Principles of Physical Metallurgy
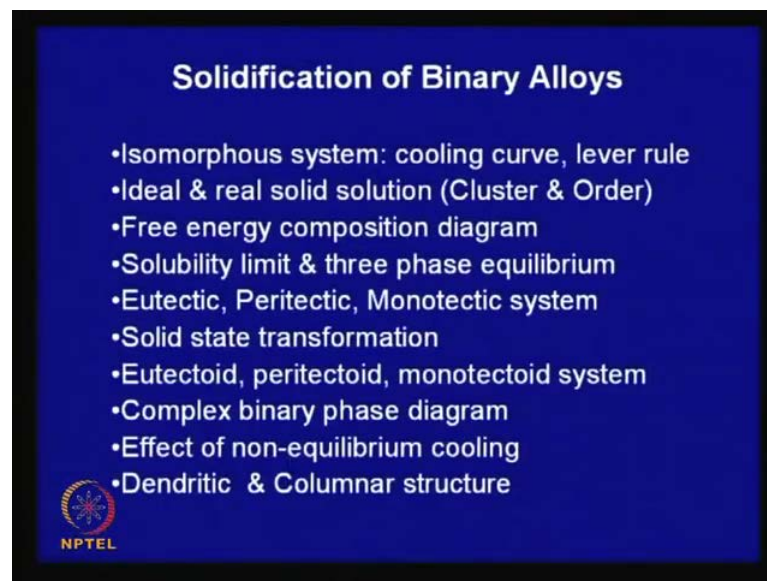## Prof. R. N. Ghosh
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Lecture No. # 18
Solidification of Binary Alloys

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Good morning. Today we begin a new chapter, and this chapter is on solidification of binary alloys. Now the topics which are to be which will be covering a listed here; we will first start with isomorphous system, you will define what it is? What is the cooling curve? We will also derive an expression which helps as to find out phase percentage which is known as lever rule. Then we will make a distinction look at what kind of material; say suppose in ideal what is ideal and what is the real solid solution. We will also know about we have introduce a concept of free energy, which defines the stability of phase, we will see that how the stability of phase changes with composition.

Then we will look at the solubility limit and three phase equilibrium, and under this some of the common three phase equilibrium, we will take up is Eutectic, Peritectic, Monotectic system. We will talk also about transformation that can occur in solid state, and under this we will consider few cases like Eutectoid, Peritectoid, Monotectoid

system. Then we will try and look at how we can how to interpret or how to construct complex binary phase diagram involving many of these transformation processes, which are listed here and until this we will consider that the solidification process proceeds in a very slow manner.

So that at every point there is equilibrium is maintained thermodynamic equilibrium is maintained. Then we will look at if there is a departure from equilibrium, what kind of effect do we get in the process of solidification and this structure that evolves we will talk about Dendritic and columnar structure, and we propose to cover this in around seven to eight lectures.

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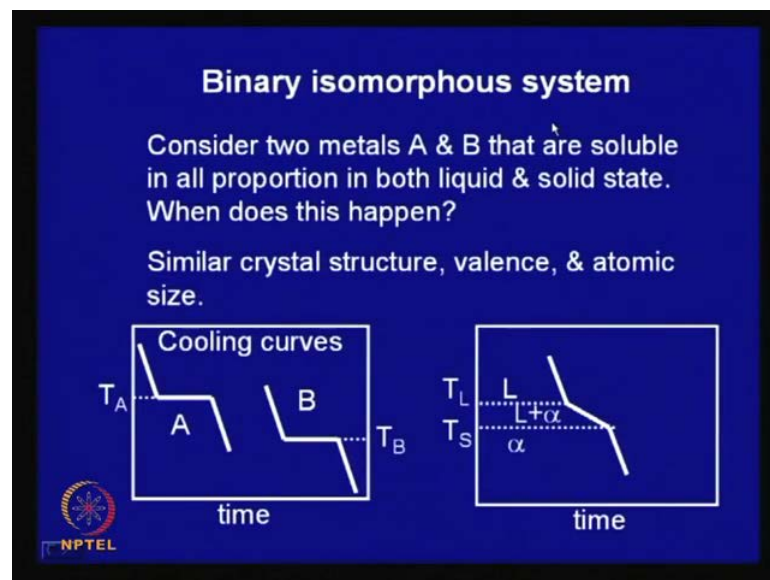
Now first let us look at I mean binary isomorphous system. Let us consider two metals A and B that are soluble in all proportion in both liquid and solid state. Now we have looked at it earlier while dealing with crystal structure when can this happen. In liquid state now visibility is well known most metals they are soluble in each other in all proportion and but in solid state only those metals they are soluble in all proportion, where certain conditions are satisfied like both metals have same crystal structure, same valency almost similar atomic size.

So these are the criteria which determines the extend of solubility of one metal in another. Now let us consider an ideal case of two metals, which are soluble in both liquid and solid state in all proportion and we looked at we learnt about thermal analysis and

this is the powerful tool in determining the transformation processes in alloys and let us look at the typical cooling curve of pure metal A. If here it is liquid and as you start cooling the solidification begins at the temperature and after certain times when solidification completes again its starts cooling down.

But when the solidification precedes the temperature nearly remains unchanged and this is the melting point of A; so let us say we write it as T A. Similarly, metal B if you cool it also will have identical or similar cooling curve and here the melting point this step in the cooling curve indicates melting point that is T B. Now what happens if it mixes up the two metal A and B in the liquid state? Now in a liquid state it is much easier to mix metal because a part from diffusion we did learn about talked about diffusion primarily in solid state and we found that diffusion is a very slow process of mixing in solid state.

So all alloys I mean by melting and mixing and when you makes apart from diffusion you can metal and then the diffusion sense the diffusion also depends on state of the from state of the matter in liquid the diffusivity is much higher. Therefore, mixing is much faster and once they are mixed in all proportion and then you start cooling the metal that alloy made up of A and B and you say if you look at that cooling curve it may if have behave something like this. It does not have a step has over here and this solidification possible you will begin this alloy at a temperature, which is little lower than depending on the composition lower than the melting point of A and it will be completed that process of solidification will be completed at a temperature will be little higher than the melting point of B.

So this we can say that key L we say define that this is a temperature at which solidification begins, when crystals of an alloy alpha we say that this is a solid solution of B in A or vice-versa whatever you may say. So this is the solid solution, which is forming and so there will be a temperature range when both the phases can coexist liquid and solid liquid and solid can coexist over a temperature range and after the solidification is complete it starts cooling almost may be nearly same rate as this. So by performing this experiment an alloy we can get two temperatures T L and T S and these are functions of composition. Both of these are function of composition that means we determine this particular case T L and T S we determine for a particular composition.

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Let us say fifty percent A, fifty percent B <mark>fifty percent B</mark> so for this so that means T L this is a function of composition; so also T is also a function of composition and here we conduct most entire experiment because we are conducted at constant pressure and we will consider that constant pressure to be one atmosphere one atmosphere pressure, which is because most processing will be done at a fixed pressure. Now having determine T L and T S for a given composition we can repeat the same experiment for a set of alloys for different values of X, X 1, X 2 and all that and then if we get this data and we plot it an a diagram like this.

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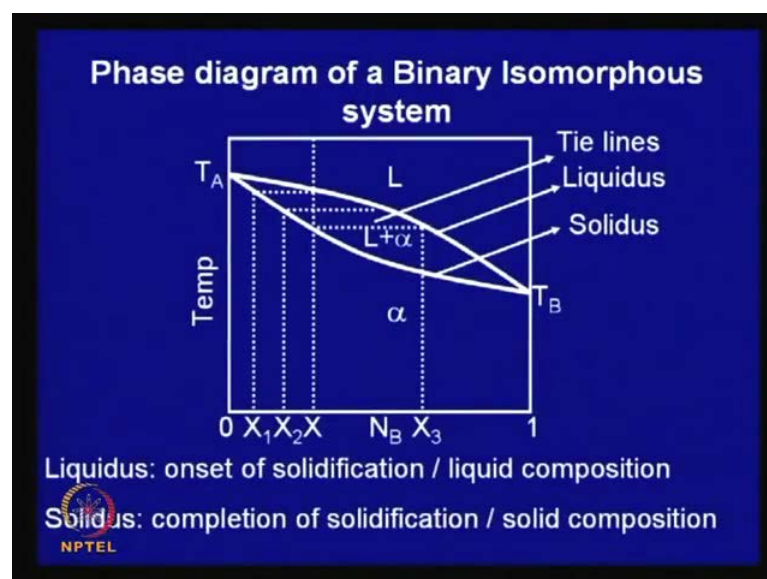
Here this Y axis is the temperature axis X axis is the composition axis. So let us say capital N B this represents atom fraction B atom fraction B it is starts with zero; this is one we can also do it for weight fraction. Now atom fraction B and suppose we have done it for this alloy X; so alloy X so this actually is the T L where so this is the T L where the solidification begins this is T S, where solidification is completed.

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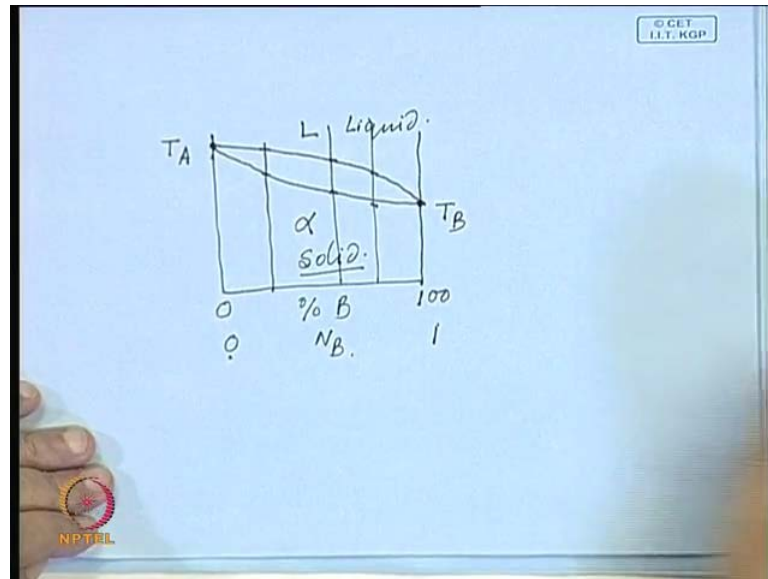
So, in fact what you can think about is what you can do is you pick up a set of alloys for each alloy you plot T L here T S, here T S here T L here T S here and say suppose this is your melting point, this is melting point of A this is melting point of B and this is a composition or weight percent B or mol fraction B. So this is zero B this is hundred percent B or one atom fraction zero here atom fraction B is 1 and then if you join this you get a diagram, which says that above this temperature state of the material it is liquid it exceeds in entirely in liquid state and below this T S temperature it exceeds in solid state.

So here it is solid and here it is liquid. So the phase diagram gives as you can say the solidification range describes the solidification range of an alloy and this case of binary isomorphous system; this is the typical phase diagram that T L line that represents that temperature at which solidification begins is called liquidus; this line is called liquidus and the line which represents temperature at which solidification process is complete is

called solidus and now here look at this solidification process of this alloy X. So when the solidification begins here it can be in equilibrium so sums solid will precipitate out.

What will be the composition of that solid? So that liquid from the liquid some solid will be precipitate out and this solidus line actually; if you draw an horizontal line this signifies then alloy this X 1 this represents the composition of the solid that precipitates out from the liquid and mark this has lower concentration of B. Obviously, the liquid will get enriched in B; so that means liquid will now start following this composition as it cools down composition of liquid will change along this, composition of solid will change along this.

But we have seen that diffusivity composition of a solid can change only by the process of diffusion. Now in liquid state diffusivity are several orders of magnitude higher. So this composition change in liquid will be quite fast but the composition change in solid will take time. Now let us say that we allow this alloyed to cool in furnace or a cool at a very slow rate. We call this slow rate as the equilibrium cooling rate under this condition we give enough time for the composition of this solid to change and follow this particular line.

An ultimately say somewhere at intermediate stage here we can draw another tie line and here it represents at this particular temperature, the composition of the liquid must have change from its original composition from here to this point and composition of the solid has change along this line from this point to this point and we will see later it is also possible as the solidification process continues here it is almost entirely liquid here it is a part liquid parts solid and similarly, when the temperature approaches solidus; then the solid composition will also change along the this line.

It reaches the composition of the alloy and virtually the liquid also compositions also have changed and almost reach here. So but point is that is solid which is precipitated out here there amount of liquid will be extremely small virtually non-existent. So if it cools under equilibrium condition the amount of solid goes on increasing as the temperature goes down and here and the initial composition of the solid is this; but as it cools down composition of this solid keeps on changing and when the entire solid composition reaches this in that case the liquid virtually disappears and the solidification process is complete.

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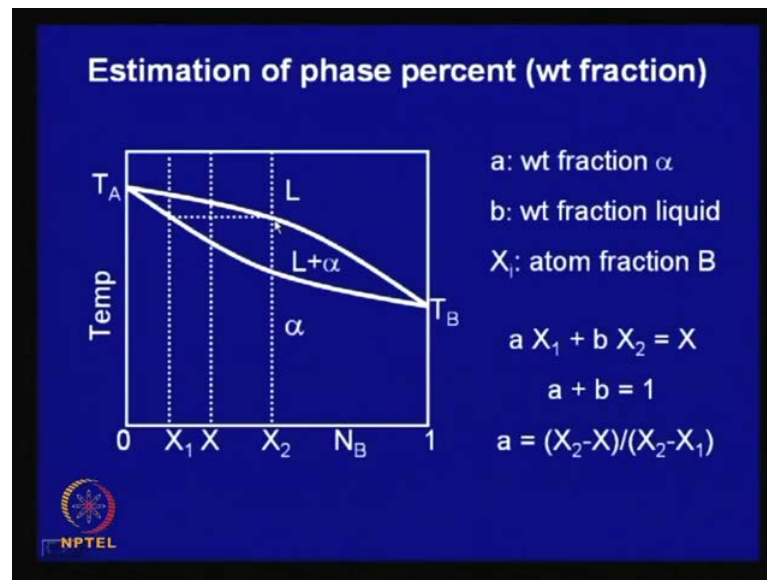
Now, let us see is it possible to estimate say some intermediate temperature you have drawn a pie; this tie line and then is it possible to calculate from this diagram. What is the amount of <mark>what is the amount of</mark> solid and liquid at this temperature? Now let us say a represents let us say weight fraction of alpha, b represents weight fraction of liquid at this temperature and X 1 represents atom fraction b in alpha. So that means this is X 1 and X 2 represent atom fraction b in liquid. Now what you can do you can try and find out what is the total amount of b in the alloy is X.

X represents weight fraction b in the alloy; in that case you can simply write this equation. So a is the weight fraction alpha times the X 1 is the amount of b so multiply this by X 1; so this is the amount of b in alpha and this is X 2 is the liquid composition and b is the weight fraction liquid. So this product will give you the amount of b in liquid and the both should add to X and again this weight fraction a and b they are related a plus b equal to one.

So if you just substitute here say b you replacing in terms of a and you do a little bit of algebraic simplification, you will find a comes out to be X 2 minus X. So look at what is X 2? X 2 is this and X is here so amount of a is proportional to this and whereas, X 2 minus X 1 is this entire length. So this is proportional to you can say that entire amount hundred percent you can say X 2 minus X 1 is the total amount. So weight fraction alpha

is equal to this weight fraction alpha is proportional to this on and weight fraction similarly you can show weight fraction of liquid is proportion to this on.

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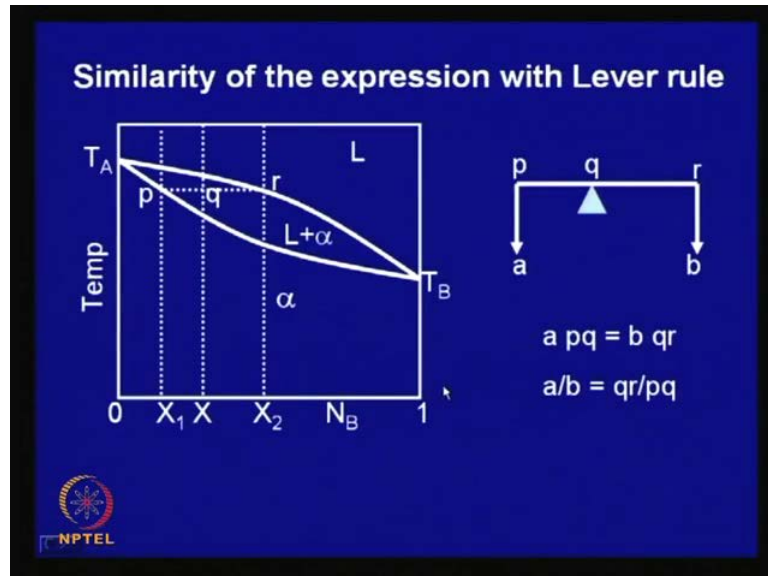
In fact, this is something which is very much similar to what you call in the case of a lever say basically imagine say this is a tie line you can say that this q point is the Carl cram you have a lever and this weight fraction a represents a represents weight fraction alpha over here and this point we call it p q r q is the Carl cram, p where this weight is a plot. Similarly, r and at this place this b is the weight of the liquid and you balance both take the moment. So a over b equal to q r over p q; so this is base so in fact you can say that the expression, which we derived here is also exactly similar you can find out for b also there will be a similar expression take the ratio a over b then what you get is this.

So that is why this rule in phase transformation or is often known as lever rule and we will apply this to any of this phase transformation processes wherever the transition takes place from one phase to another over a temperature range. This helps you to find out amount of the percentage of transformation or amount of a particular phase at any temperature.

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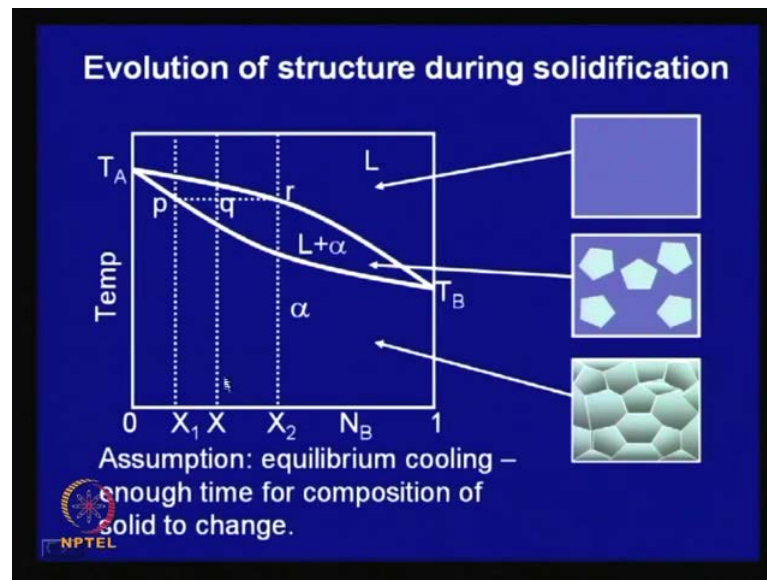
Now let us see how does this structure involved. Now consider this alloy X here now if it is at this temperature as long as it is liquid you can say it is uniform all through and then when the solidification starts you have crystals of alpha forming and which is shown over here. Note that the develop all on sudden it will nucleate and grow and this is a continuous process and take place over the temperature range and these number these particles they growing in size new particles also nucleate.

And they also will keep growing as the temperature cools down and if you assume that cooling rate is a equilibrium cooling rate whatever solid nucleates of forms at a particular temperature it composition also keep on changing. So that means it will composition is here it is linear in b as its cools down it will become richer. So that means b must diffuse from the liquid into the solid and it must diffuse from the surface to the center core of the crystal and this process to allow this process to take place; you have to cool it very slowly.

And ultimately you will have a structure something like this you will have different crystals differently orientated and they will be meeting along some boundaries call green boundary and it we look like if you look on the microscope it may appear something like this and later on as we proceed; we will look into the shape of this crystals later.

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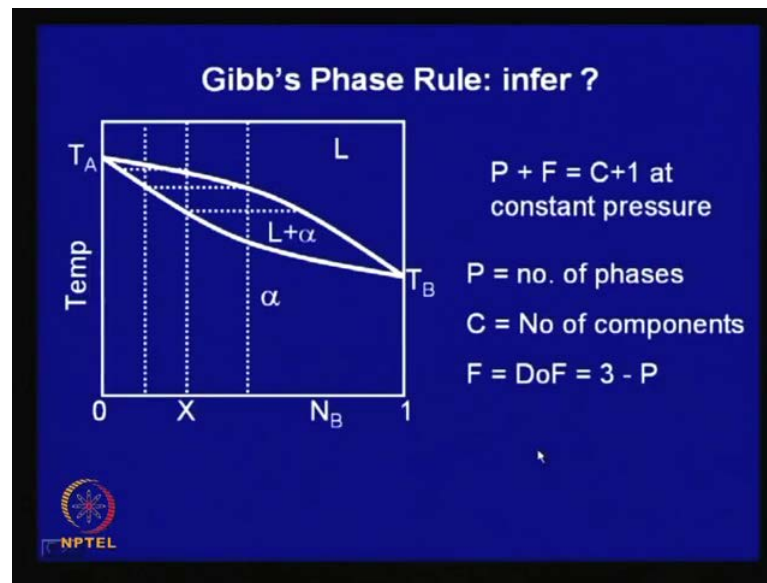
Now while dealing on with solidification of pure metal we introduce the concept of phase rule gives phase rule and what do you infer from Gibb's phase rule. Now which is illustrated here Gibb's phase rule it is stated as P plus F equal to C plus 1 at constant pressure. Now here P is the number of phases, C is the number of component and F is the degree of freedom. Now we are considering a binary alloy binary alloy means number of component is two. So C is 2 so C C plus one is three. So degree of freedom is three minus P that is number of phases which are co-existing.

So if you consider the system somewhere here if you want to define a system what is it made up of. So you see that you it is made up of liquid only but in that case to define the system you need to fix up to value. It is not only enough to say defines the state by stating that it is liquid we have to say that liquid and its temperature is let us say T, which is given here so its temperature an its composition. So you have to define two variables to define this state. Now suppose similarly, if you want to define a state somewhere here if you define an alloy you say it is solid solution A that does not mean it can be it anywhere any alloy over this.

So you have to define here also a particular temperature and a particular composition; so unit two variable to define the state completely. But what happens if we consider the case when two phases are co-existing say suppose somewhere here. Here two phases are co-existing in that case what you need to define is say the two phases are co-existing and

the temperature you define this is the temperature; then automatically the composition of phases, which are in equilibrium they are fixed.

So one is this composition another is this. So if this particular case you see if you say that my alloy is at a temperature an this temperature and it is made up of two phases then automatically phase alpha, alpha will have this composition let us say X 1 and this will have a composition X 2. So you cannot you cannot have and alpha of any intermediate composition existing here. So this is what you infer from phase rule.

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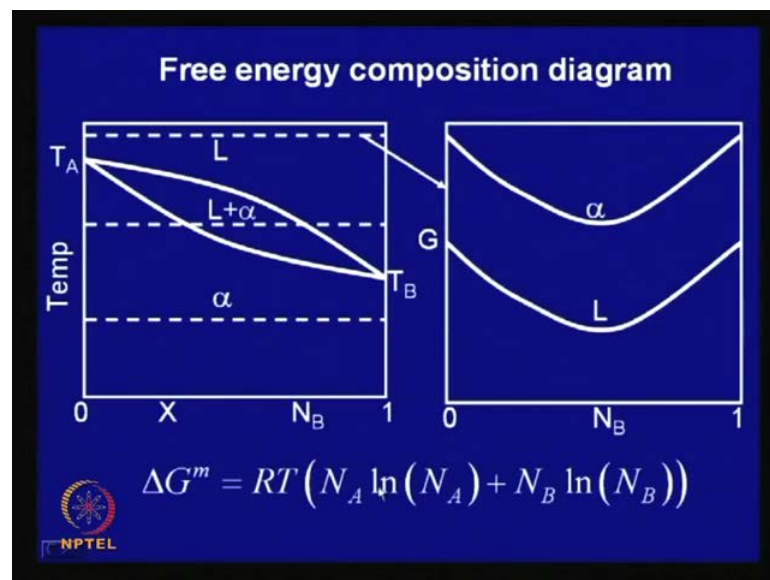
Now let us see look at the free energy composition diagram. Now we know that free energy if free energy of a solid solution is a given is a function of its composition and for an ideal solid solution; we know that free energy of mixing is given by this expression. This is R is the universal gas constant, this is the temperature, this is atom fraction of a and this is natural log ln N A N A plus N B ln N B and say let us consider this is any solution with a liquid or solid, this relation will be valid if this solution is ideal. Let us consider an ideal system we will come back to it again what you mean by ideal system.

Let us consider at this temperature the free energy composition diagram. Now here if you try and plot this free energy composition diagram, now this will come out to be. Here solid is stable say for here solid is not stable; so liquid will have lower free energy and this diagram is something like this. Whereas, liquid will have lower free energy and the

diagram is something like this and the relationship is you can say that what we are writing is a delta G of mixing; so when you mix the two this is what is happening.

But because this is a temperature, which is much above the melting point of A which has a higher melting point. So here pure metal here that free energy of alpha or A will be higher than A free energy of a liquid; so liquid has a lower free energy the liquid is stable same as this cases as well.

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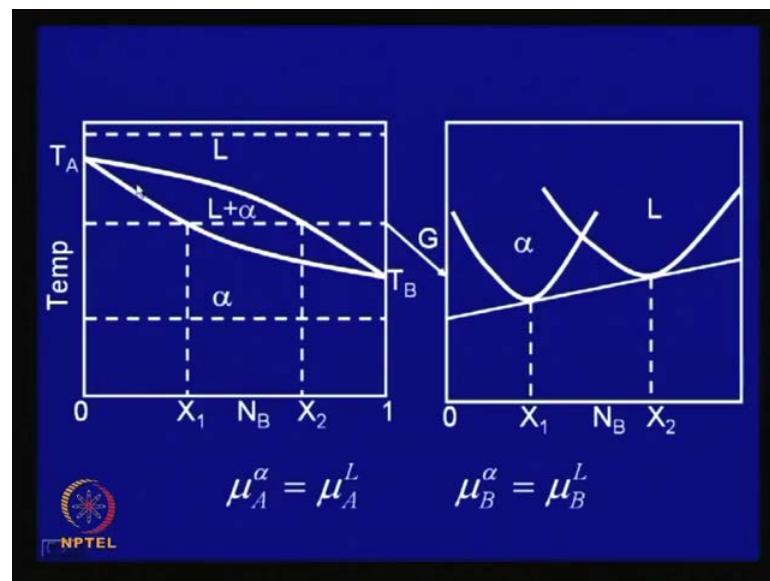
Now this is a schematic diagram not to scale and now what happens, if you come to an intermediate temperature range intermediate; temperature range something like this happens the shape of this plotted changes at a something like this is some and this is the free energy diagram of the liquid. And in a free energy plot if you draw a tangent then this intercept is known as this intercept is known as say usually free energy; it is a zero will be somewhere here this is down.

So this intercept will be known as this intercept will be known as you can say chemical potential or you can say partial molar free energy and this is partial if you draw a tangent to alpha at this point; we will say that this the chemical potential of A in alpha. Similarly, if you draw a tangent here you can also get a chemical and let it intercept this axis you will get chemical potential of A in liquid and under equilibrium the potential they are equal which is stated over here mu A alpha equal to mu A liquid similarly, it will be followed for B as well.

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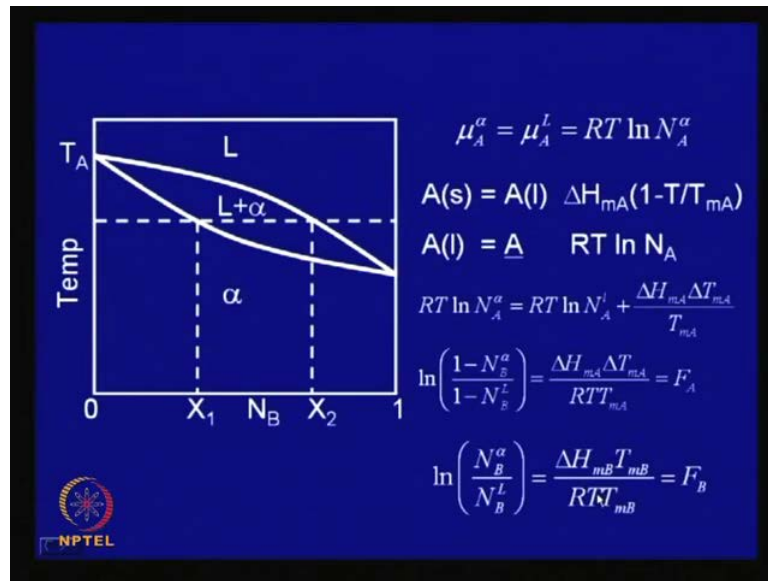
Now this concept is simple but let us try and see that if we consider the alloy system to be ideal; then how can we estimate how can be estimate or calculate this phase diagram. Is it possible to calculate the phase diagram from the basic concepts? Say and let us go through this exercise.

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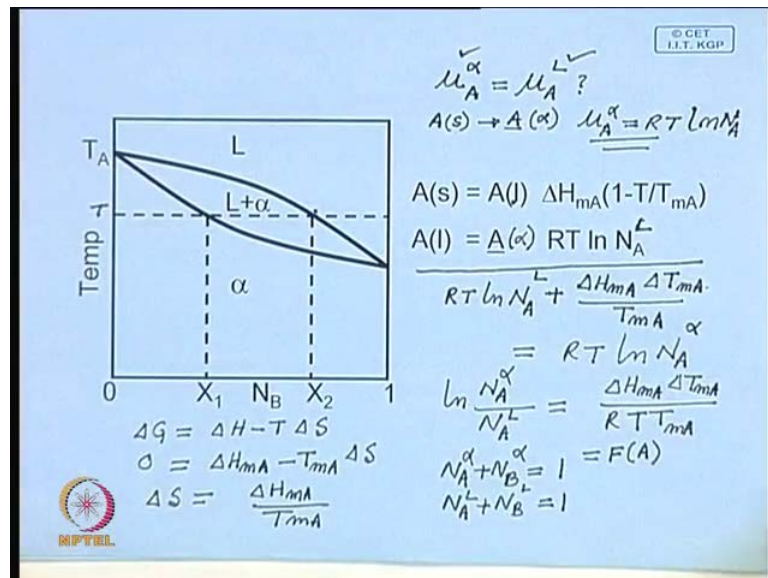
Now let us say here what you need to do you have to find out the chemical potential of the two of A and B in the two phases, which are co-existing. Suppose we say that this chemical potential of let us say A in alpha; you have to calculate equated to chemical

potential of A in liquid. Now here look at when you do this calculation it is necessary to use the same standard state. Here you can visualize solid solution of an alpha being form at this temperature T.

T is the temperature now this you can say easily you know that pure A that is solid at temperature T it goes in to solution we calls this solution alpha, which is also solid. So here you can easily say that your chemical potential of A in alpha equal to and is a free energy of mixing or partial molar free energy of A in alpha ln activity or mol fraction A. Now how do you calculate the same thing in the case of how do you estimate this; so this is easy this is done but how do you get this now here you can you have to use the same standard state we have use the standard state here pure A at temperature T.

So here if you consider pure A at temperature T this has to be transformed into liquid; this is transforming into liquid and A liquid goes into solid solution it forms alpha. So here you can say this is R T ln N A in liquid this is easy and then how do you calculate the free energy change over here this free energy change is can be estimated we know that free energy is made up of two component delta H enthalpy minus T delta S. Now at melting point pure A you know this is zero at melting point and let us say this delta H is enthalpy of melting of A this is minus this melting point of A delta S.

So you can calculate the delta S equal to delta H m A over T m A. So this is what you substitute here you get this now you add the two then what you get is R T ln N A in l plus this we call is delta m A and this also you can write as delta T with reference to at melting point of a temperature difference from here to here, this over melting point and this is and this we have found out this is equal to this is mu A l so this is equal to R T ln N A alpha. So or if you can simplify what you can say that this is N A in liquid this is equal to delta H m A delta T m A over T suffix melting point of A and R and this is the temperature.

So this we can say this is some function this is a function of some thermodynamic features of A and we also remember that in any of these phases we can say that N A alpha N B alpha these are atom fraction A in alpha, B in alpha this is equal to one. Similarly N A L N B L this also is one. So with this therefore, it is possible to construct as from the thermodynamic constants or thermodynamic parameter defining A and B; basically the enthalpy change in melting and melting point this is what you need, then

you can reconstruct on equation one equation one like this and an another equation, which is given over here.

This you can do exactly in the same way by equating what you need here; you need to equate this repeat the same thing for chemical potential of B you try B in alpha, B in liquid. In this case you have to also select in the same way that appropriate standard state and here you should select this is a standard state that is pure B liquid at T is the standard state with the same standard state; you equate and formulate this equation and if you solve you will get the equation which is shown here.

Now it is very simple to setup a spreadsheet or say tabular a table construct a table and calculate these values let us say F A and F B for different temperatures having done that you can convert it you know you can try and solve and find out this you can equate the two; these two if you equate you can eliminate one of the variable; you will get N B L if you eliminate this just re-write this expression and it is possible say what you need to do is you can always say that this is l n.

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So one way is one minus you convert the first one N B alpha this is equal to exponential let us say F A; this function this and times one minus similarly, the other one you can say that N B alpha equal to exponential.

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This should be now here if you equate you get one expression for you get this as A 1 function similarly, you can also get N B alpha also a functional form. So in fact you have two equations two unknown and it can be solved and this is what you can easily do on a spreadsheet, which is shown here. So these are this constants which are listed here the melting point what you need to know the melting point and let us say that melting point of A is 800 degree kelvin; enthalpy of melting this is 30000 joule per mol. Then melting point of B you take 500 and this enthalpy you can set it up in a spreadsheet and you that or is approximately 8.3 joule per mol per degree kelvin. So everything is known so what you can do is setup a spreadsheet.

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You calculate for various temperatures say setup a table for T it is starts with 800 say may be 20 degree interval come down to 500 for each of these temperature; you calculate the function that from the thermodynamic parameter of A. Similarly, you calculate this from thermodynamic parameter of B and then it is possible you can find out atom fraction of B in liquid and you will see that same entire thing if you just invert it take reciprocal. So may be if you calculate A minus A or something and then you can get N B alpha.

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T	F(A)	F(B)		F(-A)	F(-B)	
800	0	-1.803375	0	0	1.803752	0
775	0.145464	-1.70678	0.16057	-0.14546	1.706776	0.029135
750	0.300625	-1.60333	0.305098	-0.30063	1.603335	0.061393
725	0.466488	-1.49276	0.433973	-0.46649	1.49276	0.097536
700	0.644197	-1.37429	0.547679	-0.6442	1.374287	0.138574
675	0.83507	-1.24704	0.646789	-0.83507	1.247038	0.185858
650	1.040626	-1.11	0.731977	-1.04063	1.110001	0.241229
625	1.262626	-0.962	0.80401	-1.26263	0.962001	0.307234
600	1.503127	-0.80167	0.863751	-1.50313	0.801667	0.387462
575	1.76454	-0.62739	0.912153	-1.76454	0.627392	0.487074
550	2.049718	-0.43727	0.950252	-2.04972	0.437273	0.613668
525	2.362056	-0.22905	0.979148	-2.36206	0.229048	0.778707
500	2.705628	0	1	-2.70563	0	1

where T_{mA} = 800 K, ΔH_{mA} = 30000 J/mole, T_{mB} = 500 K, ΔH_{mB} = 20000 J/mole, R = 1.98, 8.316 J/mole/K

And this is what is shown here and in the spreadsheet and now what you do you plot, this is the composition, this is the liquidus composition, this is the solidus composition.

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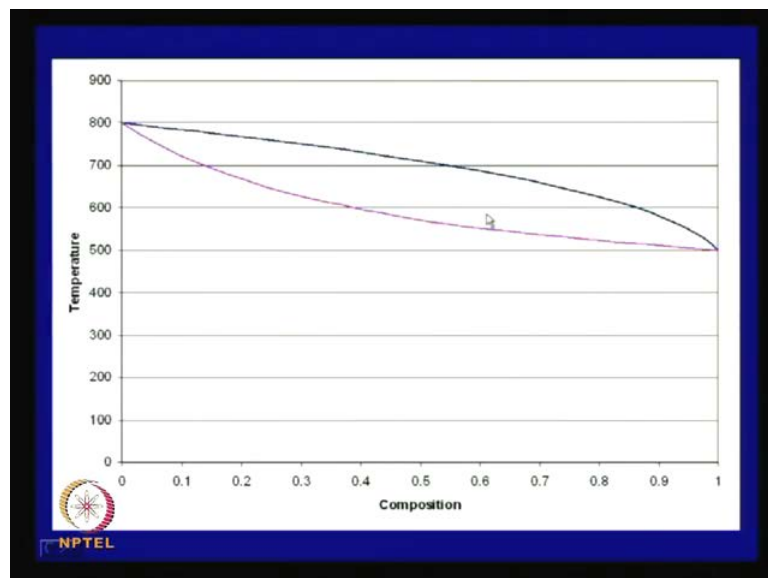
If you plot this you get this type of phase diagram. Now if you do it in a spreadsheet it will be interesting to change some of this do some sensitivity analysis, change the enthalpy of A, change the melting point of A and B and see how what happens to the nature of this phase diagram.

Now here all this calculation has been done with the assumption that the solution is ideal. An ideal solution means ideal solution means we say that free energy of mixing that activity, which is effective concentration of this species A is equal to mol fraction A, whether it is a liquid or in solid. Similarly, we consider both this is similarly the activity of A in alpha equal to N A alpha; so that means you have an ideal liquid solution an ideal solid solution and both are ideal.
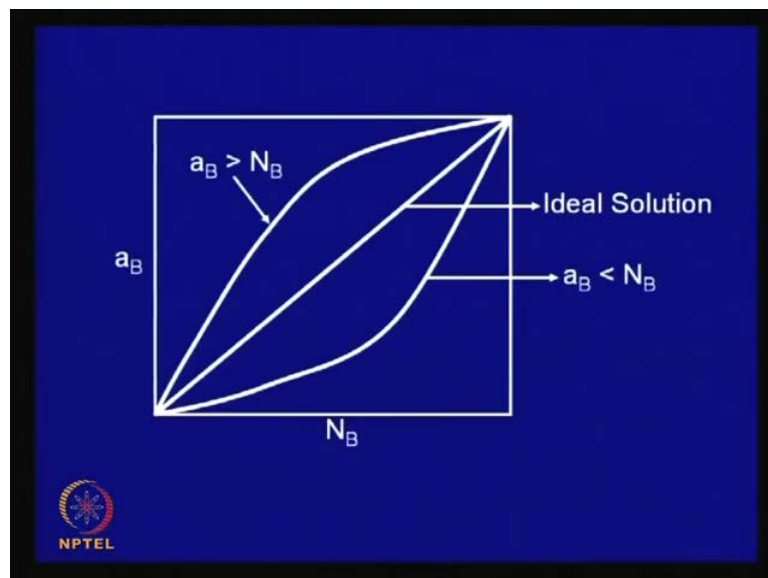
And in fact this is the famous I think you must have done this in thermodynamics. So you plot axis in one axis activity of B in this axis activity and this is the atom fraction B in this axis.

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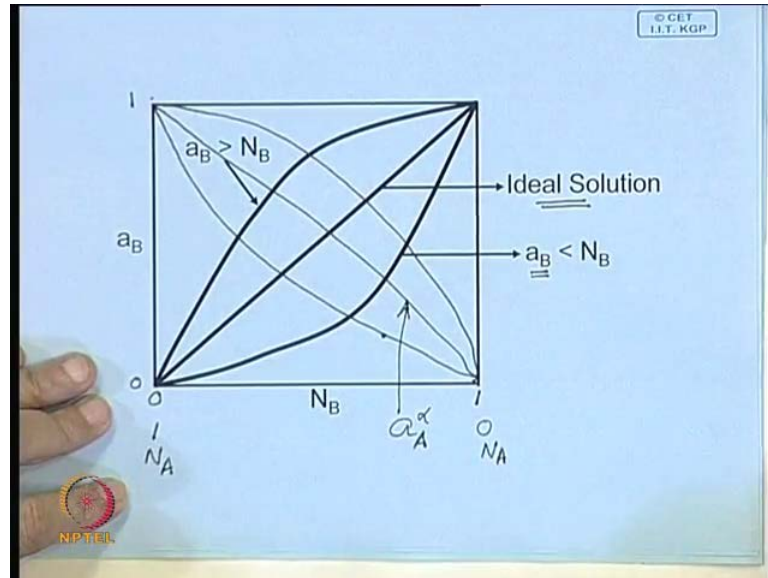
So here this activity is zero this is activity is one, atom fraction of B is zero atom fraction of B is one and that means if both are equal that means this is the line, which represents ideal solution. Now in reality this is never happens and you get both positive and negative deviation. So in one case here let us say you have activity means in one way you can say the effective concentration. Effective concentration is more than atom fraction B here; so which is higher than this. Similarly, you can also have a situation where effective concentration of B is less than atom fractions B in that case you have a negative deviation.

In the same way you can plot over here the activity of A also here we have and this I leave it to you so may be this axis the straight line joining this two point; this will give activity of A and then you will also have a deviations negative deviations you can also think about a positive deviation. So this is activity of A in alpha so this is here also it is a negative deviation and here N A is zero here N A this is N A one. Now this situation when does it happens; now in a solid solution consisting of two metals A and B if they are mixed in random.

So everywhere ever you go if the atom fraction A is exactly equal the number of nearest neighbor; say suppose we say that if the crystal structure is FCC you have 12 nearest neighbor. Now suppose the alloy has 25 percent or one-fourth is one-fourth of this neighbors if they are A and in that case we say that it is a random solid solution and its exactly its composition local composition is matching that exact that is a the number of atom it has proportional to the number of atom it has and this is pictorially shown and this next one.

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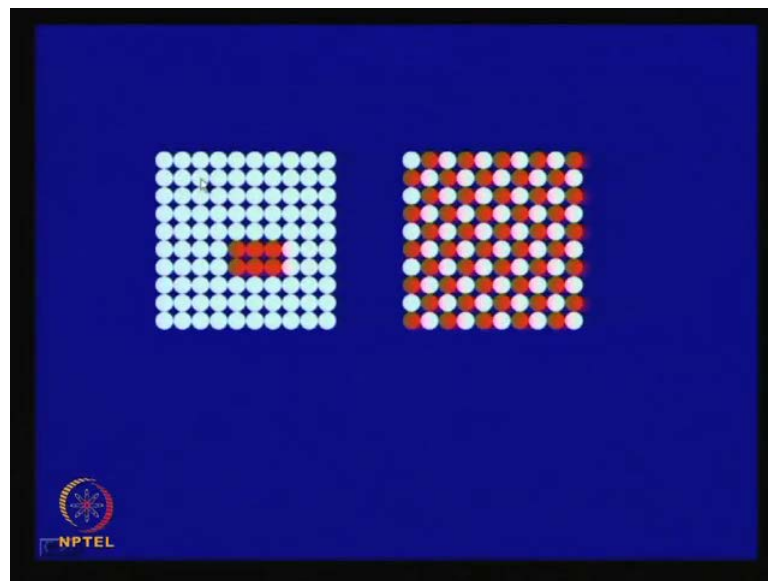
Say suppose here in this cases suppose this is a two 2D a crystal now this atom let us say one is A another is B say let us say this is A and red is B; so if this is a look at A has four nearest neighbor and it has some amount of B but look at here the number of A atoms surrounding this is more than the number of B atom, which should have been present at least say some of these should have been a whereas, locally some of these B atoms surrounding B this also is more that number of atoms, which should surround B is more than what it should be.

So that means something similar is happening some kind of redistribution as taken place in this material; we call this clustering and when you have this clustering you have a positive deviation, so that is number of a atom surrounding A is more than what it should be. Other extreme case look at here this is A atom they are surrounded by all B atom

although we know that there are some A atom here but they are not the nearest neighbor. So that means here you have A and you see that there is a regularity of arrangements.

So that means it is ordering so in the ordering case you have the other kind of unlike neighbors, you have more unlike neighbor that like neighbor. So this is the other extreme so this if you can go back so that means this is what is happening; in one case have more like number of atoms then actual. So if this is the composition this should have been the atom fraction B but actually you have more atom fraction B surrounding A B atom. Whereas, in the other extreme case you have less number of atom fraction B surrounding in A B atom and we will know about this in later in little detail.

But these are called the one is called this is called clustering; you have one kind of deviation, which is a reverse deviation in case of ordering and most real solutions you will you will have a similarity you know you have a such a situation, in fact we also talked about it during diffusion. We called we define a factor called activity co-efficient and in fact, which defines which gives you the effective number of local concentration and we will learn about it as more in detail as we go through this lectures.

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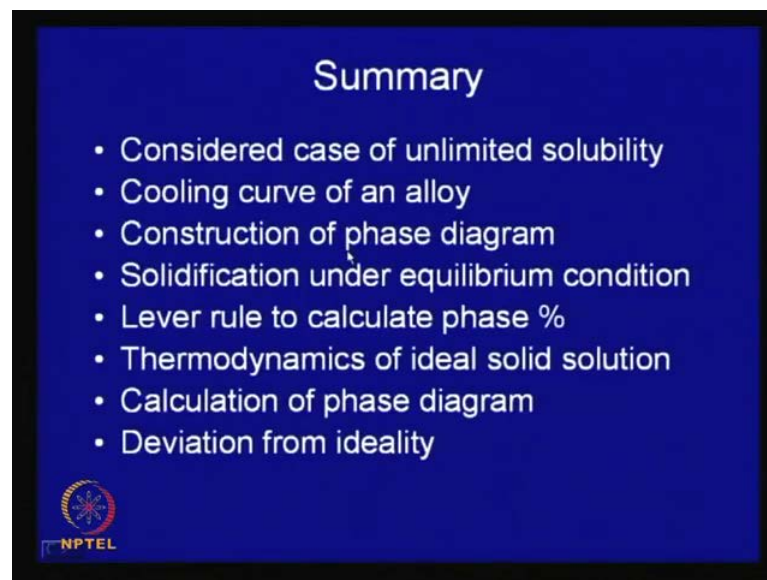
So, today to some up what we have done today we have looked at the case of unlimited solubility in both liquid, and solid state, and this type of system is called isomorphous system, we will look at the cooling curve of an alloy belonging to this particular system. We also looked at how from this cooling curve the phase diagram can be constructed,

and this phase diagram tells us how the solidification proceeds, and in this case the condition that A and this describes the process of solidification when thermodynamic equilibrium is maintain at every state.

So we can say that this can give you the structure of the alloy, if it is cooled in an equilibrium under an equilibrium condition. We also talked about lever rule, which helps as to derive and are calculate phase percentage at a given temperature, and this is a general rule and we will be using it to phase diagram to interpret micro structure evolution. We also looked at thermodynamics of ideal solid solution, and using the concept of thermodynamics, using the concept of chemical potential, it is possible to calculate phase diagram from the thermodynamic properties of metal A and B, andnd we also talked about the deviation from ideality. And next class we will talk about cases where there is partial solubility; they are not measurable in all proportion and what happens in such cases. Thank you.