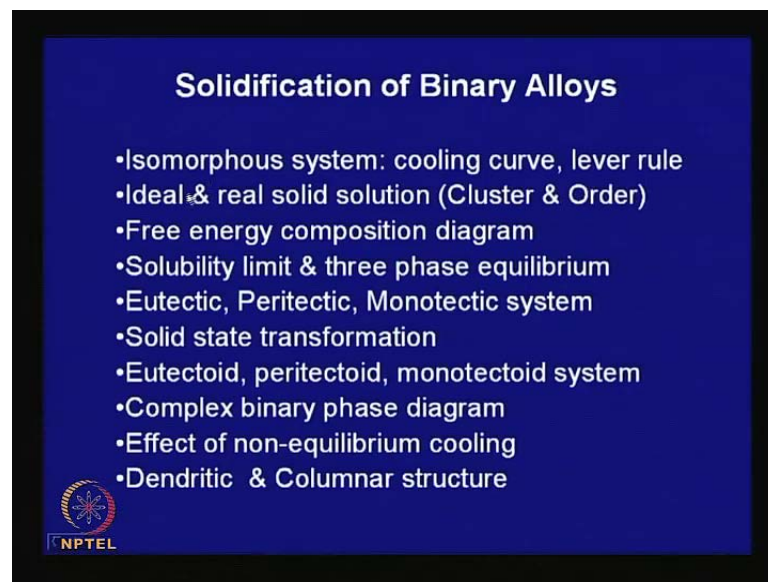


**Principles of Physical Metallurgy**  
**Prof. R. N. Ghosh**  
**Department of Metallurgical and Materials Engineering**  
**Indian Institute of Technology, Kharagpur**

**Lecture No. # 21**  
**Solidification of Binary Alloys (Contd.)**

Good morning. We continue our lecture on solidification of binary alloys.

(Refer Slide Time: 00:26)




Under this, we have primarily looked at several binary systems like isomorphous system. We also looked at the difference between an ideal and real solid solutions. We looked at free energy composition diagram of isomorphous system. We talked about solubility limit and three phase equilibrium and considered several three phase reactions that are possible in a binary system like eutectic, peritectic, monotectic. We also looked at solid state transformation; say like a not only precipitation, but also solid phase transformation; solid state transformation involving reactions where three phases are involved like eutectoid, peritectoid, monotectoid, etcetera. Then we looked at complex binary diagram. We looked at several examples. But so far we have not looked at effect of non equilibrium cooling, and today we will look at primarily a non effect of non equilibrium cooling. But before that, let us look at some of the calculations that we did with certain assumptions about phase diagrams.

(Refer Slide Time: 01:47)

### 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
- Several invariant reactions: Eutectic, Monotectic, Eutectoid, Peritectic, Syntectic, Peritectoid.
- Allotropic transformation.
- Examples of complex phase diagrams




Now, in binary phase diagrams is basically a graphical representation of phase compositions and their amounts at a given temperature and pressure. And usually this pressure is 1 atmosphere, and the system is assumed to be under equilibrium at every step. And it is a useful tool for quantitative evaluation of alloy behavior and we looked at certain examples, and these are things, which we have covered. We also looked at how allotropic transformation is represented in a phase diagram.

(Refer Slide Time: 02:28)

### Thermodynamic data for Ni-Cu

$T_{mA}$	1728 K	1455	Ni
$\Delta H_{mA}$	34096 J/mole	4.1	kcal/mole
$T_{mB}$	1356 K	1083	Cu
$\Delta H_{mB}$	25780 J/mole	3.1	kcal/mole
R	1.98	8.316	J/mole/K

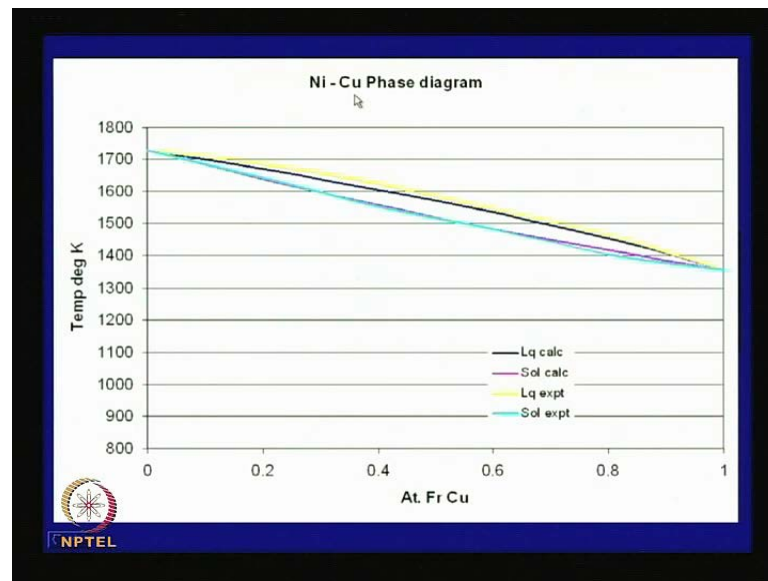
Assumption: Ni-Cu form ideal solution in both liquid & solid states



Now, we use principle of thermodynamics. Because thermodynamics is the basic science (( )) equilibrium and using certain thermodynamic data, we calculated phase diagram for an isomorphous system. And if we take that example for nickel and chromium, we get it;

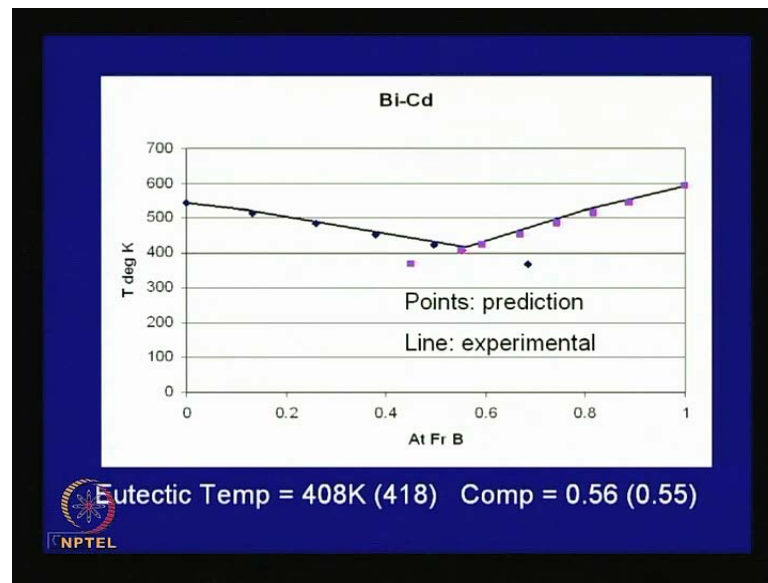
I think one of the classes with arbitrary values for A and B. But if you substitute for nickel and copper, then its melting points are known. This is the melting point of nickel; this is the melting point of copper. This is the enthalpy per mole of melting and this is the enthalpy change during melting or latent heat of melting for copper and this is the universal gas  $R$ . We make an assumption that nickel and copper form ideal solution in both liquid and solid state and using this, we calculated the phase diagrams.

(Refer Slide Time: 03:40)



And here it looks like this; this black line here, which represents the calculated liquidus line. Similarly, this  $R$  one; this line it represents calculated or predicted solidus line and we have superimposed here. The experimentally obtained liquidus and solidus line from hand book data and you look at say with these assumptions we are not getting far away although there are  $R$  deviation. But  $R$  both these ends and this is we can say that this is nearly follows an ideal solid solution; an ideal solution, I mean nickel and copper. If we assume that in liquid state deform ideal solution in both liquid and solid state, this assumption is not far away from reality.

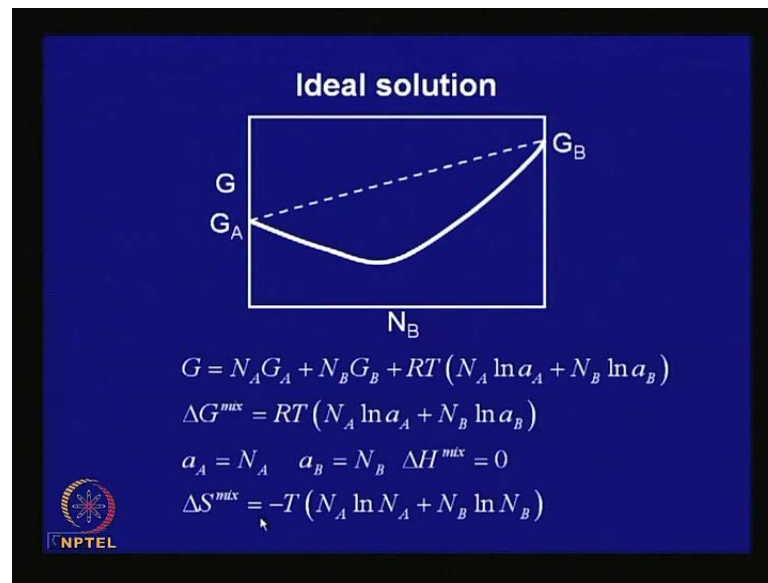
(Refer Slide Time: 04:56)



And we also looked at an extreme case of liquid or solid immiscibility. Say, we assume that for bismuth and cadmium, if you assume that in the liquid state form ideal solution and in solid state, they are totally immiscible. That means, when solidification takes place if it is in a bismuth end, you have primary bismuth precipitating out and you are on the cadmium end, then pure cadmium precipitates out when the solidification (( )). And this forms an eutectic system and with this assumption that they are totally immiscible in solid state. We did calculate the phase diagram using the concept of thermodynamic equilibrium.

And here these points they represent the predicted value and if you extend those, you also get say eutectic as around somewhere here. This is the eutectic temperature around 408 Kelvin and eutectic composition comes around 0.56. And on this, we have superimposed the experimental or actual values on hand books and if you do that, you find you are not being far off. So, that means this type of by using thermodynamic model, it is possible to calculate phase diagram. And in fact, in binary system it is using and later on, as we proceed we will find this is applicable in general. It can be used even in ternary and quaternary systems as well.

(Refer Slide Time: 06:51)



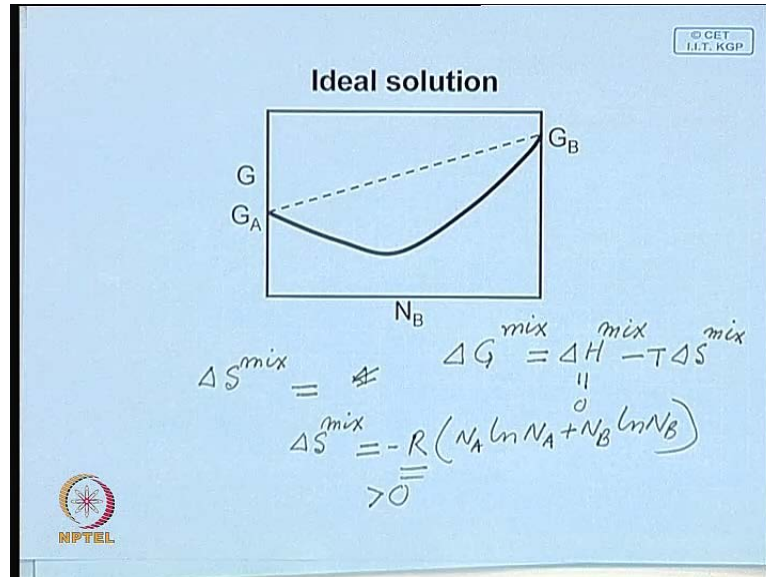
Now, let us look at the concept of an ideal solution. What is an ideal solution? Now, in ideal solution there is the primarily what we look at; say this is the free energy composition diagram, which is shown over here for an ideal solution. So, this is the axis for free energy and this is the atom fraction B; this end is pure A. This is the standard state say A has a free energy, when it is pure. B has a free energy when it is pure and if it is a mechanical mixture, they do not dissolve in each other. Then this will be the line, which will give you the free energy of the mixture; but in reality, say they mix and they mix in all proportion.

In that case, that free energy goes down and somewhere in between you will have maximum stability or the lowest free energy. Now, here that you can say that free energy of mixing can be written as this class; that we say that this is the general expression for free energy of mixing and these are in the pure form, if they mix. But if they go in solution, this will be the change. So, that means from this it goes down and here this activity is always will be less than 1. So, this will be negative. So, this will be lower than this line.

Now, an ideal solution is one, where activity is equal to atom fraction. Say, activity of A in the solution equal to N A activity and similarly, activity of B is equal to atom fraction B and there is no heat of mixing; that means, if you mix the two, there is no temperature change; that means, at so no heat evolved or heat absorbed. So, delta H or enthalpy of mixing is 0. So, therefore this term actually represents that entropy contribution and this

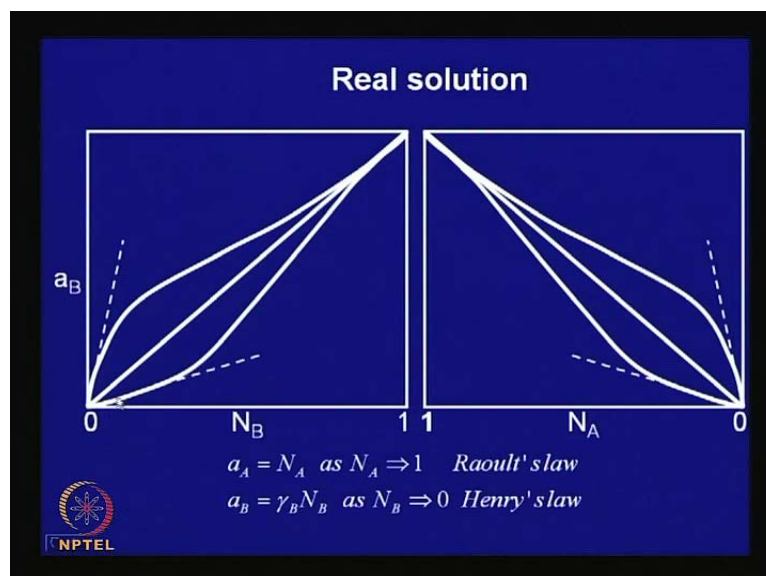
is called entropy of mixing and which is equal to... I think there is a mistake here. It should be T; it should be R. So, this is so delta H by T is actually entropy of mixing.

(Refer Slide Time: 09:44)



Entropy of mixing is **entropy of mixing entropy** is the dimension is the heat. So, we can write delta **H** mix free energy of mixing equal to delta H mixing minus T delta S mixing. Now, here we assume that this is equal to 0. So, therefore delta S mixing equal to minus R (( )) N B. So, this is the correct expression for entropy of mixing. So, what you can see this atom fraction is will always be less than 1. So, whenever you are mixing, so what is happening? The disorder increases. So, this is positive. So, delta S mixing is always greater than 0.

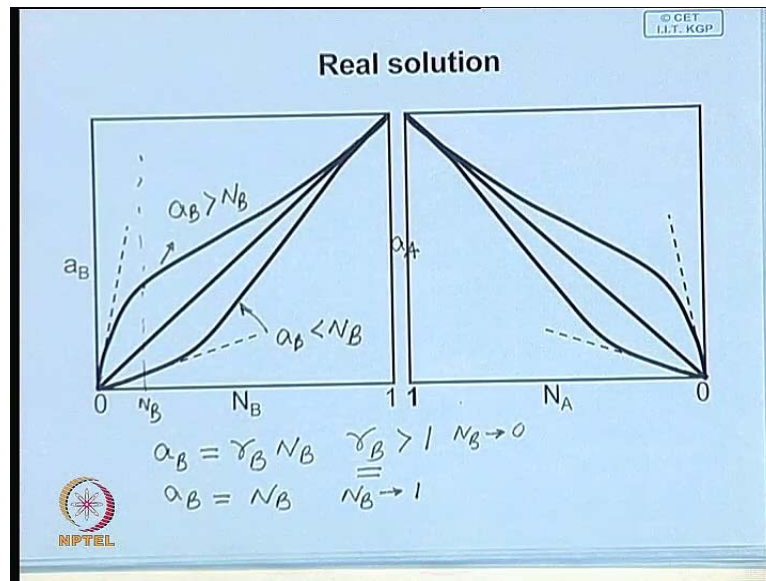
(Refer Slide Time: 11:14)





Now, if you plot the **ideal** activity of ideal solution; if you plot the activity against atom fraction; say in that case, the activity equal to atom fraction is given by this line at 45 degree. So, this is the case for ideal solution and here this is the activity and in reality, usually have some deviations; either a positive deviation that is activity is greater than atom fraction and it describes a path like this. It can also be other way; the activity of B is less than the atom fraction B and it follows this type of path. Actually, what is happening here?

(Refer Slide Time: 12:12)



In this part, you have activity is greater than  $N_B$ ; here any point you take, this is  $N_B$ ; this is the activity. So, here this **part** bottom part you have activity of B is less than  $N_B$ . Now, activity you can see that it actually gives you an approximate composition or you can say local concentration up **(( ))** atom **arounding** around B. So, if activity B is greater than  $N_B$ ; that means there are more number of more than expected number of the atom around B; whereas here there is less than expected number of B atom around B. This is what it means physically. In the same way, you can also plot activity of A in this axis and atom fraction N here.

So, in that case atom fraction here it is 0 and here the ideal solution curve is like this. Now, whenever there is a deviation, you can still make approximation at two ends. So, one is the approximation in this end, where you can see that activity of B is linearly proportional. So, there is an activity coefficient  $N_B$  and here this  $\gamma_B$  is greater than 1 and this is called activity coefficient. So, this part follows like this; whereas in the other end, this part it is nearly approaching the ideal behavior. So, that means this part it

is N B. So, this means where N B is approaching 1, this is the behavior and where N B is approaching 0, then this is the behavior.

So, and this is called... So distinctly we can divide this zone in to two parts. (Refer Slide Time: 11:14) One, we can say where it follows ideal behavior, then we say that it follows Raoult's law and the dilute solution region, it follow Henry's law. So, with this assumption also, you can make further corrections to the phase diagram that you calculate and and it is possible. I mean vice versa; either you can calculate the activity coefficient from the phase diagram; it is experimentally determined or if these activity coefficients they are known, you can calculate the phase diagram.

(Refer Slide Time: 15:12)

**Regular solution**


$$\Delta G^{mix} = \Delta H^{mix} - T \Delta S^{mix}$$

$$\Delta S^{mix} = \Delta S^{ideal} = R(N_A \ln N_A + N_B \ln N_B)$$

$$\Delta H^{mix} \neq 0$$

$$\Delta H^{mix} = n_{AA} \epsilon_{AA} + n_{BB} \epsilon_{BB} + n_{AB} \epsilon_{AB}$$

How can you evaluate this?



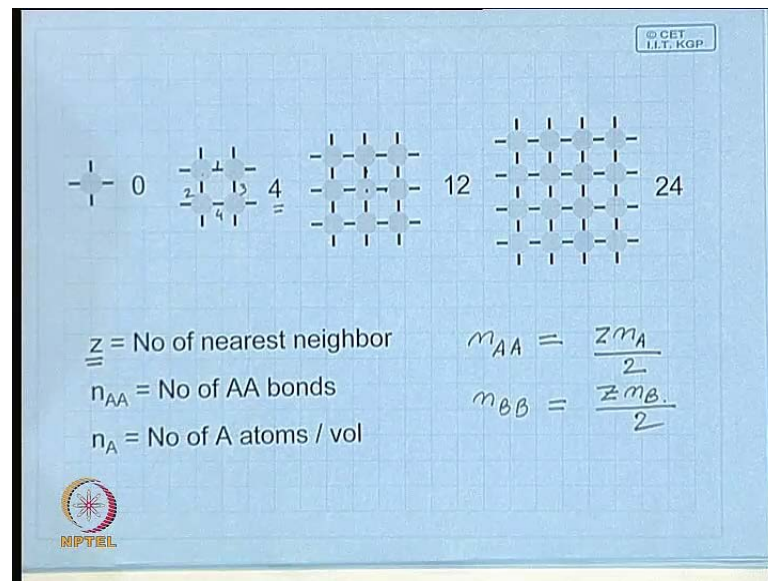
And let us consider a case, where there is some deviation from ideality. So, here you have taken a taken up a case of a regular solution. Now, what is a regular solution? This is free energy expression; general expression of free energy of mixing. You have an enthalpy term; you have an entropy term; T delta is the entropy and here for a regular solution assumption is the entropy of mixing is seen as entropy of mixing in ideal solution. This is the ideal solution; there is a mistake here; correct. Ideal solution and you say let us assume that in this case, this enthalpy of mixing is not zero; either it is positive or negative.

It is either endothermalmic or exothermalmic and in that case, how do you calculate this enthalpy of mixing? Now, enthalpy we can say that usually whenever there is a bond formation (( )) So, energy which is required to break the bond. So, in solid there is a



bond; say there may be two kinds of bond. If it is a binary solution of A and B, there will be AA type of bond; there will be some BB type of bond and there will be some AB type of bond. And enthalpy of mixing is equal to the total bond energy, where  $n_{AA}$  represents number of AA bond and this is the energy of each AA bond. So, this is how you can write the entire I mean that enthalpy of mixing. Now, is it possible to calculate this theoretically. Let us see how this is termed?

(Refer Slide Time: 17:20)



Now, when you form bond say **say** here **2 Di** 2 D representation of a bond formation. This is an atom and A let us say and it has 4 bonds. In that case, here there is number of bond formation is 0. Now, here if bond forms with similar atom, which is shown over here; so few of this bond forms; here number of bond this is **this is** 1, 2, 3, 4 bond form and this are yet to form bond. But if you go on adding more and more number of atoms, you will find that number of these bonds increases. And it increases much more, then the bonds which are free and this is the way, if you can go on adding. Finally, we will find say if say it is possible to calculate the number of bond if you mix; so certain number of A atom. Let us say that  $z$  is the coordination number; number of nearest neighbor.

So, here we can say this atom can have 4 nearest neighbor. Consider this; this is 1, 2, 3, 4. So, this is the nearest coordination number or we can say number of nearest neighbor. How do you calculate  $n_{AA}$ ; that is number of  $n_{AA}$  atom? Then you can find out, if you have  $n_A$  number of A atom. Each has coordination number  $z$ ; so  $z$  times this; there will be so many bonds. But when actually bond formation takes place here; **you know** this is counted twice, if you count like this. So, number of a bond will be this over 2. So,

similarly, you can find number of B B one. This will be z times n B over 2 and now if you mix these together, then how will you find out the total number of bonds. I think I leave it to you.

(Refer Slide Time: 19:48)

$z = \text{No of nearest neighbor}$   
 $n_{AA} = \text{No of AA bonds}$   
 $n_{BB} = \text{No of BB bonds}$   
 $n_A = \text{No of A atoms / vol}$   
 $n_B = \text{No of B atoms / vol}$

$$n_{AA} = \frac{z}{2} n_A$$

$$n_{BB} = \frac{z}{2} n_B$$

$$n_{AB} = z n_A n_B$$

NPTEL

And infact, what can be shown that this is how you will calculate this number of AB bonds. I think, this should be AB **AB**.

(Refer Slide Time: 20:03)

### Enthalpy of mixing: 1 mole of solution

N = Avogrado Number

$$N = n_A + n_B$$

$$\text{Atom fraction A} = N_A = \frac{n_A}{n_A + n_B}$$

$$\text{Atom fraction B} = N_B = \frac{n_B}{n_A + n_B}$$

$$E_0 = \frac{Nz}{2} N_A \epsilon_{AA} + \frac{Nz}{2} N_B \epsilon_{BB}$$

$$E = n_{AA} \epsilon_{AA} + n_{BB} \epsilon_{BB} + n_{AB} \epsilon_{AB}$$

$$= \frac{Nz}{2} N_A^2 \epsilon_{AA} + \frac{Nz}{2} N_B^2 \epsilon_{BB} + z N N_A N_B \epsilon_{AB}$$

$$\Delta H^{mix} = E - E_0 = \frac{Nz}{2} (N_A - 1) N_A \epsilon_{AA} + \frac{Nz}{2} (N_B - 1) N_B \epsilon_{BB} + Nz N_A N_B$$

$$= Nz N_A N_B \left( \epsilon_{AB} - \frac{\epsilon_{AA} + \epsilon_{BB}}{2} \right) = Nz \epsilon N_A N_B = \Omega N_A N_B$$

NPTEL

And now, with this let us try and try to find out how do we calculate that enthalpy of mixing. (No audio from 20:13 to 20:24)

(Refer Slide Time: 20:27)

© CET  
I.I.T. KGP

### Enthalpy of mixing: 1 mole of solution

N = Avogadro Number

$$N = n_A + n_B$$

$$n_A = \frac{m_A}{m_A + m_B}$$

$$n_B = \frac{m_B}{m_A + m_B}$$

$$E_0 = \frac{z N n_A}{2} \epsilon_{AA} + \frac{z N n_B}{2} \epsilon_{BB}$$

$$E = \frac{z N}{2} n_A^2 \epsilon_{AA} + \frac{z N}{2} n_B^2 \epsilon_{BB} + z N n_A n_B \epsilon_{AB}$$

$$\Delta H^{mix} = N z n_A n_B \epsilon = \Omega n_A n_B$$

$$\epsilon = \left( \epsilon_{AB} - \frac{\epsilon_{AA} + \epsilon_{BB}}{2} \right) \quad \Omega = N z \epsilon$$

$\Omega > 0 \quad \Omega < 0$

NPTEL

Now, so in this case what we say that when you mix, then you have total number of atom is  $n_A$  plus  $n_B$ . And if you consider that this is the 1 mole of solution, then you can say that  $N$  is the Avogadro number. Then you will have that atom fraction **atom fraction** in A. So, this will be  $n_A$  over this total number of atoms; make this smaller  $n$  and atom fraction B will be  $n_B$  over  $n_A + n_B$ . So, this and then when they are not mix; so before mixing there will be total bond energy, which you can find out that; if there is an avogadro number of atom, out of this if you multiply, this is the number of A atoms. You multiply this by the coordination number divide by 2. So, this is the number of bonds of type AA and this energy is AA.

Similarly, you can do it for BB type of bond. So, this is  $n_B$  divided by 2. Now, when mixing takes place, then what happens? Now, here certain number of AA bond will be replaced by AB bond and how do you calculate this? Now, this will be  $z N$  by 2. This is the total number of bond,  $N n_A$ . Out of this,  $N n_A$  fraction is replaced only is now AA type of bond. So, therefore this will be this. Similarly, you will have the BB type of bond; energy due to BB type of bond will be (No audio from 23:21 to 23:31) BB plus that will be  $z N n_A n_B$  types. So, this is what is (Refer Slide Time: 20:03) written here. If you... So, this is the total energy. Now, when you mix, the net energy change; Enthalpy of mixing will therefore be given by  $E$  minus  $E_{naught}$ ...

When you do this and (( )) simplification will be able to show that enthalpy of mixing is equal to **that enthalpy of mixing is equal to** avogadro number times coordination number then  $n_A n_B$  and there is an energy term. And this energy term **this** is nothing but the


bond AB type of bond formation energy; even AA epsilon BB and we usually represent this as  $\omega N_A N_B$ . Now, look at this term. Now, if the tendency of ordering is more; so if AB so this is more than this, then epsilon is positive. In that case, this omega you can say this omega is equal to  $N_A \epsilon$ . So, if omega is this is positive, then omega is greater than 0; whereas if AA type of bond is preferred than AB, in that case this is less than 0. Now, when you have this, how does this free energy composition diagram look like?

(Refer Slide Time: 26:18)

### Regular Solution Model

$$\begin{aligned}
 G^{\text{mix}} &= N_A G_A + N_B G_B + \omega N_A N_B + RT (N_A \ln N_A + N_B \ln N_B) \\
 &= N_A G_A + N_B G_B + \omega N_A N_B (N_A + N_B) + RT (N_A \ln N_A + N_B \ln N_B) \\
 &= N_A (G_A + \omega N_B^2 + RT \ln N_A) + N_B (G_B + \omega N_A^2 + RT \ln N_B) \\
 &= N_A \mu_A + N_B \mu_B
 \end{aligned}$$

$$\begin{aligned}
 \mu_A &= G_A + \omega (1 - N_A)^2 + RT \ln N_A = G_A + RT \ln a_A \\
 \mu_B &= G_B + \omega (1 - N_B)^2 + RT \ln N_B = G_B + RT \ln a_B
 \end{aligned}$$

$$\begin{aligned}
 \ln \gamma_A &= \frac{\omega}{RT} (1 - N_A)^2 \\
 \ln \gamma_B &= \frac{\omega}{RT} (1 - N_B)^2
 \end{aligned}$$


So, this is what has been worked out, the regular solution model. If you substitute this and with a little  $\left(\left(\right)\right)$  simplification and here what we have done? We have multiplied for the simplification. What we have done is multiplied this by  $N_A + N_B$ ; these are atom fraction A, atom fraction B and they add up to one. And then this  $N_B^2$  times  $N_A$  this is  $\left(\left(\right)\right)$  with this, then you get this entire expression can be algebraic and you simplify and written like this. So, you have now two parts; this is the free energy that you can say this is partial molal free energy of A in the solid solution. This is the partial molal free energy of B in the solid solution and these two are written like this. So, in the way so what you have is for a regular solution, we get it is possible; assuming this assumption that nature of bond and how do they form.

(Refer Slide Time: 27:32)

© CET  
IIT KGP

### Regular Solution Model

$\Omega = 0$  ideal.

$$\mu_A = G_A + \Omega(1-N_A)^2 + RT \ln N_A$$

$$= G_A + RT \ln a_A$$

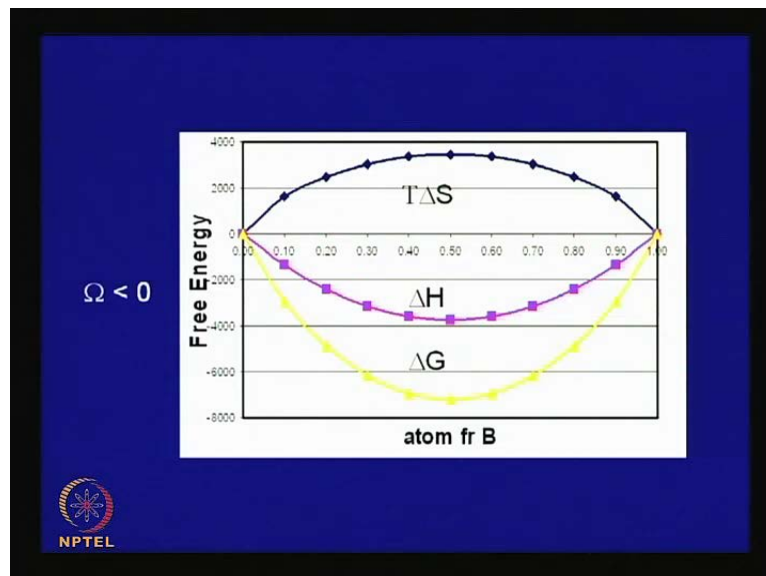
$$a_A = \gamma_A N_A$$

$$\ln \gamma_A = \frac{\Omega}{RT} (1-N_A)^2$$

NPTEL

And from the bond energy, it is possible to derive an expression for activity **activity** of specific atom A and B in a regular solution model. So, this is A is equal to you can say this is **this is** the standard state; then you have  $\Omega(1-N_A)^2 + RT \ln N_A$ . So, **( )** been ideal solution; for ideal solution,  $\Omega$  equal to 0 **for ideal solution**. But in this case, this is this. So, therefore this is equal to you can write that  $G_A + RT \ln$  activity of A. So, therefore one can show that activity A is equal to activity coefficient A times atom fraction and therefore,  $\gamma_A$  will be 1 minus...

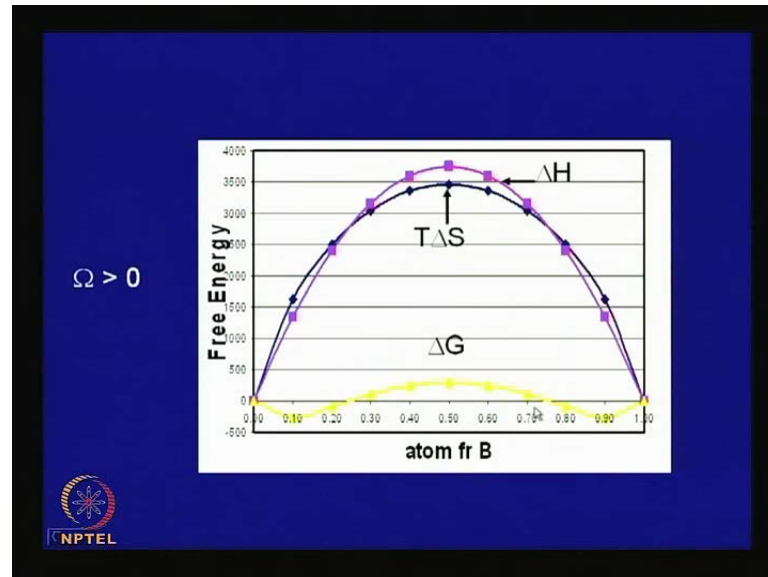
(Refer Slide Time: 29:17)





With this, it is now possible to calculate, let us say that free energy enthalpy and entropy of mixing and they are plotted here, and this is the nature of the plot looks like this. So, when it is gamma is less than 0, this is the type of deviation that you have.

(Refer Slide Time: 29:39)



Whereas, if omega is greater than 0, then this is the type of free energy composition diagram you expect. Here both enthalpy and  $T\Delta S$  both in the positive directions and they add up. So, you **you** get this type of diagram.

(Refer Slide Time: 30:04)

### Limitation of phase diagram

- Represents structural evolution under equilibrium
- Gives no information on rate of transformation
- Time Temp Transformation Diagram provides complementary information

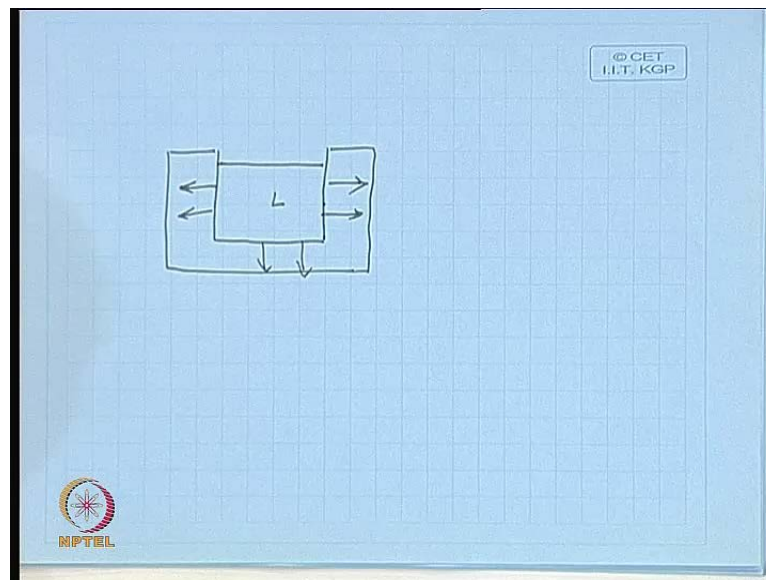
The NPTEL logo is in the bottom left corner.





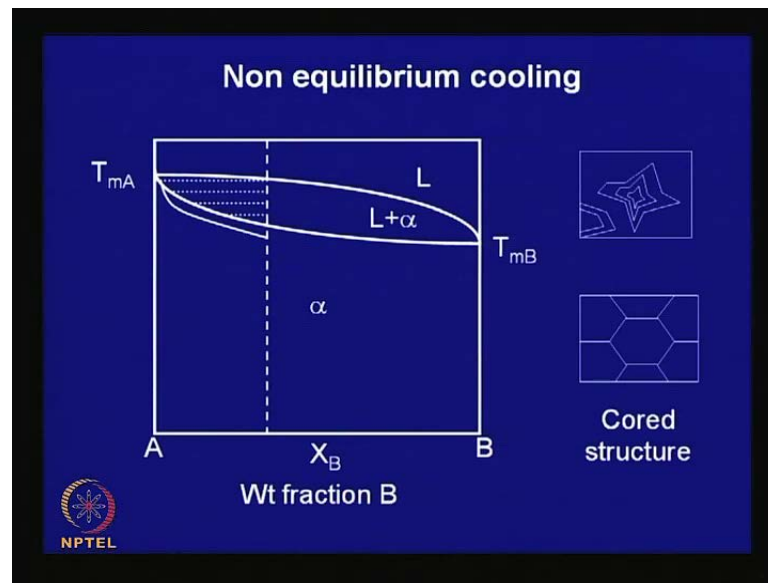
And now, let us say with this I think we have completed more or less the simple binary phase diagrams. Before we proceed further, let us look at (( )) certain limitations of phase diagram, which are given here. This phase diagram gives you structural evolution; no doubt; but only when the system is cooled at a very slow rate. This gives no information on the rate of transformation. There is another variety of diagram, which is called time temperature transformation diagram or TTT diagram, which provides complementary information and later on, when we look at we will separately look at this at a later stage. But when you actually make an alloy, there are certain constraints; say suppose when you make an alloy, what you do? You will melt and you will pour.

(Refer Slide Time: 34:17)



Pour it in a mould. So, in so this is the liquid and now, heat will flow through the mould. Now, the way that heat is extracted that will determine how the structure will form and we have also seen for solidification to start, some amount of super cooling is necessary. So, in that case the way the structure forms, it will depend on the way the heat is extracted from the liquid and let us look this in a little more detail. (Refer Slide Time: 30:04) we will look at it in a little more detail.

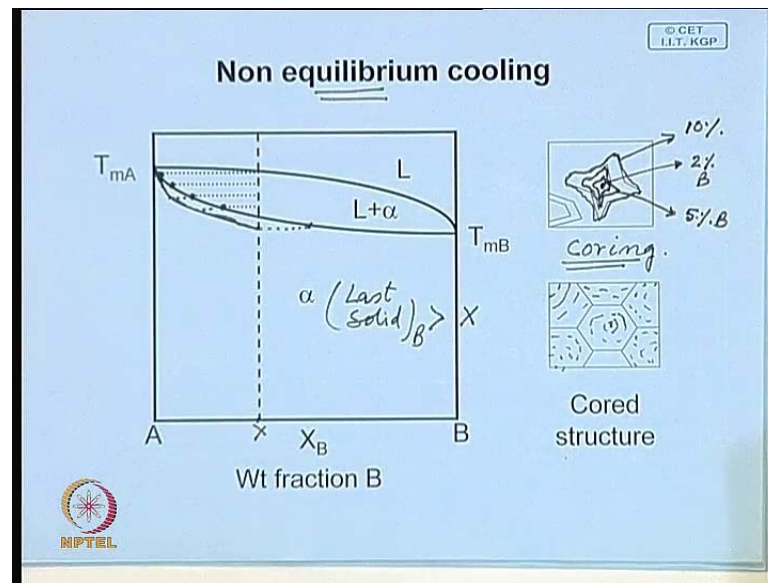
(Refer Slide Time: 35:12)



And now, let us say that we can use phase diagram to understand effect of non equilibrium cooling and which is shown here. First, let us take up the case of an isomorphous system. Now, in an isomorphism system, the situation is... So, you have liquid and we also know that (( )) of atom is equate is must faster; diffusivity is several order of magnitude higher in liquid. And therefore, we can assume make an assumption that liquid composition can change must faster than that in solid. Now, here when the solidification begins, the first solid that solidifies for this particular composition; alloy composition. Composition of the solid will be given by this point.

You draw the tie line or horizontal line; it intersects solidus here. So, this is the composition of first solid that precipitates out. Now, when the temperature comes down say suppose here, then the next solid which will precipitate out at this temperature must have this composition. Now, what happens to the solid that has solidified earlier and if we assume that the diffusivity in solid is very small.

(Refer Slide Time: 36:40)



In that case, what we can think say the first solid, which precipitates out here. Say, may be this is the first solid; it has certain composition. Say, suppose this has 2 percent B. Now, the next solid that precipitates out surrounding; say, now the next one; say this is let us say this is 5 percent B. Now, if we make as a assumption that diffusivity in solid is extremely small. So, this composition (( )) take very, very long time for it to change. In that case we can say that next solid; it is surrounded by each that has the crystal (()). It is surrounded by solutions, which are richer in B and this is the next one; next layer will be even richer in B.

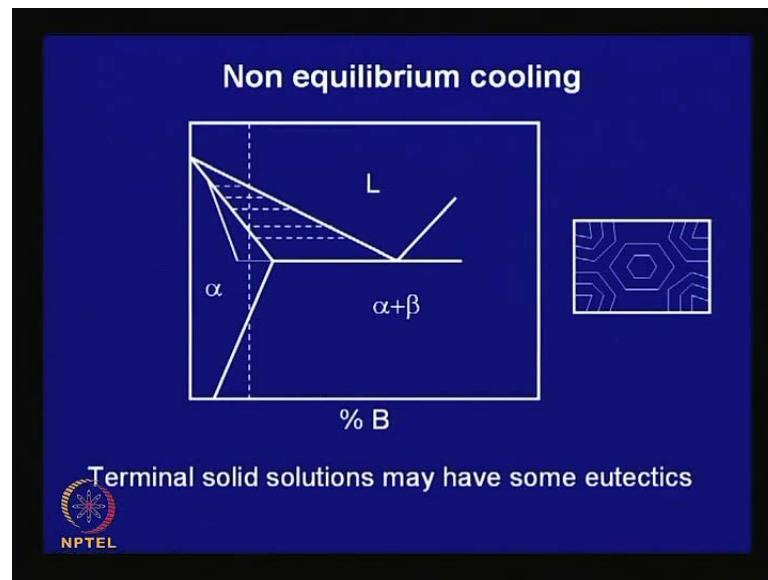
So, let us say this is 10 percent. So, as you go loop from the centre of the crystal to the periphery, you will likely to find that composition goes on changing. So, in a way what we can say that the solid composition; so here the first solid, which precipitate as this composition; next solid as this; next solid as this; next layer as this. But when the average composition if you try and calculate, it will not be. Had you if it were possible to cool it very slowly, it would have followed this line; then it would have move from here to here. Now, instead of moving here, then we can say the average composition lies somewhere here.

So, that means if there is a departure, what will happen? The average composition of the solid will follow a different line. The solid is a **comp** is not able to change its composition very fast as far as **as** it is expected. Therefore, the average line follows this and the last liquid which solidifies here. Solid, it will have a **it will have the** composition, which is richer than even that last solid will have more B. So, B in last solid will be

greater than actual composition; average composition of the alloy and the phenomena is known as coring. So, that means using the simple concept; so that assumption that even if you can use to some extent to understand.

The structural change that is likely to take place, when we there is a departure from equilibrium cooling. And finally, what you have a cored structure? You will have different compositions from centre to periphery. So, you will have so normally if you look at the micro structure, we can say that differently different composition. There will (( )) it will differently. So, you will get a gradation of contours say which means basically represents which basically represents non uniform composition. Now, same thing you can extend it to eutectic structure.

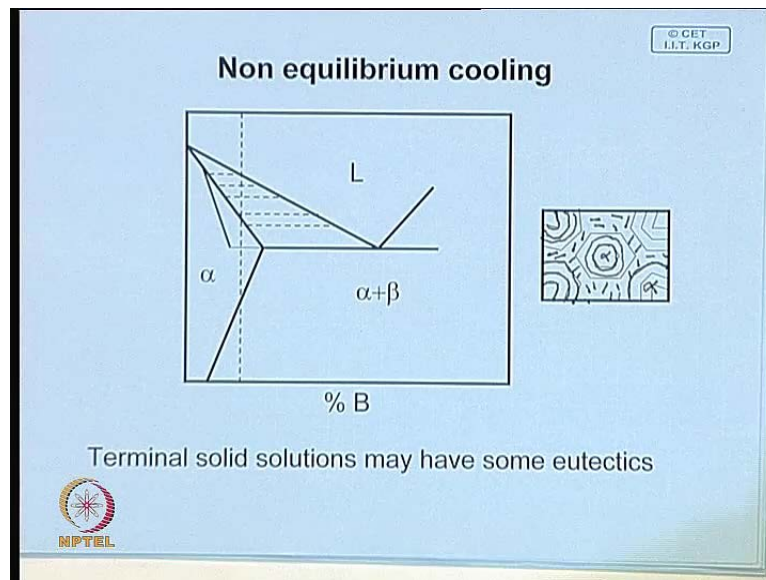
(Refer Slide Time: 40:23)



So, eutectic say suppose here; we consider this is the case and what is the non equilibrium cooling in case of a eutectic system? Now, let us look at this terminal solid solution. Now, here that initial composition that precipitates out, when the temperature goes below the liquidus. So, this is A; this line represents pure A; this is pure B and when this liquidus line temperature goes below this liquidus, the first solid that precipitates out as this composition. As it goes to the next temperature here, the solid precipitating out will have this composition. So, new crystals or new layers of alpha which is forming; they will follow this composition, whereas the old if you assume older will not get enough time to change its composition.

Therefore, effectively what will happen? The average composition of the solid will follow a line; a solidus which is different from this and this is the departure from equilibrium and ultimately, what it may have? When it has reached, the eutectic temperature possibly there may still be some amount of liquid left. So, this is the amount of liquid, which is from this point to this point. This is the amount of liquid, which remains even when the temperature reaches eutectic temperature. So, this will now solidify as eutectic having alpha of this composition and beta of this terminal solubility somewhere here. So, therefore the structure will look like. You will have primary code grains of alpha.

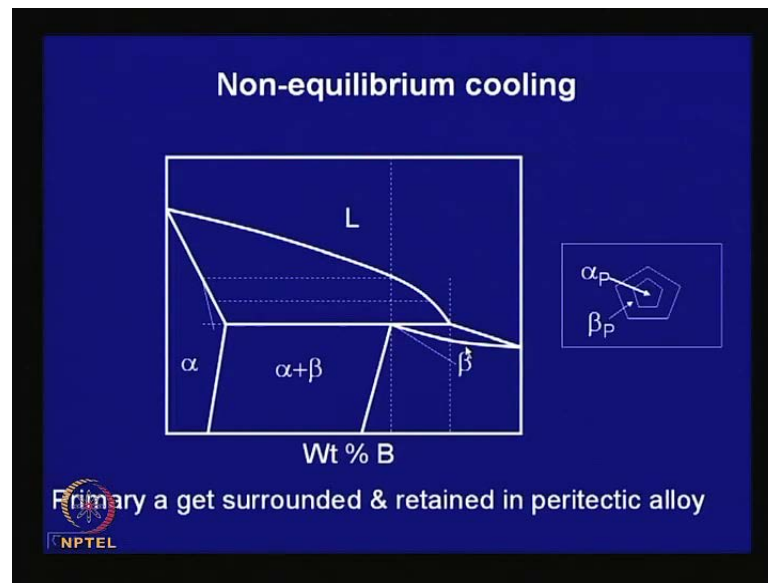
(Refer Slide Time: 42:24)



Let us say, this is alpha. This represents the different composition contours. These lines represent different contours. This is one grain of alpha; this is another grain of alpha. These are contours; composition contours. So, these are alpha and still there is some amount of liquid, which is you solidified as eutectic. So, there will next case of alpha, beta. So, normally so what effect of non equilibrium cooling in these cases, you can get eutectic (Refer Slide Time: 40:23) even in composition; even in terminal solid solutions, where you will under equilibrium cooling, you do not expect a eutectic. So, this is one important departure which is expected, if the cooling is not very slow; if the alloy is not cooled at a very slow rate.

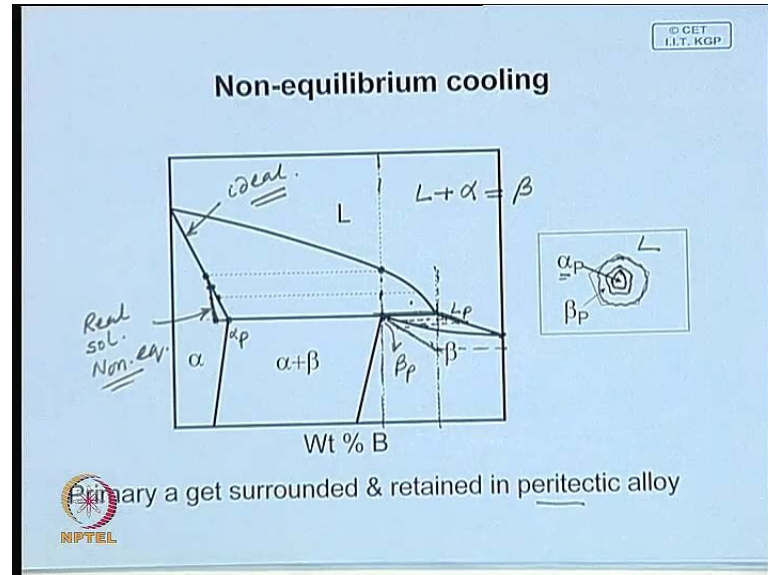


(Refer Slide Time: 43:29)



Now, let us look at the peritectic system. Now, what happens in a peritectic system here? Same concept we can apply in the peritectic system and let us consider in the peritectic system this alloy. Now, this **this** is the peritectic point.

(Refer Slide Time: 43:56)



Now, in this peritectic alloy; so that means here; this is the alloy composition. Now, the first liquid which precipitates out will have this composition. Now, when it comes here, then its composition of the **liquid** solid will be this and the average composition will be this. When it is here, then the new solid, which precipitate out as this and average composition is this. So, here also it follows the solidus actual solidus real solidus, this you can say that real solidus. This is ideal case, when it is under equilibrium and here it

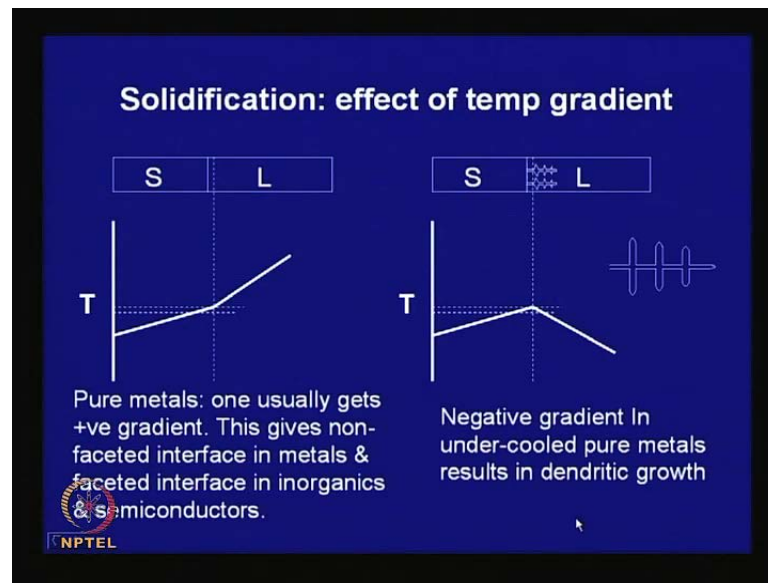
is real solidus that is non equilibrium. Now, it follows in that case, what you have now? You have this is where you have come.

Now, here the amount of liquid is... There is some amount of liquid here; even here. Amount of solid at eutectic at the peritectic temperature is proportional to this part; amount of liquid is this part and what happens? Now, this amount of solid alpha at peritectic temperature that is liquid will react with that alpha and will give you beta. So here what is happening? There is coring; no doubt. So, that means that primary alpha which has formed it as the cored structure. Now, when peritectic reaction takes place what is happening? That liquid surrounding reacts with alpha at the peritectic composition, alpha p.

This is the liquid peritectic composition. This will give you beta of that peritectic composition and this beta will form surrounding this. So, let gets (()). Now, this alpha if that has to react with the liquid, now it is becomes quite difficult; because that is not in contact with the liquid. So, what is likely to happen? Some amount of primary alpha will get surrounded and retained even in this peritectic alloy and once the peritectic reaction is complete, then what is happening? This composition peritectic composition is this. Say, there is substantial amount of liquid and here now the liquid now has this composition. Now, this starts changing like this. The liquid composition will follow this part.

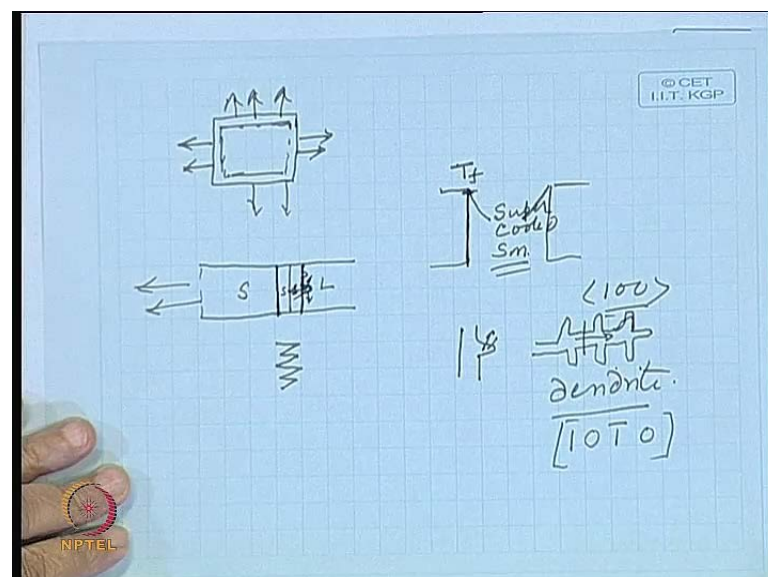
Because diffusivity in liquid, the movement of atoms in liquid is faster is able to change; adjust composition decreasing temperature. But solid is not able to adjust the temperature; adjust composition decreasing temperature. So, here also that average composition will follow this line and ultimately, the solidification will be completed somewhere here; that is at temperature much lower than the melting point of B. So, here it is little more complex. So, in case of a peritectic reaction, if there is in any system if there is a peritectic reaction (Refer Slide Time: 43:29) you will have you will have prime primary alpha will get surrounded; primary this is alpha get surrounded and retained even in peritectic alloy.

(Refer Slide Time: 48:10)



Now, let us build up all this. So, that means we can use to some extent equilibrium diagram to understand what will be the nature of the **structure** actual structure in a real alloy. So, that means composition if you cool at a normal rate, composition is not going to uniform. So, all class metals they will have some amount of the... I mean from point to point composition may vary. And if you want uniform composition, you have to give some heat treatment after solidification and we will come to it later as well. Now, let us look at the effect of temperature gradient. We talked about solidification in a mould and when solidification takes place in a mould, the nature of the structure that develops will depend on the way heat is extracted.

(Refer Slide Time: 49:18)



So, that means if you and for simplicity, let us take in a real mould heat may be flowing in a real mould, if you have like this. Heat will be flowing in this direction; different directions. So, therefore the structure will be... solidification will start from this end as well as this end. And we can assume that here as (( )) which is exposed or if it is covered also here also that if it is in case in a metal (( )) coming in all sides. So, this side also the heat will flow. Similarly, you have to depend on the top how you are maintaining; is it open or is it also in contact with metallic mould. So, that rate of cooling will be determined on the nature of mould and nature of the surrounding.

Let us take a simple case, where this is the one part; this is the solid; this portion is liquid and this is the solid liquid interface and heat is being extracted from the solid; only along this. In that case, if it is a pure metal and we have this type of a gradient, this is that interface of solid and liquid and gradient is like this. The heat will flow from higher to lower temperature from this end to this end. So, that is why (Refer Slide Time: 48:10) here the temperature is lower and in the liquid is at a higher temperature and you have a positive gradient here like this. In this case if it is a pure metal, we will positive gradient.

This will be non-faceted or planar interface; that interface this plane will (( )) and move like this. Initially, it is as a temperature goes; it comes here. It comes here; this becomes solid. So, here even if there is a (( )) to say somewhere it tries to go like this. In that case, when this solidifies, it will that to be latent heat which has to be extracted. If it comes this side, you can that you can go this way also. It will heat up and melt. So, it will **it will** not be stable; this kind of any departure from the planar interface will not be stable in the case, where you have this type of gradient. But there are certain materials like some inorganics, where **you know** this phase can also be this kind of a faceted like this.



This kind of a faceting can take place in inorganic and some semi-conductors. Now, it is also possible to maintain a negative this type of gradient as well, which is little difficult. We can visualize suppose in a mould; take a mould and you have super cooled **super cooled** let us say (( )). For solidification, it is necessary to have some amount of super cooling. This is super cool; in this case which is possible to maintain a temperature gradient. So, it is super cooled; when you pull it and then solidification starts. Then temperature goes up. So, here we have the temperature may be like this.

This is the temperature and this is the temperature; you can say, this is the freezing temperature of that metal. So, something likes this. So, in this case what is happening

since the temperature nearby area is less? In this case, if this is the interface; if there is a deviation like this, this temperature is lower. So, when it solidifies, the heat can flow in this direction as well. So, this is stable. So, in this case you have this type of a tree like structure developing. They are called dendrite; ((C)) it means tree like. So, this is called dendrite. So, this type of shape of (Refer Slide Time: 48:10) this primary crystal is also possible.

(Refer Slide Time: 54:00)

**Relation between interface morphology & entropy of melting**

Material	$\Delta S_m/R$	Morphology	Schematic
Most metals	< 2	Planar no facets	S   L
Metalloids Si, Ge, Bi	2.2-3.2	Faceted	S  L
Most inorganics	> 3.5	Faceted	

Growth direction: FCC & BCC <001> HCP <10.1>

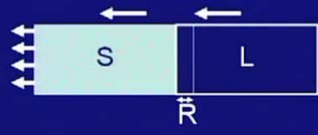
NPTEL

And all this will be determined by the thermodynamic characteristics of the material and there are certain correlations, people have found out and looking at the thermodynamic database, if you find that there is some correlation with entropy change. This entropy over R; so this is dimensionless number, entropy over R and if you try and find out for most metal, it is less than 2. In this case, you get planar interfaces between solid and liquid and which is represented schematically. Some metalloids like silicon, germanium, bismuth and certain other materials, where this is in this range you get faceted structure.


And most inorganics, this is much higher and they are invariably get this kind of faceted structure and the crystal growth is also depends on **on** the directions. And the growth direction is fastest along this cube direction in FCC and BCC. So, these planes so when these crystals are growing (Refer Slide Time: 49:18) so this plane or plane normal this will be one of the cube directions in FCC and in **in** hexagonal close packed structure, this is 1 0 1 bar 0. This is the direction or that plane; this is the plane on which the crystal growth (Refer Slide Time: 54:00) takes place.

(Refer Slide Time: 55:36)

**Effect of heat flow on interface movement**



$R$  = interface movement rate  
 $L$  = Latent heat  
 $\rho$  = density


$$-k_s \left( \frac{dT}{dx} \right)_s = -k_l \left( \frac{dT}{dx} \right)_l - L\rho R$$
$$R = \frac{k_s \left( \frac{dT}{dx} \right)_s - k_l \left( \frac{dT}{dx} \right)_l}{L\rho}$$


Now, (()) the flow of heat flow on has an important effect on that interface movement and which is represented here. This is the heat conduction through solid; this is the conduction through liquid and this is the latent heat that comes out when solidification takes place; rho is the density and R is the rate at which, this interface moves. So, assuming this to be planar, this type of equation can be setup and we will build up on it and we will see how this affects evolution of structure during solidification in the next class.

(Refer Slide Time: 56:19)

**Summary**

- Comparison of simple phase diagram: experimental & calculated
- Reasons for deviation
- Non-ideal solution: regular solution
- Limitation of phase diagram
- Effect of non equilibrium cooling on solidification



Let to sum up today we looked at comparison of simple phase diagram which are calculated theoretically from simple model, and experimental diagram. There are some



derivations, we learnt about why there is a derivation. We went little higher order of calculation using regular solution model, which will get better fit, and we looked at limitation on phase diagram. And also looked at effect of non equilibrium cooling on solidification. Thank you.