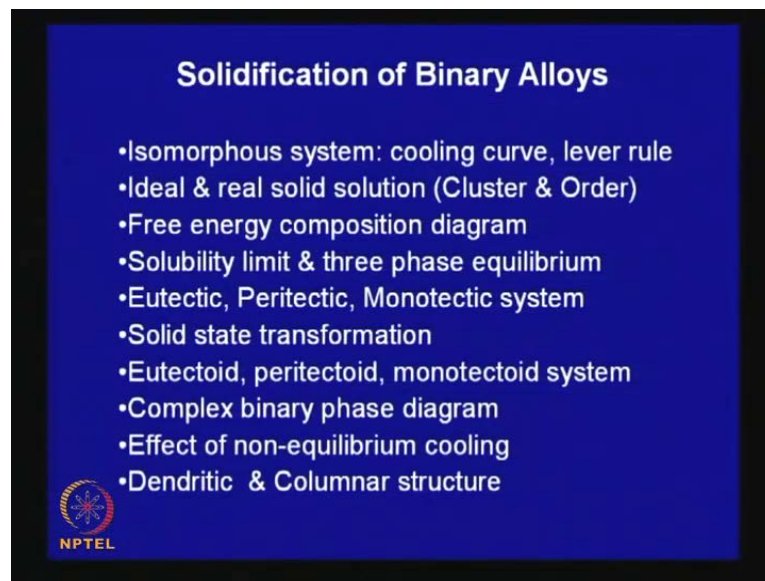


**Principles of Physical Metallurgy**  
**Prof. R. N. Ghosh**  
**Department of Metallurgical and Materials Engineering**  
**Indian Institute of Technology, Kharagpur**

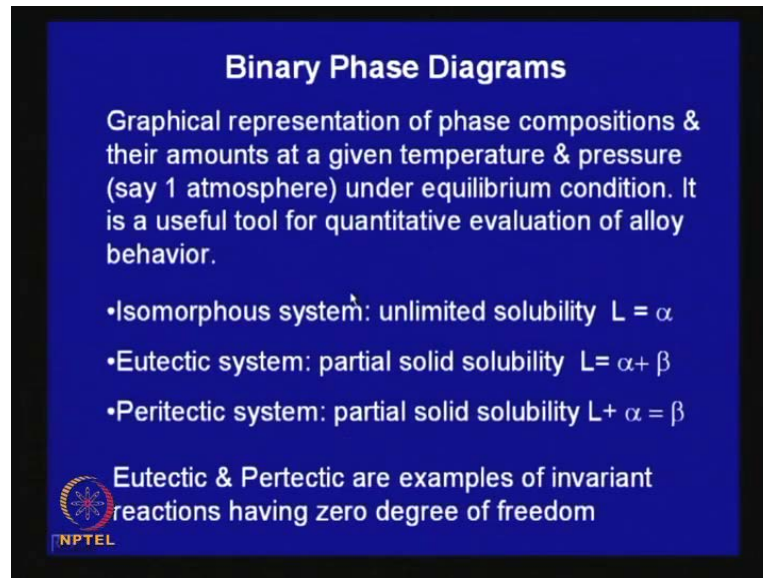
**Lecture No. #20**  
**Solidification of Binary Alloys (contd.)**

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Good morning, we continue our lecture on solidification of binary alloys. Now we have, so far looked at isomorphous system, its cooling curve; we also looked at the lever rule, which can be applied to find out the percentage phases, which are present in a particular case, I mean wherever you have two phases coexisting. We also looked at the difference between an ideal and real solid solutions. We talked about free energy composition diagram in the case of isomorphous system. Then, we moved over to cases, where there is solubility limit, that means, two metals, they are not soluble in solid state in all proportions; in those cases, there will be a situation, where three phases can coexist. And we looked at two particular cases; eutectic and peritectic system. And **and** we looked at how this structure evolves in detail in eutectic and peritectic alloy. Now we will continue for here onwards

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**Binary Phase Diagrams**

Graphical representation of phase compositions & their amounts at a given temperature & pressure (say 1 atmosphere) under equilibrium condition. It is a useful tool for quantitative evaluation of alloy behavior.

- Isomorphous system: unlimited solubility  $L = \alpha$
- Eutectic system: partial solid solubility  $L = \alpha + \beta$
- Peritectic system: partial solid solubility  $L + \alpha = \beta$

Eutectic & Peritectic are examples of invariant reactions having zero degree of freedom



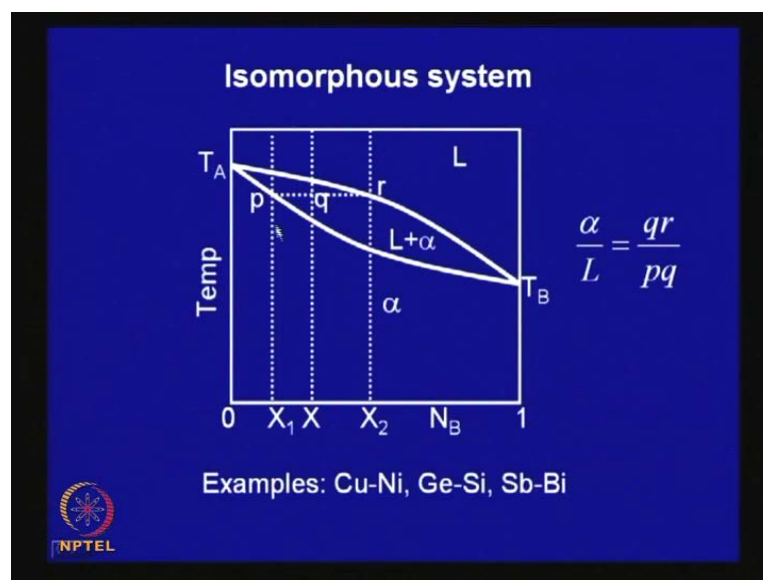
And basically, what we have seen that the transformation that takes place during solidification of a binary alloy is represented in the form of a diagram, which is called binary phase diagram. This is a graphical representation of phase compositions and **and** their amount at a given temperature. And often we do it at constant pressure, and usually the pressure is one atmosphere. And one important condition here if we assume that the cooling is very slow, such that at every stage, there exists an equilibrium between liquid and solid.

And these binary diagrams, they are well useful tool for quantitative evaluation of the micro structure of the alloy; and hence, it can also in for some thing about its mechanical and other physical behavior of the alloy. Now, in the case of an isomorphous system, where there is unlimited solubility, and both liquid and solid state, the phasing takes place over a range of temperature, we looked at this. We looked at eutectic system, where there is a partial solid solubility, and here there will be a some stage, a liquid, which dissociates into a mixture of two solids - alpha and beta; in phase diagram we always represent liquid using an this roman alpha that L represents liquid, and Greek alphabets are used to be represent phases. Now, we also looked at a peritectic system, where **...** And this is also a case, where there is a partial solid solubility; there is a limited solubility in the solid state, but unlimited solubility in liquid state.

And here, on the second conditions over a range of competition, the liquid reacts with solid, which has precipitated out to give a different solid; like in this particular case, liquid reacts with alpha to give beta, where beta has entirely different physical characteristics and structures from that of alpha. Now these two cases - eutectic and peritectic, these are examples of invariant reactions; and in fact, at 1 atmosphere pressure, if three phases are coexisting in a binary system, that in binary system, where number of component is two; in that case, if you applied this phase rule, you will find the degree of freedom is 0. So, that means this type of equilibrium can coexist at a fixed temperature and between a fixed composition of liquid and to solids. So, there is no variable that can be altered. So, in fact, in principle from the thermodynamic characteristics, it is possible to calculate these temperatures. And we will see today, one such example.

Now, there will be several order invariant reactions as well, which are possible apart from this, but basically similar to that, that one phase is separating into two phase or two phases reacting to give a third phase. So, this type there are certain other possibilities as well, and we will look at them in subsequent part of the lecture. And also we will look at some different variants of isomorphous system.

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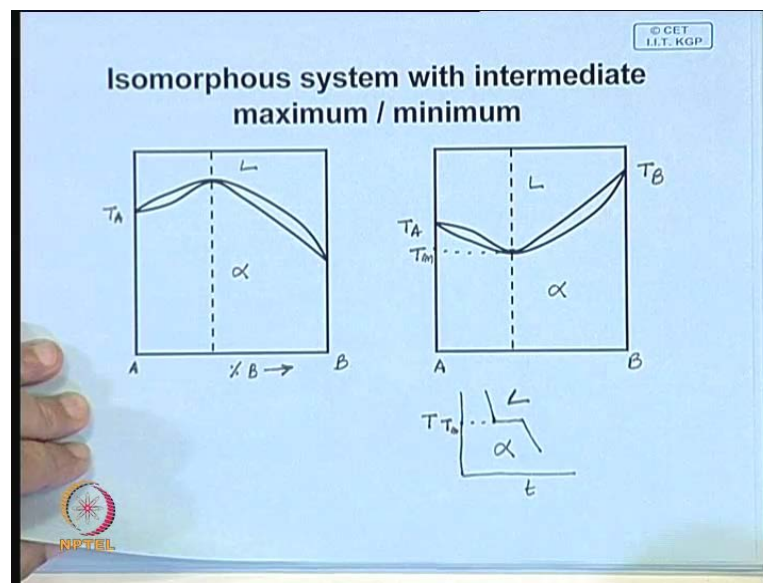


First start with this isomorphous system in the phase diagram, you know just to recollect that, this is that phase diagram of an isomorphous system. And in the two phase region,

one can apply phase rule, that lever rule; one can apply the lever rule to find out proportion of alpha and liquid, which are coexisting; like over here, the alpha of this composition given by that point p, that composition is X 1. So, this can coexist with a liquid of this composition X 2; and in this case, in using lever rule you can say that alpha, amount of alpha is proportional to  $q r$   $q r$ , and amount of liquid is proportional to  $p q$ . And there are certain alloys, which exceed it this kind of phase diagram, which are listed here, like one of the common alloy, is copper nickel.

And here, if you look at both copper and nickel, they have identical crystal structure, they have nearly similar lattice parameter, difference is less. So therefore, atomic size's difference is less, so there exhibit unlimited solubility. And same, I think will be valid, and for you to check up what are the crystal structures, and lattice parameters of these cases germanium-silicon, antimony-bismuth, they also exhibit a similar isomorphous behavior; this kind of table will have at least in the half; until solidification is complete, they will exhibit this type of phase diagram

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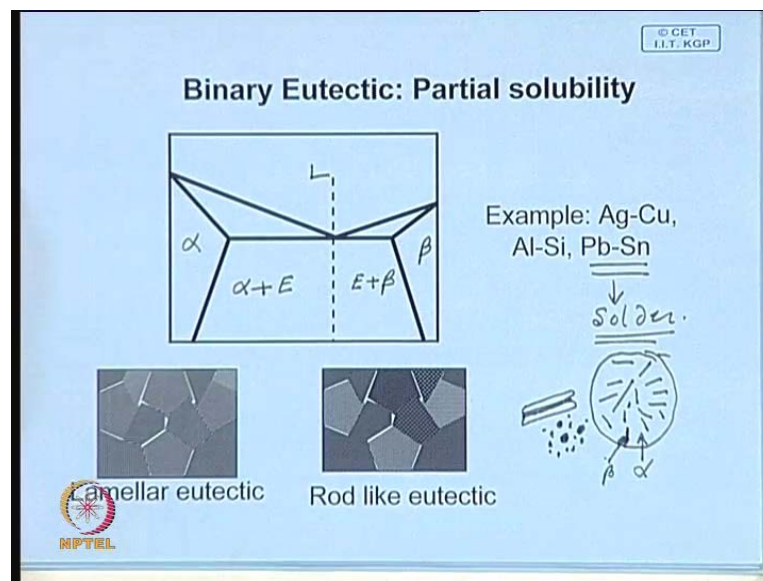


Now, there are cases where this type of isomorphous system can exhibit maxima or minima; so that means, in between an alloy, there can be an alloy, which has in this particular case, higher melting point than both A and B; and which is shown in this diagram. And we will look at it here, say suppose this is actually T over A, this is B, you have percentage of B with percentage plotted along this axis, this is melting point of A,

here it is liquid, and here it is alpha. Now, here you have a maxima, at so that means, you can look at it as if it is two isomorphous system, one this side, another this side.

You can also have a case something like this, exactly similar; here you have liquid, here you have alpha, and here this is  $T$  over  $A$ , this is  $T$  over  $B$ , this is melting point of  $A$ , melting point of  $B$ ; at in between, you have an alloy, which melts in exactly same way as that of pure metal. If you try and plot, it is cooling curve of this alloy, it will actually be a temperature and time; its plot will be more or less exactly similar to that of pure metal. So, this is the melting point of this law, let us say, this is the melting point; and it will exactly, I mean, its solidification behavior will be similar to that of pure metal. So, this kind of deviations from an ideal isomorphous system, they are result of deviations from **ideal** deviations from ideal solid solutions. And we will later on, we will see how we can express this deviations in a more quantitative fashion.

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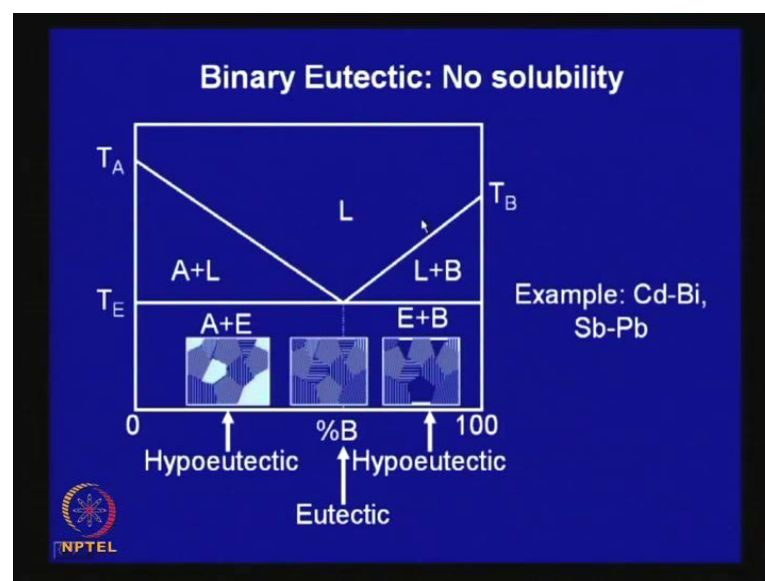


Now, binary eutectic will looked at eutectics, an in this particular cases, where **where** we have two fields, alpha, beta these are terminal solid solution, this is liquid; here you have alpha plus eutectic, here you have eutectic plus beta. And the two cases, you know, there are certain binary alloy system will exhibit this kind of behavior like silver-copper, aluminum-silicon, led-tin, they have this type of phase diagram; and this is a common solider alloy, this is used as led-tin is **is** a solder alloy, it is a low melting material.

And the type of structure that you can get in eutectic is shown here; and we can look at this, say one type of structure in eutectics, say this alloy, here it is totally liquid; and once it solidifies, solidification is complete, you will have a structure, which will give you really an intimate mixture of two phases alpha and beta; here, suppose if see alpha solidifies, surrounding liquid becomes rich in beta, so automatically, the beta solidifies; so in fact, one after the other, it will start forming as so, you have a layer of alpha and that a layer of beta will form; say something like this, you **you** have a layer of alpha forming, then within that, you will have beta, then again alpha. So, this is be a lamella structure can form.

Similarly, you can also have this type of structure; if alpha is precipitates out, surrounding **if alpha precipitates out, surrounding** is beta, again alpha precipitates out. So, you can have this kind of a very intimate mixture of this kind of a rod like this precipitate, which is chromatically shown in this diagram mixed one here. You can also have certain irregular structures are also possible, where maybe one phase is like this; regular structures are also possible; but what it means that eutectic will be an intimate mixture of two phases. So, this is the say beta, this is alpha, and this pattern can be regular or irregular, and this depends on certain physical characteristics of the two metric A and B.

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Now, **you can** it is also possible to have one extreme case, where the solids are totally invisible like here; this is a level diagram of an binary eutectic, where there is no solubility in the solid state. There are certain clear examples like cadmium-bismuth, antimony-lead, which exhibit this kind of phase diagram. And here, the eutectic will be an intimate mixture; the hypoeutectic, you will have primary alpha, primary that means, A crystal of A and eutectics; and here in the hypereutectic alloy, you will have primary B crystals of B and then eutectic.


Now, use in thermodynamics, it will also possible to calculate if suppose, we take the case of cadmium-bismuth; if you know the melting point of cadmium and bismuth unknown, the latent heat of fusion of cadmium and bismuth is known; in that case, if we assume that liquid is an ideal solid solution, it is possible to calculate from this thermodynamic data that means, melting point and heat of fusion. The composition as well as the temperature, that eutectic temperature and eutectic composition, it is also possible to plot this liquid as line, this liquid as line as well as this. And we will see look at one such example of calculating this type of phase diagram; in fact, we have seen one such example in the case of isomorphous system, where both liquid and solid are assume to be Raoult's law; that means, both liquid and solid are assume to be ideal solution.

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**Determination of Eutectic Diagram from Thermodynamic Properties**

Bi-Cd are soluble in liquid state but insoluble in solid state. Estimate its eutectic composition & temperature. The melting points & latent heats of fusion of Bi & Cd are given below. Assume the liquid to be an ideal solution.

$T_{mA}$	544 K	271	Bi
$\Delta H_{mA}$	10878.4 J/mole	2.6	kcal/mole
$T_{mB}$	594 K	321	Cd
$\Delta H_{mB}$	6401.52 J/mole	1.53	kcal/mole



So, let us look at the determination of eutectic diagram from thermodynamic properties. Now this is a problem bismuth-cadmium, they are soluble in liquid state, but insoluble in

solid state; estimates its eutectic composition and temperature; the melting points and latent heats of fusion of bismuth and cadmium, they are given below. Assume the liquid to be an ideal solution; and since pure bismuth and pure cadmium are precipitating out, we can assume that their activity, you will be equal to 1. And these are given over here; this is the melting point of bismuth is 271 degree centigrade, its heats of fusion that is (( latent heat of fusion is 2.6 kilo calorie per mole; cadmium melting point 321 degree centigrade; and its latent heat of fusion is 1.53 kilo calorie per mole. And let us see, how we proceed with the calculation. So, here the main principle is that you have to calculate the free energy of this transformation.

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**Solution**

std state  $\rightarrow$  Pure A out T.

$$RT \ln N_A^A = 0$$

$$A(s) = A(L) \quad \Delta H_{mA} \left(1 - \frac{T}{T_{mA}}\right)$$

$$A(L) = \underline{A} \quad RT \ln N_A^L$$


---


$$A(s) = \underline{A(L)}$$

Since these are in equilibrium the net free energy change should be zero.

And look at a case in the phase diagram, consider a temperature over here. If you are in this region, you have pure A a equilibrium, pure A is in equilibrium with solution; that liquid consisting of liquid or as a liquid solution of B in A. Now, how do we calculate the free energy of transformation, which is illustrated here; say suppose in this particular case, you take that pure A as standard state; in free energy calculation, definition of standard state is quite important; and we take the standard state that is pure A at T, temperature T.

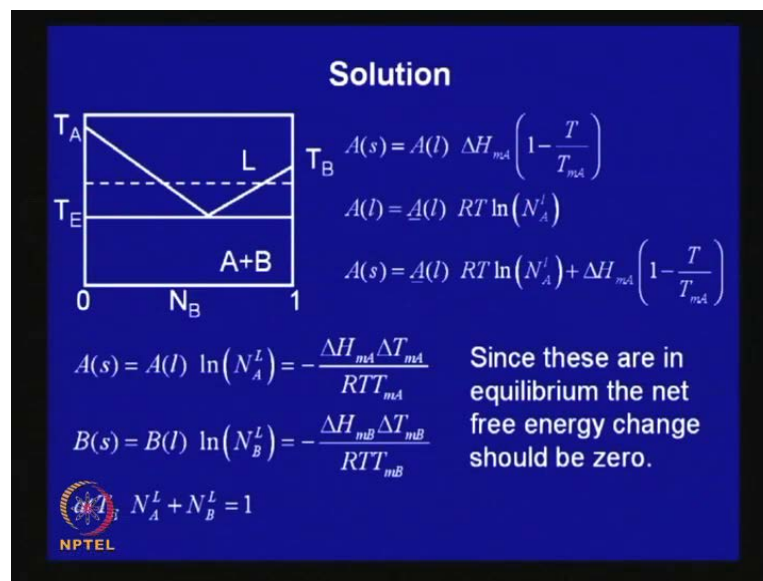
Now, in **this case in** that case, what is the free energy of pure A? Say since it is a mixture, it is  $RT \ln$  activity of A; so we write it mole fraction of A and activity is equal to mole fraction. So, in that case, this is 1, because it is pure A, so this is 1, so therefore,



for pure A, this is 0. Now how do you calculate the free energy of that liquid or let us say partial we want to find out partial free energy of A in liquid; how will you find out? In that case, you take first pure A - solid, it transforms into liquid; and then we assume that this A liquid goes into solution. So, in that case, you can easily write it down, you can check up your earlier notes.

And this particular case, here that free energy will be delta H of that melting of A times 1 minus T over melting point of A; whereas, this is RT ln we assume ideal solution; solution to be ideal, then this is the atom fraction A in liquid. So, you add the two, this is the free energy, so this is the partial molar free energy of A in liquid, and this should be equal to this. So, that is the chemical that partial molar free energy is also known as the chemical potential; and this two potential should be 0. So that means, over this, if you sum these together, so you assume that this is some kind of a chemical reaction, and you add the two, and they are in equilibrium. So, therefore, these two should balance; and with this, what you get is listed here.

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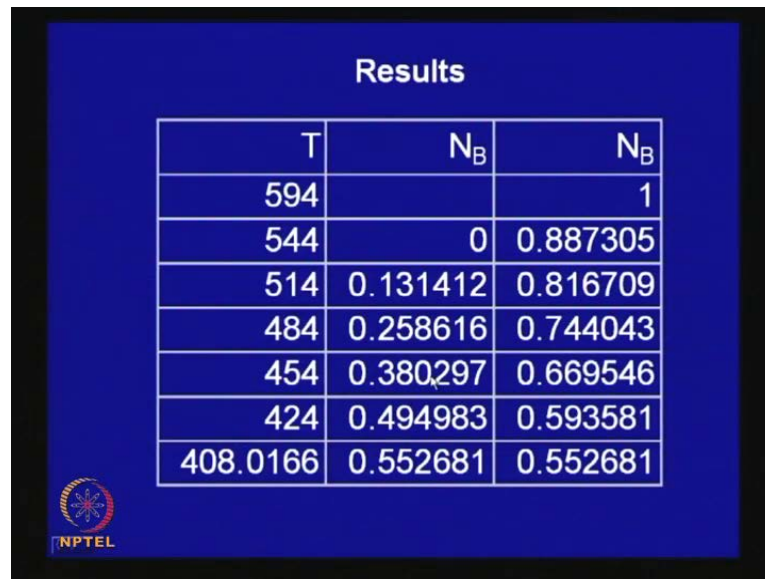


In this particular case, you can see that atom fraction, the large atom fraction A in liquid will be a function of which is shown over here. So, this you can just algebraic simplification, this is equal to this; and you can apply the same concept to this region of the diagram, and then you get similar expression for this. Now, if here, so all these are known, this is known, this is known, this is known, temperature is fixed. So, it is possible

to calculate  $N_A$  that is composition of the liquid as a function at any given temperature  $T$ . And if you do that, you will be able to generate this plot.

In this same way, if you try and solve this, then you will be able to generate this plot; and wherever these two meet, so this is where composition of the liquid, which is in equilibrium with A is exactly same as the composition of the liquid, which is in equilibrium with B. So, in this particular case, the sum total of this will be 1. So, in this case that **that that** you have to possible to find out the eutectic temperature as well as eutectic composition, and for this you can easily set it up in a spreadsheet, and then and these results which are shown here, on the next one.

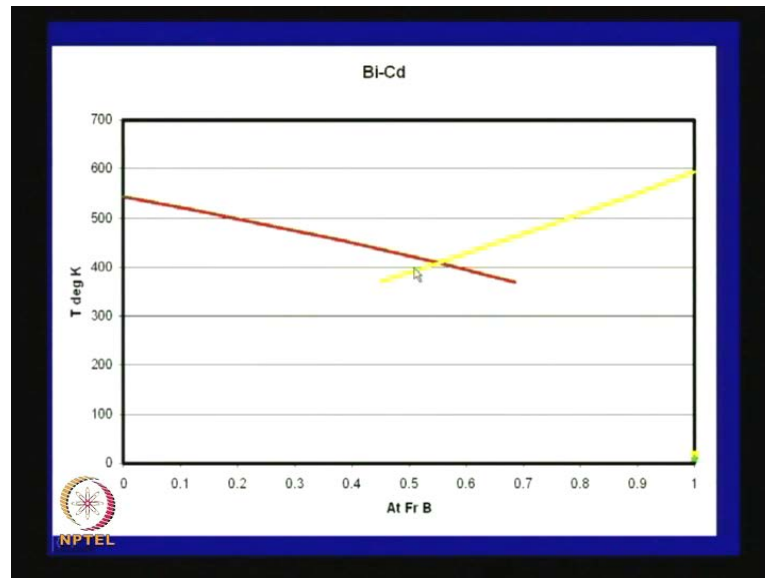
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T	$N_B$	$N_B$
594		1
544	0	0.887305
514	0.131412	0.816709
484	0.258616	0.744043
454	0.380297	0.669546
424	0.494983	0.593581
408.0166	0.552681	0.552681

So, these are the different temperature; this is the melting point of 1 or the 2, which is the higher; and this is in kelvin, degree kelvin; and you calculate that  $N_B$  - atom fraction B; and this is the other one.

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And if you plot the two, then you get this is the diagram you get, and this eutectic composition comes out to be close to around let us say 0.55 atom fraction, and this temperature comes out to be 408 degree kelvin.

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The figure shows a table titled 'Results' with three columns: T,  $N_B$ , and  $N_B$ . The data is as follows:

T	$N_B$	$N_B$
594		1
544	0	0.887305
514	0.131412	0.816709
484	0.258616	0.744043
454	0.380297	0.669546
424	0.494983	0.593581
<u>408.0166</u>	<u>0.552681</u>	<u>0.552681</u>

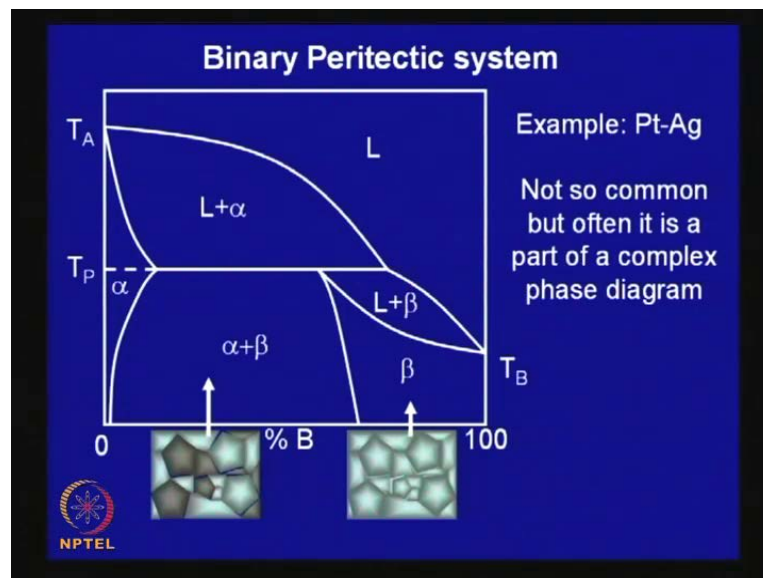
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So in fact, if you check up this diagram, you will find **you will find** that although this, there is a good match between this atom fraction, this composition is exactly seen as **as** given in the phase diagram, which is experimentally found out. But this temperature is possibly, is a slightly lower; what is there we have found out by this. So, in that case,

why is this deviation, why it is not matching? So, one possible explanation could be we have made on assumption that the liquid is ideal, second is we are assumed that there is no solubility.

So now, it is a question of is there a slight, which is extremely small amount of A is soluble in B or B in A, these are some of the possibilities, we can think about; so that means, you have to question this assumptions only, but in the procedure, this is a procedure which is applied; and in one way, you can see that thermodynamic properties are also evaluated from the phase diagram. So, actual experimentally you determine, and then you try to conclude whether that liquid, a solution is an ideal or not; if it is not ideal, from this it is possible to calculate, how much is its deviation from ideality?

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Now, next we also looked at the binary peritectic system. Now, binary peritectic system you know, this is one way, you can when you look at the phase diagram, you said this is a very useful tool, you know by which you can know about the phase percentages, you make some quantitative estimates, like say in this particular case, say this alpha beta region, you know how well its property depend? Suppose we assume that alpha is softer, beta is harder. So, there is a possibility, what we can see? You can apply the rule of mixture to find out its properties.

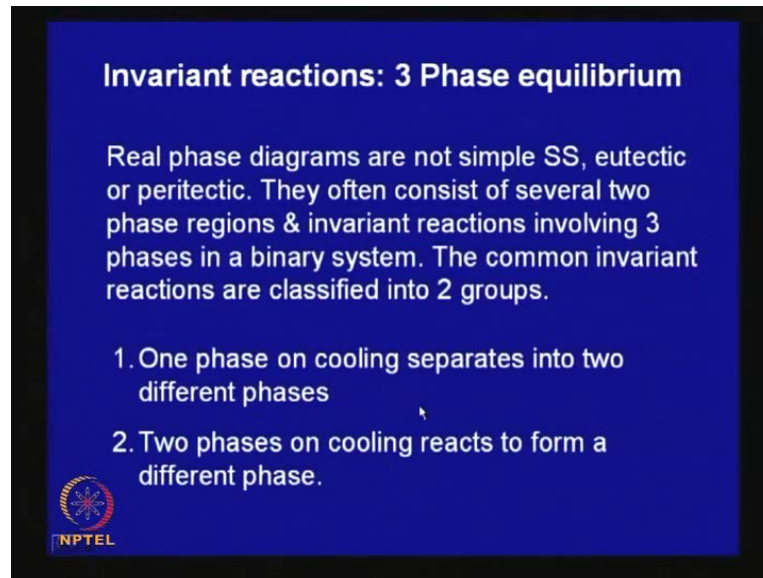
So, if you know percentage alpha, it is possible to... And to find out the property of the mixture; say suppose we are we say that a particular composition say say and this, we try

and find out that on this axis, we super impose tensile strength or hardness. Say suppose beta has a certain hardness, say of beta of a particular composition, this composition has certain hardness, say let us say, this is the value of this hardness; and then alpha has certain hardness, in that case in this region, as amount of beta increases, if you go along this, it will follow is **some** something like this, a linear dependent. So, if you know percentage beta, you will be able to find out such properties.

And also, if you look at the micro structure; say suppose of this diagram is not known, it is also possible to find out or locate **this composition** these compositions from micro structure, analysis of the micro structure. So, what you have to do? Look at two micro structure or two compositions, look at this micro structure, find out percentage alpha here; find out percentage alpha here. And in both cases, both the two phases alpha and beta, say here as it is shown here, they will have a composition, alpha will have this composition, beta will have this composition. So, using few a lever rules, you can set up one equation with these compositions.

And secondly, follow the second alloy, you can write a similar expression; in that case, and once you know have two equation, two unknown, you will be able to find out these compositions. So, it is both way possible; if the phase diagram is known, you can find out its properties from phase percentages if or else if phase diagram is not known that you find that, this is the region you have two phase structure; then you find out at least make two alloy in the similar in the region, and then find out percentage alpha and beta. And from that, you will be able to find out the compositions that is of this solvers, that is solubility limit of alpha and beta.


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**Invariant reactions: 3 Phase equilibrium**

Real phase diagrams are not simple SS, eutectic or peritectic. They often consist of several two phase regions & invariant reactions involving 3 phases in a binary system. The common invariant reactions are classified into 2 groups.

1. One phase on cooling separates into two different phases
2. Two phases on cooling reacts to form a different phase.

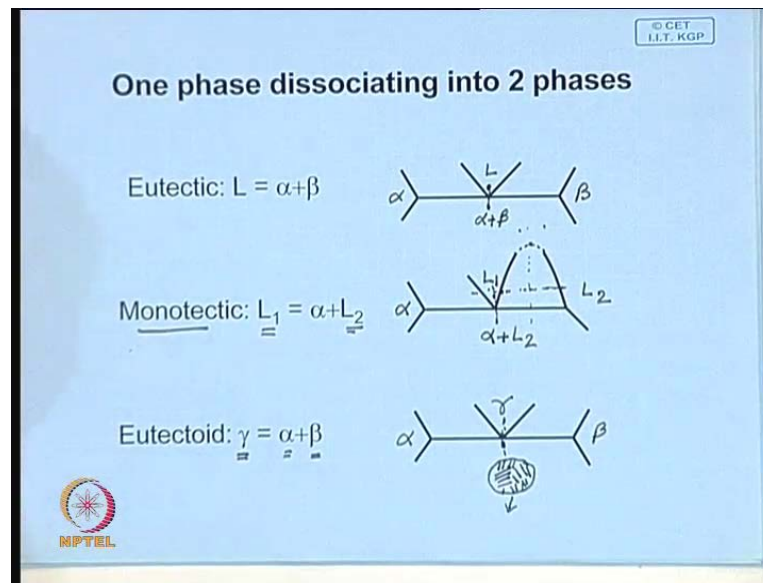
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And now, let us look at we have looked at two types of invariant reaction; see one is a eutectic, where liquid dissociate into a mixture of two different phases, two distinct phases having different physical and properties physical mechanical properties; a crystal structure like alpha and beta. And we also have looked at a peritectic system, where two phases say liquid reacts with alpha giving giving a totally different crystal say beta, a different phase called beta. So, these two cases, we had looked at.

But real phase diagrams are not see basically, not not simple solid solution or eutectic or peritectic, they often consist of several two phase regions, and invariant reactions involving three phases in a binary system. Now, these commonly invariant reactions, you have some invariant reactions other than eutectic and peritectic, and we will look at them. And we can broadly classified this invariants into two groups in one case, one phase on cooling separates into two different phases like that in eutectic; and another case, two phases on cooling reacts to form a different phase like in peritectic.



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Now, let us look at the first ((C)) that is one phase dissociating into two phases; now this example we have looked at in detail, say that is eutectic; and here this shows a small part of that eutectic phase diagram we eutectic isotherm. So, like here this is eutectic, you have two solid solution alpha and beta, and this is the liquid, and this dissociates here. So, here it is totally liquid, and here it is a mixture of alpha and beta; and they are intimate mixture. And now we we can esteem this, in cases where the liquids also can have solubility limit, there are several examples in liquid, which you can think about try and makes all and water, they do not makes.

So, study the possibility that there can be in these two phases, if you are trying to makes in the liquid state, they may not be soluble in each other; they may, and there or they may be partly soluble in each other. So, there can be several such examples. And let us generalize that we have a liquid, and it dissociates into two different liquids having different composition; one we represent as L 1 and another we represent as a L 2. And if we have a reaction say one liquid L 1 dissociates into a solid another different liquid, and which is shown over here; here this is alpha, this is L 1, and this side, it is liquid is L 2, and this is the miscibility gap; so that means, liquid here, in this particular composition liquid, if it has this composition at this temperature, they will not mix and they are not totally miscible, they are not... They will dissociate into two liquid L 1 and L 2.

So, if you extend this, there may be a possibility that higher temperature chance of miscibility is higher. So, here they are miscible, if you go down this temperature, there is a miscibility gap, it dissociates into two liquids L 1 and L 2, this is a miscibility gap. So, in this particular case, this liquid is here, it is reacting, it is **it is** dissociating as you cool this temperature is dissociating into alpha, another liquid; and this type of reaction is called monotectic reaction or this is also an invariant, because you have three phases coexisting in a binary system.

And you can have amount of variant, it is not bad, it is only liquid can dissociate on cooling into a mixture of two phases, you can also have a solid, say gamma; on cooling, it dissociates into two phases, two other solid different solid phases, alpha and beta; and this diagram is shown is here. So, gamma is dissociating into alpha and beta, so here. So, this structure say like eutectic, this structure you will call it eutectoid structure; and structurally also it will be very similar to that of you take T, it is a one very common example could be this type of lamellar structure; **lamella structure** and this is called the eutectoid structure.

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### Two phases react to produce a third phase

Peritectic:  $\alpha + L = \beta$

Syntectic:  $L_1 + L_2 = \beta$

Peritectoid:  $\alpha + \gamma = \beta$

Now, next is the second case, where two phases react to produce a third phase. We looked at peritectic, where alpha reacts with liquid giving you beta, which is shown over here. Now, there are several variants of this, and which, from which you can derive in the same way as that from the eutectic reaction. And here, say like in this particular case,

peritectic, here you have alpha, this side is liquid, and here you have alpha and liquid, these two react, and it form a different solid solution beta.


Now you can think about liquid in miscibility that means, if there is a liquid in miscibility like this, the liquid here dissociates into two liquids L 1 and L 2. Now, these two can react and form a solid. So, this is a possibility, and this is called syntactic reaction. And like eutectoid, it is also possible here also, the two solid phases reacting and producing a third solid phase, and this is called peritectoid. So, here usually here this is alpha, this is gamma, here you have alpha and gamma coexisting in this region, and in this particular composition, this two react and give you a different phase beta. And this part you will have alpha plus beta, this part you will have beta plus gamma, this is called peritectoid reaction.

So, there are several ways, I think there are possibilities that means, and we looked at the common three phase, **the** that is a reactions, which are possible in binary systems; and each of these reactions involved in three phases, they are invariant. So, they can takes place at a fixed temperature, and **and** it is possible that type of equilibrium is possible between liquid and solids of between phases, three different phases of having or having definite compositions; so that means, at one atmosphere pressure, so this temperature is fixed, composition of the phases, which can coexist they are fixed. And now a real phase diagram as has been mentioned, they will consist of may consist of several of these reactions.

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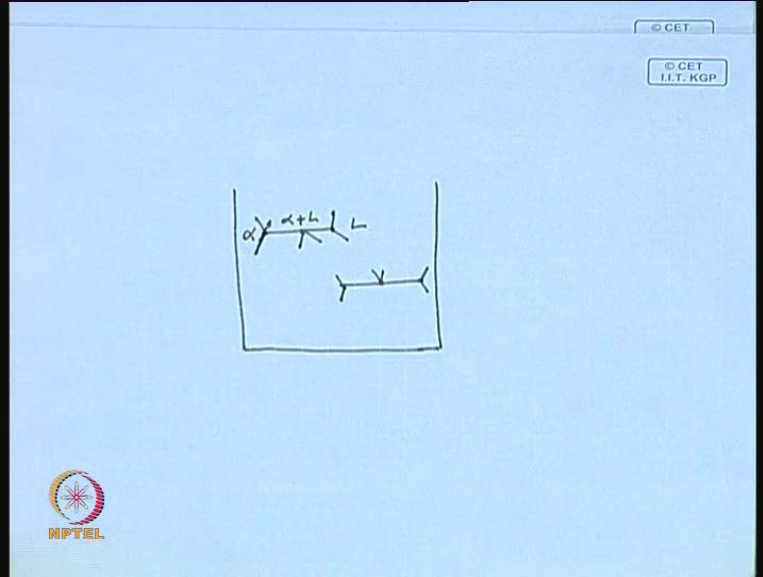
**Construction of complex phase diagram:  
examples**

Draw a binary phase diagram having one peritectic & one eutectic invariant reactions.



Now, let us look at some examples, where construction of complex phase diagram. So, one example, so let us first take a case, where we have to draw a binary phase diagram having one peritectic and one eutectic invariant reaction. How will you do it? So, in this particular case, so what you need to do? You have to say one eutectic and one peritectic.

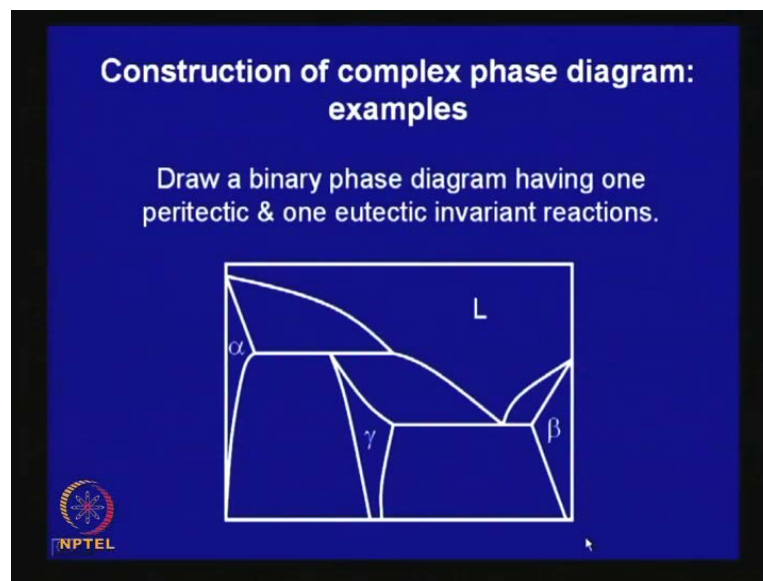
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So, what you try? See you **you** draw this diagram, see one, see you draw this isotherm first; say one peritectic, another eutectic; say suppose we draw a peritectic here. So, this is a two phase, and similarly eutectic that also will be at a fixed temperature somewhere

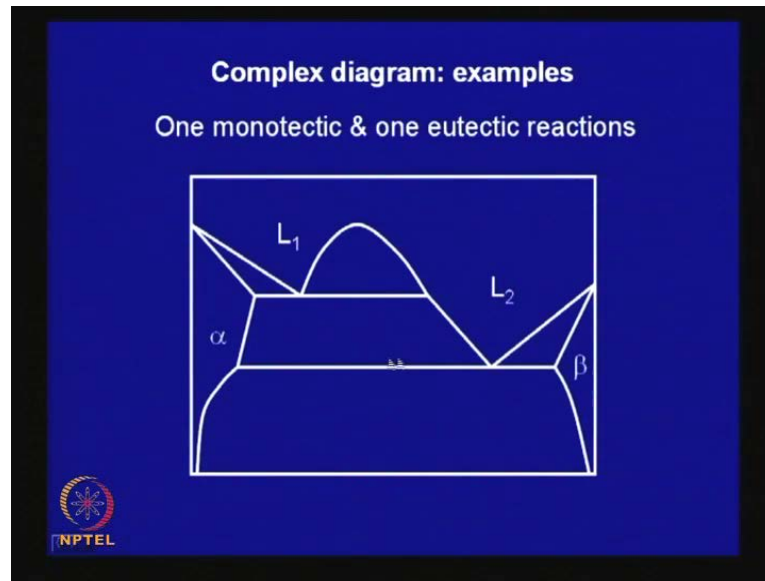
you draw this, then you have, and then you try and join. So, this is... So, so you may have to, and then you follow certain rules like the two phase region should be separated by single phase regions. So, this is say suppose this is this is alpha, this is liquid, so this is two, so this is two phase; and if you extend this line, which is the boundary single phase and a two phase, we should extend in this portion here; this cannot go to a single phase region. So, certain some of these rules you follow, and then it is possible to construct a diagram.

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And which is shown here; in this particular case, if you this is pure A, this is pure B, this is liquid, this is one terminal solid solution alpha; and here alpha, this is a peritectic reaction, alpha reacts with liquid giving you an intermediate solid solution gamma; and this is a terminal solid solution beta, and you have an eutectic reaction, isotherm over here.

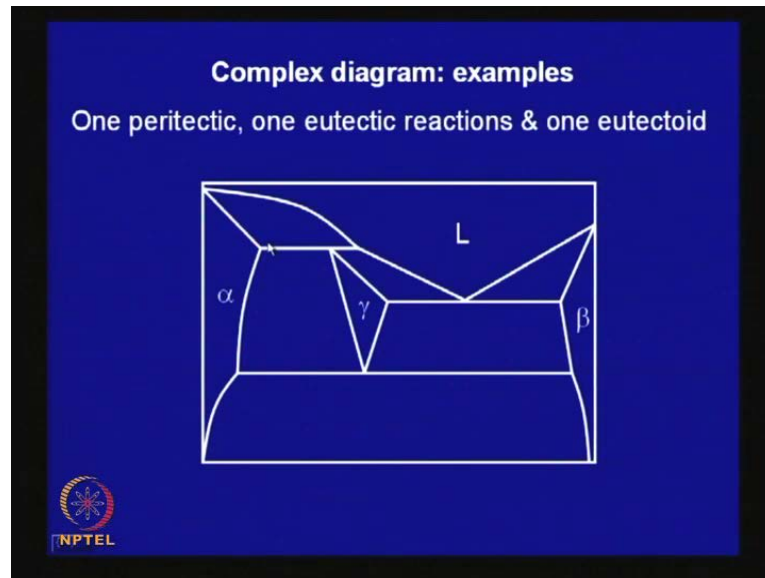
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Similarly, let us take up a case (( )) one monotectic and one eutectic reactions; how will you draw, I think you follow the same principle; and then you get a diagrams say one example, so this part, this is monotectic. Now, if you look at this monotectic, now you should be able to level this diagram or leaving this as an exercise. So, this single phase regions, they have been leveled, but I have left out so suppose, you say that which is the liquidous line, so liquidous line changes with composition is top portion; this is the liquidous line. Similarly, what is the solid as line? So, solid this part is solid, but here it is not solid. So, solidous, this is solidous, so here, this is isotherm, this is a solidus line; similarly, solvers you can say these are the solvers line, these are the solvers line, and these are the regions of two phase region. So, this region is alpha plus beta, this region is alpha plus L 2 this is L 2 plus beta.

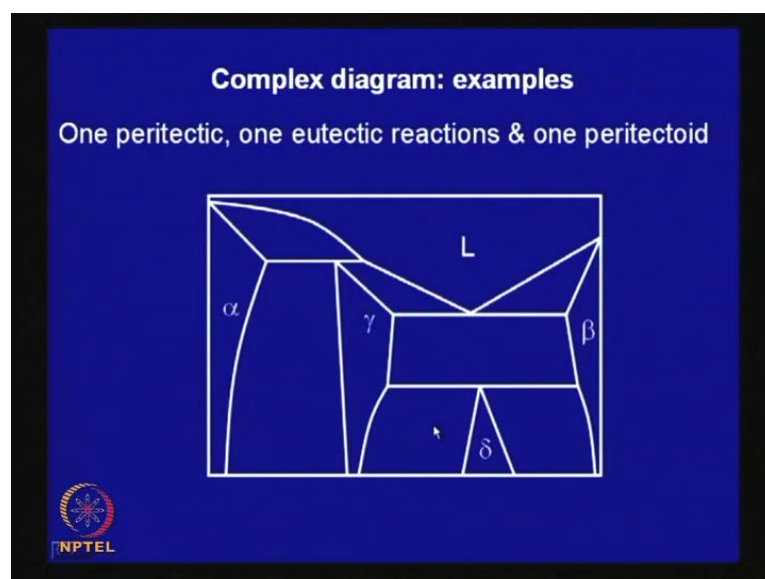


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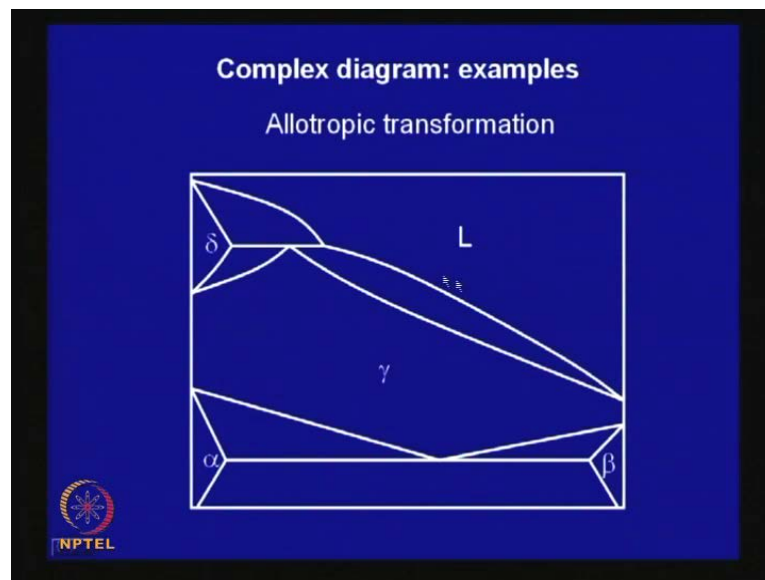
Now, let us take up a case, where to, there is one peritectic reaction and one eutectic reaction, and another eutectoid reaction, you have three isothermal reactions. Now how do you synthesis this? So, one example which is given is this. Now, these are the single phase region, which are then leveled, I leave it to you to level the other. So, this is one peritectic, this satisfies the peritectic, you have one eutectic, this is the eutectic liquid dissociating into gamma and beta; and this is an eutectoid reaction, a gamma dissociating into a mixture of alpha and beta. Now, when we look up some of the real system, you will see that some **to some** of the cases, you have diagrams very similar to this kind.

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So, we have looked at eutectic, peritectic, monotectic, eutectoid; let us try an ... And try to draw one diagram, where there is one peritectic, one eutectic, and one peritectoid reaction. Now this is one such case, this is pure A, pure B, and these are the single phase region alpha, gamma, delta and beta. And you have free invariant reaction, this is peritectic, where alpha reacts with liquid giving gamma; this is eutectic, where liquid of this composition dissociates into two solids gamma and beta, and this is peritectoid, where two solids gamma and beta; gamma of this composition, beta of this composition react together to give you delta of this composition. Now many metals, they undergo a allotropic transformations, so different temperature, they have different crystal structure.

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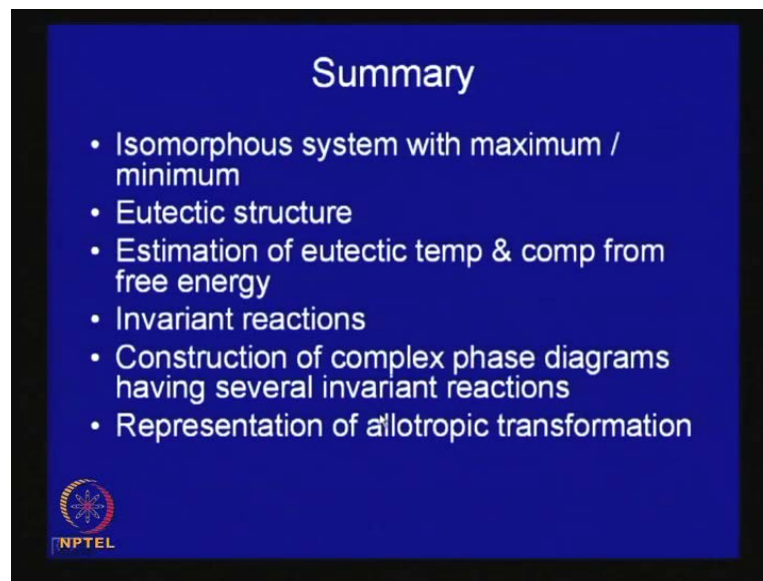
And one common example, we looked at is that of iron. So, there will be such cases, in many binary phase diagrams, you will come across such situation, where pure solid also undergoes transformation - solid state transformation. So, a higher temperature, it may have one crystal structure; at lower temperature, it has another crystal structure. As we have seen pure iron, when you cool initially, it solidifies into a body centered cubic structure, then it gets converted into a face centered cubic structure, and on further cooling, it again transforms into a body centered cubic structure. So that means, pure iron has two such allotropic transformations.

Now how are these transformations represented in the phase diagram? So, let us look at one example, where there is allotropic transformation; let us say we have both metal A

and B undergoes one allotropic transformation. And so I have not specified any of these previous phase diagrams, I mean when it is just solidifies, but one example I am giving here; say here first this liquid solidifies using say simple it is a peritectic system, which shown over here; and once it is solid, it is gamma. But pure A which is solidifying here first as delta, it is solidifies as delta; and then again it transforms into alpha; then gamma again transforms into alpha.

So, pure A in this particular case has that solid A has one undergoes, one allotropic transformation delta to gamma at this temperature; and again from gamma to alpha at this temperature. And there is a eutectoid transformation at a lower temperature, where gamma dissociates into a mixture of alpha and beta. So, in this particular case, if you try and I mean, there the cooling curve of this pure metal, you will get one isotherm here, one step over here, second step here, third step here; whereas pure B you will get a one step for solidification, and second step over here, now phase diagrams.

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So with this, we have looked at several types of phase diagrams, we have looked at; we have looked at isomorphous system with I mean, we also looked at some of these variations of isomorphous system like one showing maximum and another showing minimum; we looked at eutectic structure, the eutectic structure can be some regular, so lamellar, rod like, or irregular type of microstructure it can have, but nevertheless eutectic will be an intimate mixture of two distinct phases. When we also see that is one

particular case that eutectic temperature, we have calculated eutectic temperature and composition from thermodynamic concepts; from free energy of transformation, we have estimated for cadmium-bismuth system.

When we looked at several invariant reactions, several invariant reactions we looked at, and broadly these invariant reactions have been classified into two groups that is one similar, one in which a single one particular phase is dissociates into two at a particular temperature; and the second category, two's phases react together to form a third distinct phase on cooling. Then we also looked at construction of complex phase diagrams of several invariant reactions. And we also looked at representation of allotropic transformations.

Now here most of these diagrams, for a binary system, you **you you** may wonder how are these determined? And here, this we learnt about it, in our initial classes on their experimental, a experimental techniques. And there we talked about thermal analysis in detail; and thermal analysis provides the basic I mean, primary be tool for evaluation of phase diagram, we you can recall that one is a simple cooling curve, and which we have been referring to in trying to find out your how this structure evolves during solidifications. But there are better variants of thermal analysis like differential thermal analysis or DSC - Differential Scanning Calorie metric can be used.

And so they give us accurate determination of this transformation temperature that means, when solidification begins, when it is completed, when solid state transformation takes place; and apart from that also, you can use any other physical properties, also to determine phase diagrams like you can do a resistivity measurement anything, any physical properties, which is a function of crystal structure and composition **will be** can be used to determine the phase diagram. And we also **we also** have illustrated that one particular case discussing that peritectic phase diagram, that even simple micro structure and analysis also can help you to identify the phase boundaries.

With this, we stop here this today's lecture and **and** we will continue still with couple of more classes on the binary phase diagram. I think, next class, we will possibly look at the deviations from ideality, the thermodynamics. And **and** we also will look at what happens, because so for we were discussing the evaluation of structure, when the alloy is cold at a very slow rate; aware at every stage, equilibrium is maintained. So, liquid the

composition change, it can easily adjust to composition change, because you are the movement of atom is much faster than that in solid. But once a solid forms, solid for the composition to change, you have to allow sufficient time; and if you do not allow that time, what happens? I think we will look into these in subsequent lectures. Thank you.