 2. And this basically in a binary system implies single phase equilibrium for point B well let us not say B because B is the composition. So, anyway that is I think it does not matter. So, let us say it is point B.

So, at point B what we have is two phases. So, P is equal to 2 C is anyway equal to 2. So, in this case F is equal to 1. So, which means only 1 parameter meter can be varied independently. So, you can vary either temperature or pressure independently. So, what it means is that if you go, if you are at point B the composition of 2 phases is given by these 2 points. So, this is the liquid composition C_L this is a solid composition C_{β} . If you vary temperature for example, to this point; if you vary the temperature the composition is automatically fixed. If you are varying a composition and template now, if you move along this line, if you move along that line you vary the proportion, but your temperature come.

So, composition remains fixed here temperatures or so, if you vary temperature your composition is automatically fixed. So, the only variable is only one independent variable because, you move along the line. So, when you move when you go to this point or the point below the compositions are automatically fixed.

So, the only parameter that you can there is only one independent variable that can be changed in case of 2 phase equilibrium. You can apply the same logic to you know eutectic phase diagrams; in case of eutectic phase diagram by technique phase diagram there is like difference slight difference because, you have invariant points because you have 3 phase equilibrium that we will see in the next lecture.

So, basically to summarize what we have done in this lecture is we have understood we have derived the phase rule Gibbs phase rule which correlates the number of phases number of components with the number of independent variable to predict the phase equilibrium in a given system. Or to maintain a phase equilibrium what kind of variations can be done in the parameters and which parameters can be varied. And, we have looked at the examples in the context of unary and binary system in case of isomorphous phase diagram. We will extend this to eutectic phase diagram in the next lecture.

Thank you very much.