Phase Diagrams in Material Science and Engineering
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Lecture – 04
Phase Rule-I

So, let us first discuss now why do I get parabolic shape of the (Refer Time: 00:20).

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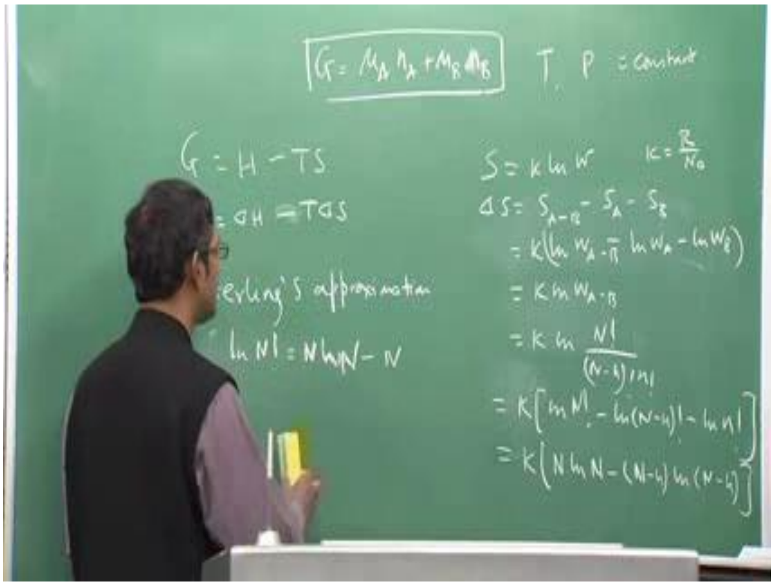

We know that G is equal to H minus T S. Right. So, therefore change of free energy can be written as delta H minus T delta S. Now, delta H is can be easily obtained by (Refer Time: 00:40) means using the C P of the system. We know the free energy; heat capacity of the system can be used to calculate delta H. But for a solution containing more than one component, delta S is also function of compositions. So, that needs to be measured or obtained using rules and regulations of entropy. How do I do go about it?

We know that S or the entropy as per Boltzmann formulation is given as K l n w; K is Boltzmann constant. And, K is also can be written as R by N 0, where R is the universal gas constant; N 0 is the Avogadro number and w is nothing but number of, you know arrangements, popular arrangements possible in a system.

Suppose if I have four balls, three a and one b and I have four different positions to keep these balls. How many number of ways I can arrange them? There are only four different ways to be (Refer Time: 01:44). You can do this games with yourself. You buy four different balls; three of green colour and one red. And then, try to put it in a box containing four different places. You will find that there are only four ways to arranging them. There will be no other ways of arranging that. Correct.

Similarly, if I have two a and two b or there is two red and two green balls, we will have six different steps of arranging them. So, this w means that; w means how many number of positions for arranging these systems. So now, and suppose if I have N, capital N, number of A-atoms. This is number of A-type atoms; A-atoms. And, N minus small n number of B-atoms. And, I want to arrange them in a lattice containing n sides. So, what will be the probability? Probability will be N factorial divide by N minus n factorial and n factorial. How do I get this number? This is basically from permutation and combination. That is what you get. And, I could not have time to discuss in detail of that. This is simple by permutation and combination; you can get this.

So, therefore this is the number of positions arranging in A-atoms, N minus small n B-atoms in a lattice containing n sides. Now, question is this. If I have to calculate delta S of a system, let me just do it there. Delta S of a system. Suppose delta S of a system, so then I will write down S A minus B minus S A minus S B. Why? Because this is delta S is the difference; the difference of the entropy of the system containing A and B-atoms minus entropy of the system containing only A-atoms minus entropy of the system containing only B-atoms. This two must be subtracted because they are, when there is only A, only B; and there is only A, only B means, there is only A or B times of atoms present. Here only A-type, here only B-type, but here you mix of both of them.

So, now I can write down like this; K l n w A B, K I can take common, l n w A l n w B. So that means, I can write down K l n w A B. Why? Because w A is one. If I have only A-type of atoms, arranging A-type of atoms in a number of side, suppose capital N number of sides, is one. There is only one probability. You cannot put, you can only put only A-type atoms. There is no option. Similarly, for B also. So, this log of 1 is 0; log of 1 is 0. This becomes cancel; so that means, this one is like N, capital N minus.

And, I can expand this. I am using Sterling approximation. What is Sterling approximation? This can be written like this; log of N factorial minus log of N minus n factorial minus like this. And, we know the sterling approximation is; Sterling approximation I write here; Sterling's approximation is this that N log N, sorry, log of N factorial is equal to N log N minus N; N log N minus N. This is what is Sterling approximation.

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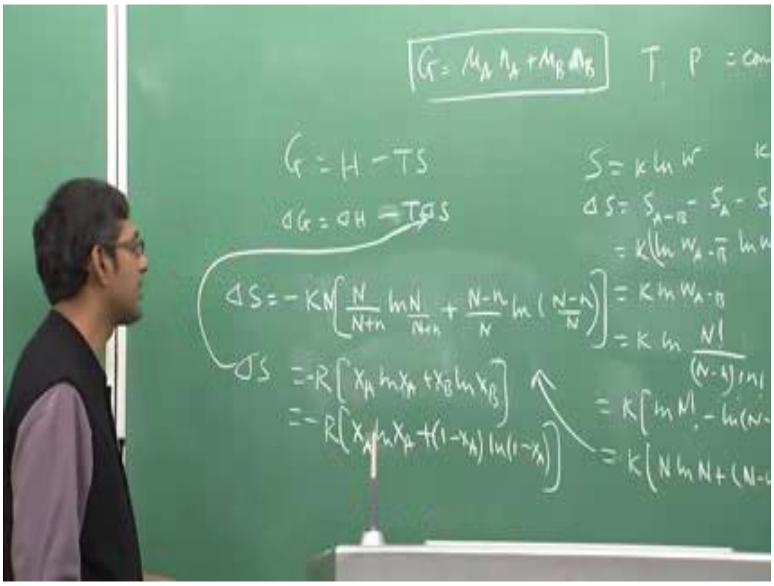

So by that time, by the way if you apply this, finally what you will get is K N log N minus N minus n log of N minus n. You will get this. And, if I take away this one, then what will I get? I will get delta S is equal to minus K N N by N plus n log of N divided by N plus n plus, this will be plus sorry, plus N minus n divide by N. Yes. log of N minus n divide by N. And, we can define this as the mole fraction of X A. So, this is equal to R, minus R because K into N 0, K into N 0 is R. So, this N is also Avogadro number of molecules. So, this become X A l n X A plus X B ln X B. That is what we get.

So, total entropy change is this. So, now this S has to be replaced here. If you see here, if I replace this one, this is X A l n X A X B l n X B. Or, we can write down minus R X A ln X A is log plus one minus X A; because X B is one minus X A, one minus X A. So, you can clearly see that this is equation of parabola. This is nothing but equation of parabola because log of X A can be expanded. See if you expand it, it will be X A multiplied by X A is X square. So, this is nothing but equation of parabola. Similarly, one minus X A will be multiplied by one minus X A. If you expand log, so that is also be X square. So, that is why actually it becomes a parabola.

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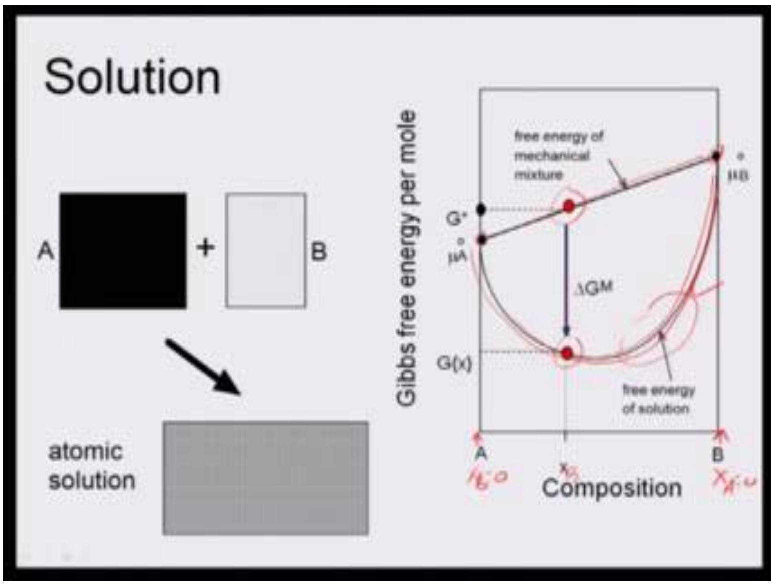

Solution

So all these curve, that is why you see here is nothing but a parabola. This is the parabola. This is why it is known, looking like this, otherwise not. So, let me now move ahead with my first derivation. This is just; just I wanted to clarify you why we get parabola. Otherwise in future you will say, “Sir, you have shown this parabola, but you have never explained why it is parabola”.

So, let me just now go ahead with a phase rule derivation here. So, we know that G is a function of temperature, pressure and your number of moles of A, number of moles of B. And, I have shown you that d G can be written as d G prime rather; because G has to be divided by number of moles.

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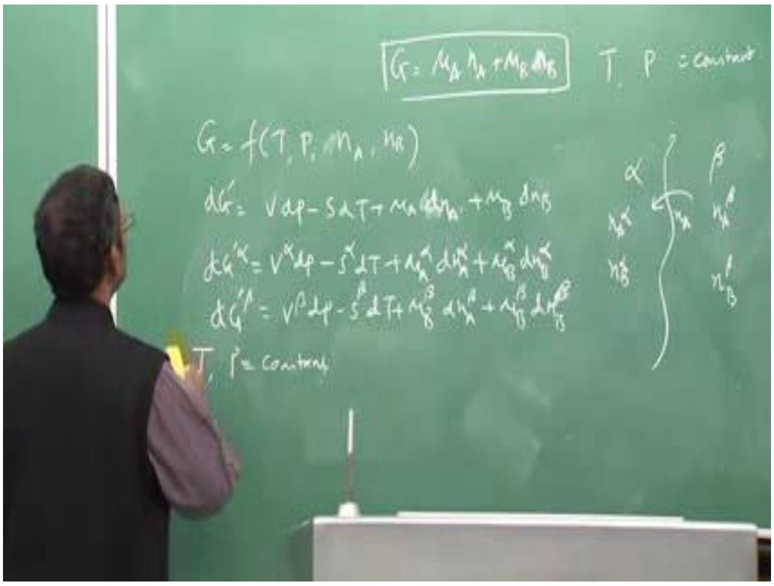

This can be written as V d p minus S d t plus mu A X A mu A d X A plus mu B. Sorry, d X A should not be written here because N A I have written. So, this will be d N A and mu B d N B. Now, let us suppose; let us assume a situation in which there are two phases; alpha and beta. I have shown you lot of alpha, example of R n and other systems. And, alpha contains n A alpha of A and n B atoms of B. Similarly, beta contains n A atoms of beta, n A atoms, and n B atoms of beta. These are the number of atoms present.

Now, suppose there is a transformation from alpha to beta, or rather, let us suppose some atoms of beta is getting transported to alpha, there is a transformation at a constant temperature, pressure. So, therefore what is the change of free energy? So, let us first write down free energy expression for alpha. This will be all alpha. I have to put alpha, all the everywhere, superscript. Similarly, beta. Sorry. You can close your eyes. I will write down all the beta superscript and get that. These are the free energy changes, when you have such system like that. At constant temperature and pressure, these two variables will be vanished; because temperature, pressure d T and d P are not changing.

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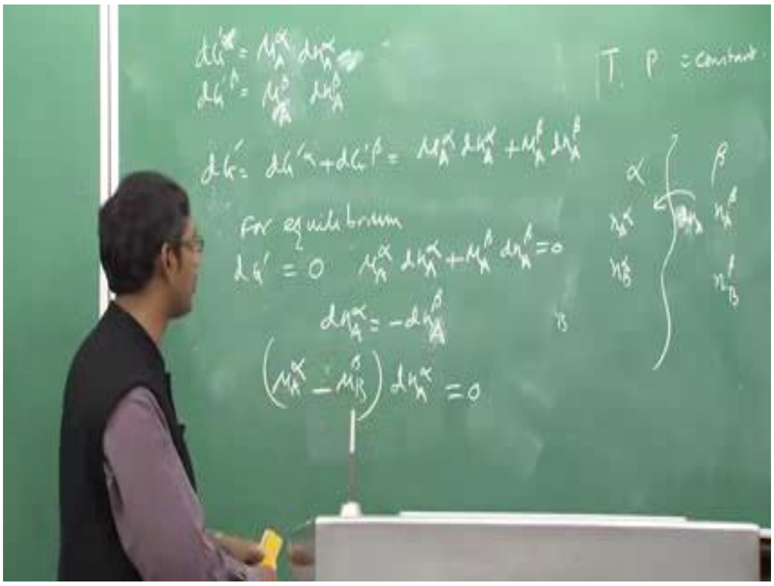

So, let us now do this calculation. If I have transporting, suppose if there is a transport of n A moles of A from beta to alpha, what will be the change of free energy? Change of free energy will be very easily written that change of free energy is for alpha will be mu A alpha, sorry, mu A alpha d n A alpha; because n A number of molecules are changing. Sorry not n A, it has to be d n A. Or, otherwise you will be confused.

So, d n A number of molecules are changing. So, alpha will be; this is the change of free energy because there is a change of B. So, therefore only this part will change. This, we have already assumed the pressure and temperature constant. So when d p is 0, d T is 0, d n B is also 0. But, there is no B molecules getting transported from beta to alpha; only A molecules transported.

Similarly, this is for G prime alpha. Similarly, for G prime beta will be mu B, mu B will not be there, mu A, sorry mu B, mu B alpha, mu B alpha. mu B beta, yes, mu B beta. Oh! I have made a mistake. This will be A. Yes, mu A beta d n A beta because all A molecules are transported. Suppose, these n B are not changing at all. I have assumed that. So, now what your total change of free energy? Total change of free energy is addition of these two. d G total is addition of these two d G prime alpha plus d G prime beta. So, that is nothing but summation of these two. Mu A alpha d n A alpha plus mu A beta d n A beta.

So, for any system to get equilibrium, the total free energy change should be crossed n. Therefore, total, for equilibrium d G, total or d G prime should be 0. If I have to make 0, this whole thing is 0. That is mu A alpha d n A A alpha plus mu A beta into d n A beta 0. As you know that I have transported d n A molecules from B, beta to alpha. So, therefore if I transport that, therefore d n A alpha must be equal to minus of d n A beta; because whatever is the molecule I am transporting from beta, only getting added to alpha. So, there is a change this way. So that means, I can write down mu A alpha minus mu A beta multiplied by d n A alpha is equal to 0. As you cannot have d n A alpha to be 0 because this is a mass. Mass cannot become 0.

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So, since I can write down d n A alpha cannot become 0, mu A alpha equal to mu B, sorry, mu A beta. This is a very important condition in Thermodynamics.

So, you can see here if two phases have to get equilibrium at constant temperature, pressure, the chemical potential of A in the both the phases must be equal. Chemical potential of A in alpha must be equal to chemical potential of A in beta. Remember this; I have not changed the subscript. I have only changed the superscript. Similarly, chemical potential of B in alpha must be equal to chemical potential of B in beta. These conditions must be satisfied. If they are not satisfied, you cannot not really talk about equilibrium conditions in solutions. This, I just want to derive B and show you how using physical metallurgy thermodynamic principle like total free energy change 0. I can derive this expression and show you that. So, now question is this. How can I use this? This is what is shown in this picture. Right.

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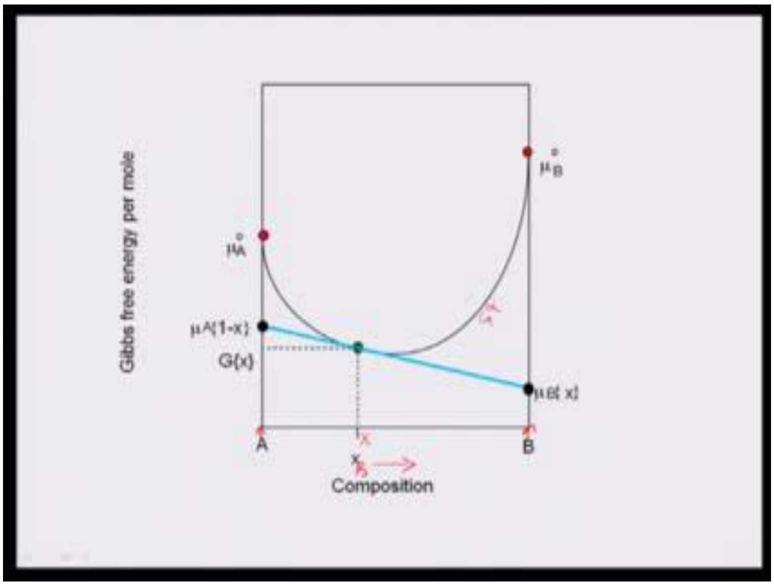

Let us do that analysis. You can clearly see that if I go back, this is my free energy curve; free energy verses composition. Composition, suppose X B. Composition increasing this way. This is my pure A and pure B and correct. So, pure A and free of energy equal to mu A 0; pure B will free energy equal to mu b 0. That you already define. And free energy will be like a; this kind of steps, I have already discussed you why these kinds of steps are there. So, if I now wanted to know free energy at a particular composition X, that is what a G X, then I can just draw a tangent to the curve. And, this tangent will be passing through this dotted line. This dotted point will be tangent to this curve.

So, in that case these two ends will give you the chemical potential of A and chemical potential of B. So, now if you consider this is for alpha, this is for suppose phase alpha, this is free energy of alpha. And, this is free energy; the chemical potential can be measured easily, graphically. Why is tangent to curve rule? That also needs to be discussed. That we will discuss later. Why it is tangent to curve? Rules, which tells you the free energy chemical potential of the two components of the ends.

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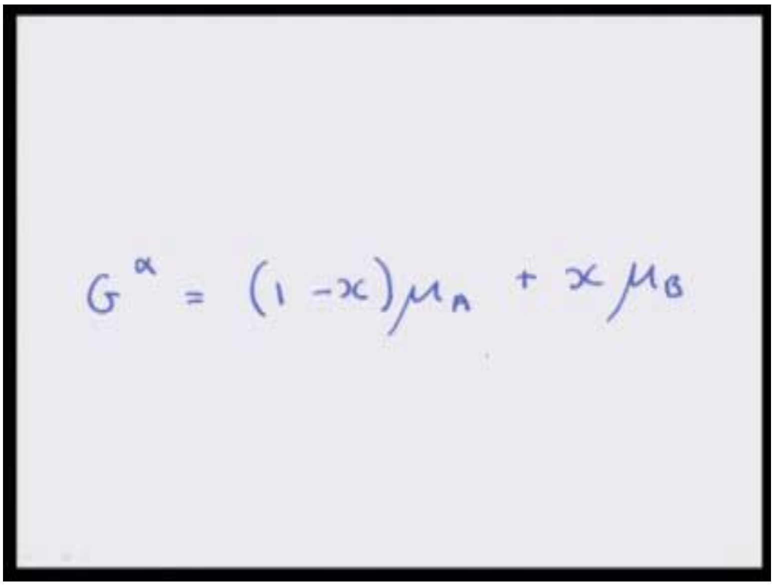

$$G^{\alpha} = (1-x)\mu_A + x\mu_B$$

Now, let us. So, this is the equation I have already shown you in the last class. This is basically equation of this straight line. This straight line as equation u and y. G alpha is equal to one minus x mu A plus x mu B; is obviously, this would be all alpha phases. The single phase has to be known. Write the superscript. Now, if I consider multiple phases, what will happen?

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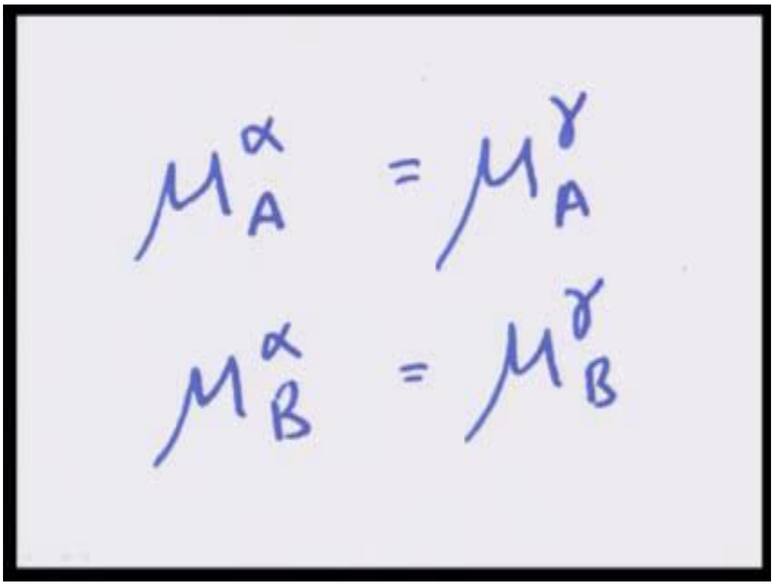

$$\mu_A^{\alpha} = \mu_A^{\gamma}$$

$$\mu_B^{\alpha} = \mu_B^{\gamma}$$

Suppose this is for. This one, I have discussed with you. Right. Now, let us apply that.

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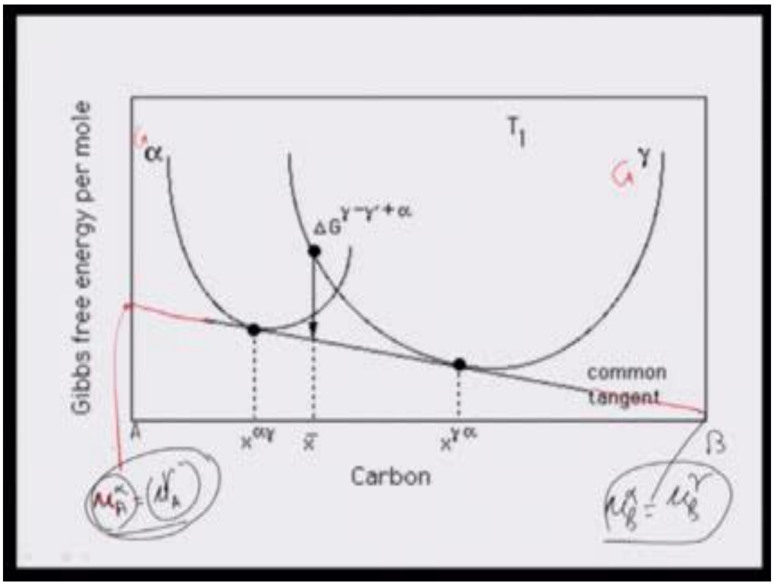

Let us apply these tools for two phases, where you have alpha and gamma. And, let us consider this is alpha iron solid solution; this is gamma iron solid solution. In, iron and carbon.

So, this is the alpha free energy curve G alpha, this is G gamma. Right. So, now this curves looks like this, again parabolic step; inverted parabola. So, now you can see here that if I want to have chemically potential, sorry, you want to be equilibrium, then this must be satisfied. What is just to be satisfied? In that case, I could draw a common tangent between these two curves, dou A, I have drawn the tangent. And, if I draw a common tangent, these points will tell me what? This point will tell me mu A alpha, mu A alpha.

This point will tell me mu A alpha equal to mu A because this is A end, this is B end, A A beta because it is a common tangent. So, therefore this curve tangent will tell me mu A alpha phase. This curve tangent will tell me mu B, if mu A beta phase. So, this I satisfy. This can be satisfied here. Similarly, here mu B alpha equal to mu B gamma, sorry this is not beta, this is gamma. Here, we have done gamma. So, you have to write down gamma. Please make changes. Similarly, so therefore these two conditions satisfy. And, this is the way we explain the phase transformations in a classical system.

This is the way we explain the phase transformations and classical system that the chemical potential of any component A must be equal in all the phases; chemical potential of B must be equal in all the phases. So, now let us quickly derive the phase rule. We will get back to you again. If you do not understand, I will again think about it and discuss. But, let me just derive whatever time I have in this class, what is the phase rule. Let us suppose I have got; I have got C components in a system; generalise. And, p phases in a system. Right. Alpha, beta, gamma, delta goes up to p.

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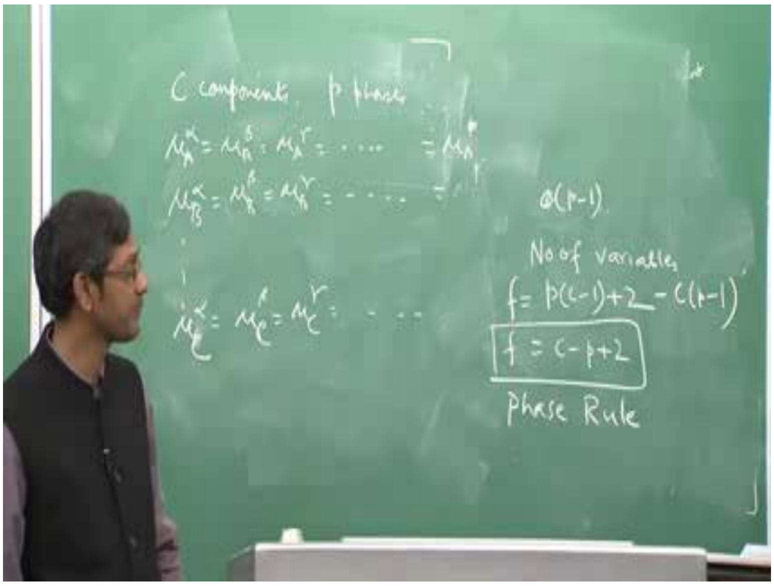

So, if I have C components p phases, the following things will be satisfied; mu A alpha equal be mu A beta equal to mu A gamma dot, dot, dot equal to mu A p because p phases are there. So, for a particular component all the phases will satisfy this rule. Similarly, mu B alpha equal to mu B beta equal to mu b gamma dot, dot, dot, equal to mu B p; p is the number of phase. Right.

So, like that I can write down mu c. There are c components. Do not think that is A, B, C. There are many things. The total number of component c; c may be any number. May be 100, 200, 300 possible. So, this will become c beta c gamma equal to mu c p. Right. So, how many equations are there? Any idea? Very difficult. Right.

Let us consider this one. In one row, how many equations are there? p minus 1 because 1 equation is irrelevant. So, there are c rows. So, therefore, total number of equations is c p minus 1. So that means, I have total number of equations which are to be satisfied for p component system with p phases. (Refer Time: 21:27) p phases is c minus p. But, what is the number of variables? When I have so many component, so many phases, number of variables are; number of variables let us write down. Number of variables is p phases c minus one component. Why? That is very simple. If I know the compositions of c minus one component, I know composition of all the c components. Why because if you recollect that thing that X A plus X B plus X c plus X d plus X n equal to 1.

So, if I have to; if I know compositions of all the X A, the mole fraction of X A, X B, X c, X n are known. The last one can be easily known because summation is equal to one. So, that is why c minus one. Now, there are p phases. Therefore, c minus one into p is the total number of variables in the system. These are the compositional variables plus you have temperature and pressure variables.

These are the total number of variables. These are the composition variables. Why because p is the number of phase. And each phase, there are c number of components. Therefore, c minus one number of composition variables. Plus, temperature and pressure is a two variables. Out of these variables, this one are fixed by these equations; c minus p c into p minus one. This is fixed. These numbers of variables are already fixed by Thermodynamics. This is what is Gibbs has done. Beautiful thing, He could have got noble prize for this. But, he died before noble prize started. That is the problem actually.

So, you can see all this equation must be satisfied. So, these are the things which already fixed by the system. If you do that, what is the number of free variables you get? Free variables are this minus this. This is the total number of variables minus fix variables. And, if you do the maths clear full, carefully, you will get this; f equal to c minus p plus two. And, this is known as phase rule in the books.

Phase rule; this is also known as Gibbs phase rule; because Gibbs has derived these equations. Very clearly, the number of free variables is equal to number of components minus number of phases plus 2. Two comes because of your constant temperature and pressure. You can consider other variables like magnetic field, little field, then two will change. But, basically composition special variables will be c minus p. Please, make sure that in your exam you do not write p minus c. Then, you will make a mistake, this is c minus p. So, therefore number of free variables is equal to c minus p plus 2. And, this is what is known as the Gibbs phase rule.

Let me also tell you one thing. In metallurgical system, we consider pressure to be constant. We have seen. Already seen that pressure is always one and most (Refer Time: 24:20).

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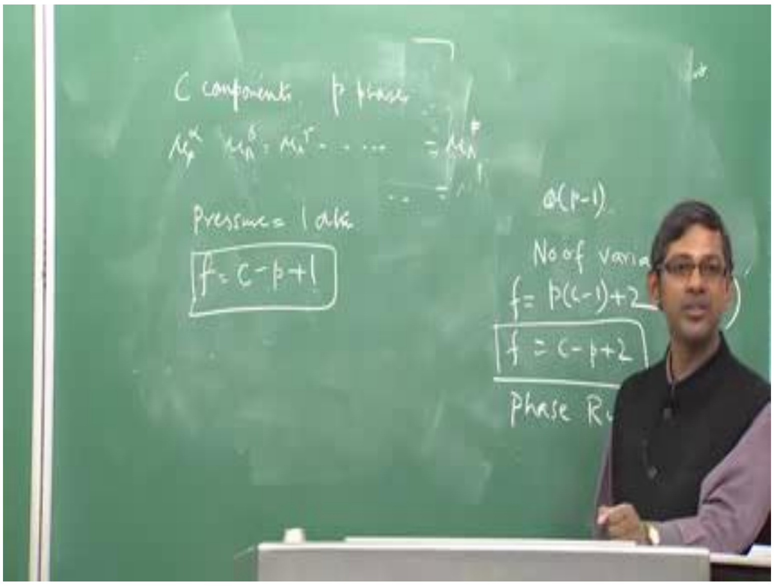

So, therefore, this phase will become c minus p plus one. This is what is this because two, out of two variables temperature and pressure, one is already constant. So, one is a free the free is temperature, so composition minus phase plus one. This is what is the free variables presents in a system.

I hope this is the very important concept. I told you how to derive phase rule and how to get an idea about and the different chemical potentials need to satisfied in a particular system. I have already discussed and showed you graphically how we can use it. In the next class, actually we will apply this rule. We will see how we can apply this rule and will also derive a new rule call lever rule to know the composition of these phases from the diagrams.