Structure of Materials
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Lecture - 34
Chapter - No. # 07
Phase Diagrams

Now, we try to understand, what we call the tie line and the lever rule to calculate the phase fractions which are present in a two phase mixture.

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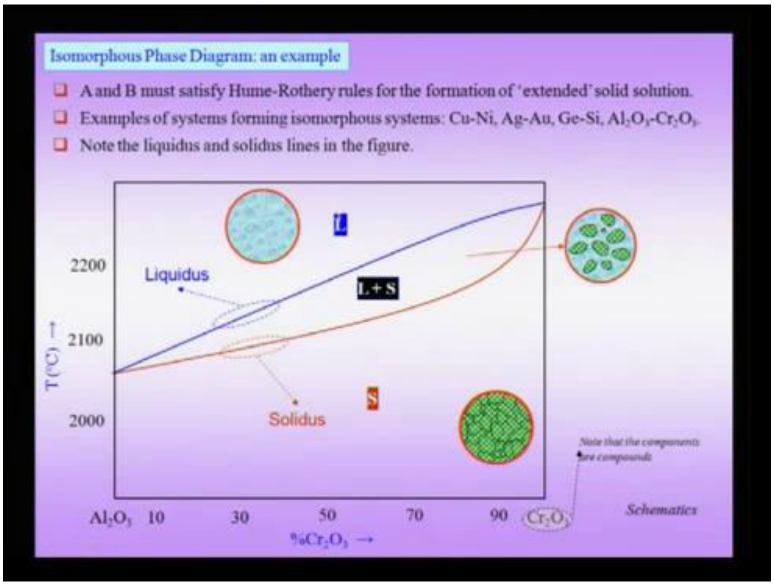

Isomorphous Phase Diagram: an example

- ☐ A and B must satisfy Hume-Rothery rules for the formation of 'extended' solid solution.
- ☐ Examples of systems forming isomorphous systems: Cu-Ni, Ag-Au, Ge-Si, Al_2O_3-Cr_2O_3.
- ☐ Note the liquidus and solidus lines in the figure.

So, suppose we are working at a certain temperature and composition and we want to find out the fraction of the phases present along with the composition of the phases. For instance, we have already seen in the case of an isomorphous phase diagram that, there is a single phase region, the liquid phase region, the solid phase region. The liquid and solid both contain components A and B, and there is also a solid plus liquid phase region, which separates the liquid and solid phase regions.

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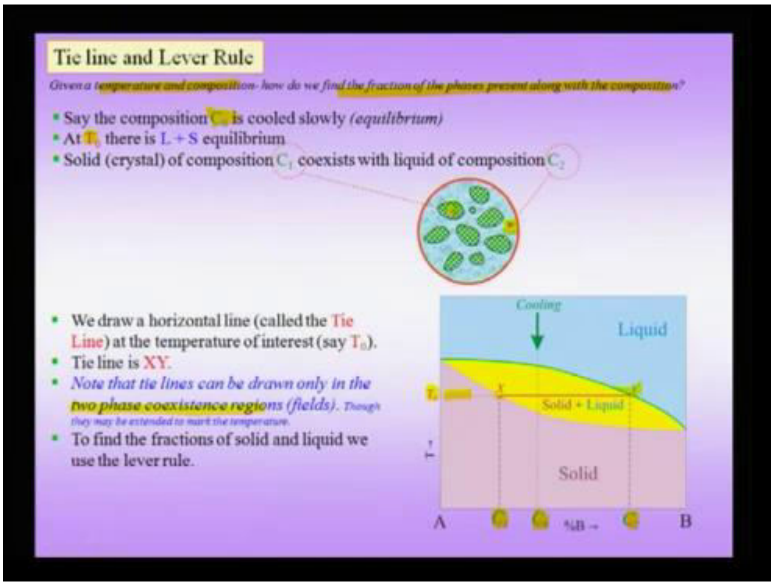

Tie line and Lever Rule

Given a temperature and composition- how do we find the fraction of the phases present along with the composition?

- Say the composition C_0 is cooled slowly *(equilibrium)*
- At T_0 there is L + S equilibrium
- Solid (crystal) of composition C_1 coexists with liquid of composition C_2

- We draw a horizontal line (called the Tie Line) at the temperature of interest (say T_0).
- Tie line is XY.
- *Note that tie lines can be drawn only in the two phase coexistence regions (fields). Though they may be extended to mark the temperature.*
- To find the fractions of solid and liquid we use the lever rule.

And in this two phase region which is marked in yellow in the current slide, we would like to know, what is the composition of the liquid, which is in equilibrium with the solid and what are the phase fractions of each one of them given that, I am starting with an alloy of composition C 0. So, I will for now assume, but of course, this assumption is not necessary and I am slowly cooling this alloy with composition C 0 and I am at a temperature T 0.

That means, I am at a temperature T 0 and I am working with the alloy of composition C 0 then, I can clearly see that I extend an horizontal line, a constant temperature line from X to y, which I call the tie line. This tie line is drawn in the single phase region, the two phase coexistence regions and often sometimes may be extended like I have done here to the left to see the temperature or mark the temperature.

But, strictly speaking, tie line should be drawn in a two phase region and in the current slide, it is the X Y which is the tie line marked in red. Now, as we are in the two phase region, there is a liquid of composition C 2 as shown schematically in the figure above, which is in equilibrium with a solid, which also been shown schematically of composition C 1. We had previously in our video, wherein we cooled stearic acid, which of course, is not an equilibrium process to be noted. But then, we could clearly see that, we could have a solid a crystal of stearic acid in coexistence with a liquid.

So, this is scenario similar to that, but only thing is that, here we are talking about an equilibrium and in that case, it was the solidification process which was occurring rather fast. So, the tie line is X Y and we are in the two phase field and I we would like to know what is the fraction of the liquid in the schematic above and the fraction of the solid. The composition of the solid and the composition of the liquid are fixed by the ends of the tie line. That means, the composition of the solid is C 1 and the composition of the liquid is C 2 and these do not change.

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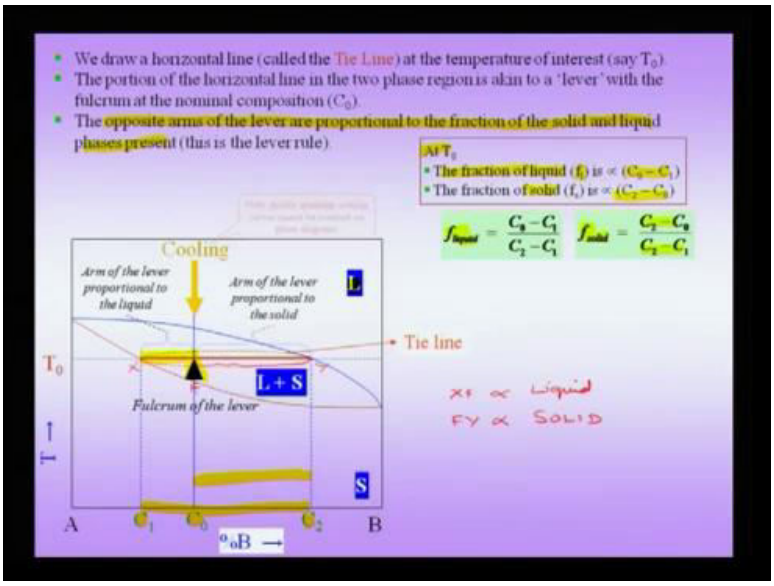

- We draw a horizontal line (called the Tie Line) at the temperature of interest (say T_0).
- The portion of the horizontal line in the two phase region is akin to a 'lever' with the fulcrum at the nominal composition (C_0).
- The opposite arms of the lever are proportional to the fraction of the solid and liquid phases present (this is the lever rule).

At T_0
- The fraction of liquid (f_l) is $\propto (C_0 - C_1)$
- The fraction of solid (f_s) is $\propto (C_2 - C_0)$

$$f_{liquid} = \frac{C_0 - C_1}{C_2 - C_1} \qquad f_{solid} = \frac{C_2 - C_0}{C_2 - C_1}$$

So, once I made a tie line construction, I will assume that, this is occur into a lever that is, it is similar to a lever and what we call a mechanical lever and I will put the fulcrum of the lever at the composition C 0. Then there are two arms to this lever, the left hand side of the arm, which as we shall note is proportional to the amount of liquid present. This is similar to the lever that the opposite arm is the one which gives the lever, advantage of the lever or the moment about the lever and therefore, here the amount of liquid is proportional to the opposite arm which is I marked in yellow.

On the other hand, the amount of solid is proportional to the other arm of the lever, which is I have marked in red. So, this right hand side, suppose I call this X Y and this is fulcrum F, so I can note that X f is proportional to the liquid and f Y is proportional to the solid. So, the opposite arms of the lever are proportional to the fraction of the solid and liquid phases present and this is the lever rule.

So, at T 0, the fraction of the liquid f 1, which we call f subscript 1 is proportional to C 0 minus C 1. And the fraction of the solid which has a composition C 1 is proportional to this arm of the lever, which is C 2 minus C 0, so this is arm of the lever here, from here it is running all the way here. And suppose, I want to calculate the fraction of the liquid then, I will divide it by the overall composition difference, which is C 2 minus C 1.

Therefore, I get the fraction of the liquid is equal to C 0 minus C 1 by C 2 minus C 1 and the correspondingly, the fraction of the solid will be equal to C 2 minus C 0 as I pointed out here, divided by the C 2 minus C 1. So, I have a simple way of having, what we call tie line construction to calculate the fractions of the liquid and the solid.

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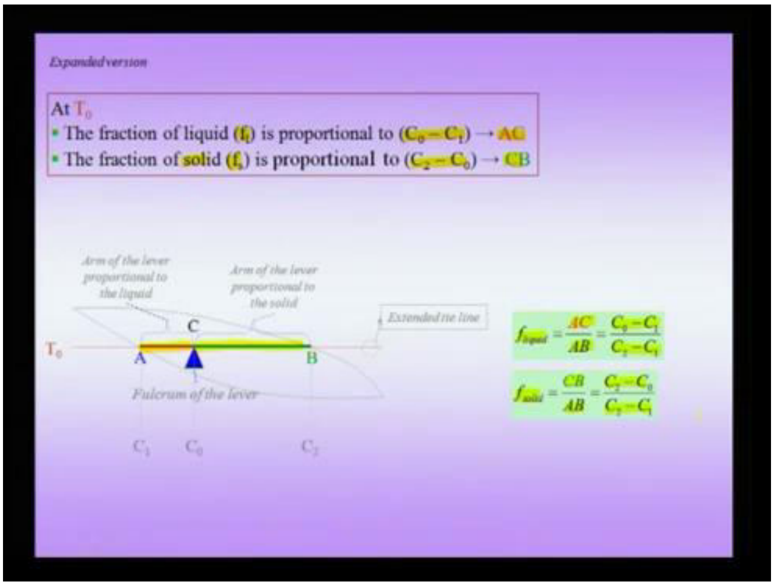

Expanded version

At T_0

- The fraction of liquid (f_l) is proportional to ($C_0 - C_1$) → AC
- The fraction of solid (f_s) is proportional to ($C_2 - C_0$) → CB

$$f_{liquid} = \frac{AC}{AB} = \frac{C_0 - C_1}{C_2 - C_1}$$

$$f_{solid} = \frac{CB}{AB} = \frac{C_2 - C_0}{C_2 - C_1}$$

So, let us look at it once more and revise it, because this tie line construction and the phase fraction calculation are often used in whenever you study phase diagrams. And therefore, I look at the extended version and I note that, the fraction of the liquid f 1 is proportional to AC, this the red arm of the lever and therefore, is proportional to C 0 minus C 1. The fraction of the solid which I write as f subscript s is proportional to C 2 minus C 0 the other arm of the lever, which is the green arm of the level and is marked as CB.

And therefore, I can write the fraction of the liquid as the arm AC divided by the length of the whole lever, which is AB or the length of the rod and fraction of the solid is CB by AB. And correspondingly, I can write these fractions in terms of the compositions as C 0 minus C 1 by C 2 minus C 1 as the fraction of the liquid and correspondingly, the fraction of the solid will be C 2 minus C 0 divided by C 2 minus C 1. Therefore, by this tie line construction, I can compute the fractions of the phases and also know the composition of the solid, which is in equilibrium with the liquid.

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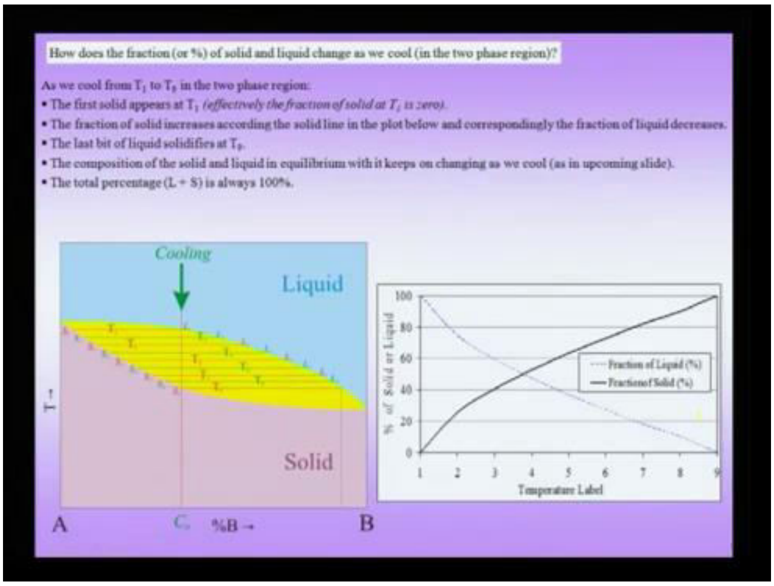

How does the fraction (or %) of solid and liquid change as we cool (in the two phase region)?

As we cool from T_1 to T_9 in the two phase region:

- The first solid appears at T_1 *(effectively the fraction of solid at T_1 is zero).*
- The fraction of solid increases according the solid line in the plot below and correspondingly the fraction of liquid decreases.
- The last bit of liquid solidifies at T_9.
- The composition of the solid and liquid in equilibrium with it keeps on changing as we cool (as in upcoming slide).
- The total percentage (L + S) is always 100%.

Now, as I pointed out, often the utility of phase diagrams is extended by what we might call a slow cooling process. That means, I may take an alloy of composition C 0 and slowly cool it from the liquid state through the two phase mixture region, the liquid plus solid region to a fully solid region. And I would like to know, what is happening to the phases, their volume fractions, etcetera and the weight fractions. So, what I do is that, I start with the alloy composition C 0 and I slowly cool that means, I am at least maintaining some kind of an equilibrium as I am cooling.

And I ask this question, how does the fraction or percentage of solid and liquid change as we cool and especially, in the two phase region, because in the single phase region, the overall composition is same as the composition of the phase present. Now, I choose some nine temperatures T 1 to T 9, T 1 being the highest temperature and T 9 being the lowest temperature. That means, at T 1 the first solid begins to form, as I am cooling from high temperatures, at high temperatures. I note that, there is purely good and the composition of that liquid is C 0 and that liquid has both components A and B in it.

Now, as I cool slowly and touch temperature T one my first solid which forms and the composition of that solid is s 1 and the liquid which it is in equilibrium is l one of course, if I make a lever rule calculation at this exactly at the coexistence line. You would notice that, the fraction of the solid is 0, so it is exactly it is like an infinitesimal amount of solid forming or that is where the solidification is expected to start and as I go lower in temperature that means, I go to temperature T 2 which is marked in green, all odd temperatures are marked in red, all even temperatures are marked in green.

So, I go to T 2 then to T 3 then to T 4 then progressively go to T 5 etc, I notice that the arm of the lever which is proportional to the solid. For instance, This is the arm of the lever which is proportional to the solid and next for instance, this arm is proportional to the solid that arm of the lever is constantly increasing that means, as I cool down as I would expect that the fraction of the solid is increasing. Here then correspondingly, the fraction of the liquid is decreasing which is proportional to this arm of the lever originally, the liquid was the whole thing was fully a liquid then at temperature T 2.

The amount of liquid came down which is this length then say for instance the T 5 this length is further decreased and when I reach s T 9 the lowest temperature I notice that the fraction of the liquid becomes 0, which is the smaller arm here and the whole thing becomes solidified. Therefore, what I can do is that I can plot the fractions of the or the percentages of the solid and liquid in the right hand curve above.

So, I have this temperature label which I have shown here and I am tracking the percentage of the solid and liquid and the solid is of course, the solid line here and the liquid is shown as the blue dotted line. So, initially when I melt a temperature T 1 the entire thing is a liquid 100 percent is liquid and there is 0 solid, but as I slowly cool I note that the fraction of the solid is increasing, but the fraction of the liquid is decreasing and of course, at some point of time there is fifty percent solid and there is fifty percent liquid.

Of course, when I say some point of time because I am talking about a cooling process I can use time, but truly speaking at some temperature there is in this diagram of course, that temperature is close to T 4. You would notice there is fifty percent of solid and fifty percent of liquid otherwise at any other temperature you would have a mixture of solid and liquid, but the net percentage total is obviously, hundred percent.

So, you notice that the fraction of the liquid is decreasing from hundred percent the fraction of the solid is increasing from 0 percent and finally, at temperature 9 you have a fully solid and there is no liquid present in the mixture.

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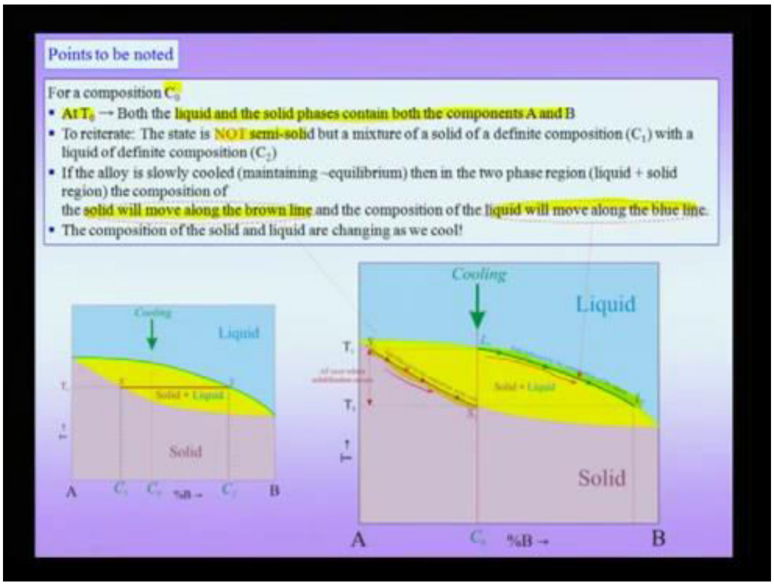

Points to be noted

For a composition C_0

- At T_0 → Both the liquid and the solid phases contain both the components A and B
- To reiterate: The state is NOT semi-solid but a mixture of a solid of a definite composition (C_1) with a liquid of definite composition (C_2)
- If the alloy is slowly cooled (maintaining ~equilibrium) then in the two phase region (liquid + solid region) the composition of the solid will move along the brown line and the composition of the liquid will move along the blue line.
- The composition of the solid and liquid are changing as we cool!

Now, what we need to consider is that how at various temperatures not only is the fractions of the solid and liquid is changing, but the composition of the solid which is in equilibrium with the composition of the liquid is also changing and this is very important. Because, the first solid which comes out for instance, here has a composition which is marked by s 1, the second solid which comes out at lower temperature T 2 has a composition s 2 that means, that the original solid which formed has to change its composition.

Now, the it has to become richer in b because s 2 is richer in b and correspondingly suppose you go to even lower temperature like s 1 which is even rich more richer in b and that implies that the solid which formed at a higher temperatures like s 2 or s 3 has to change its composition. ,so that it becomes commensurate with what is dictated by the phase diagram and I am assuming that at every temperature though I am cooling, but I am cooling slowly enough that equilibrium is maintained.

Therefore, at s 4 the composition of the solid is different from that of the liquid and this implies that because it is a solid state there has to be some diffusion taking place. ,so that the composition is made uniform corresponding to that temperature label for instance s 4 similarly, the composition of liquid also constantly changes.

I mean as we are cooling it is changing and the first liquid which is in equilibrium with the first solid, which comes out or the liquid which is in equilibrium the first solid which comes out is has a liquid composition l 1. But then it keeps changing as we go down in temperature and therefore, the liquid is also constantly changing its composition.

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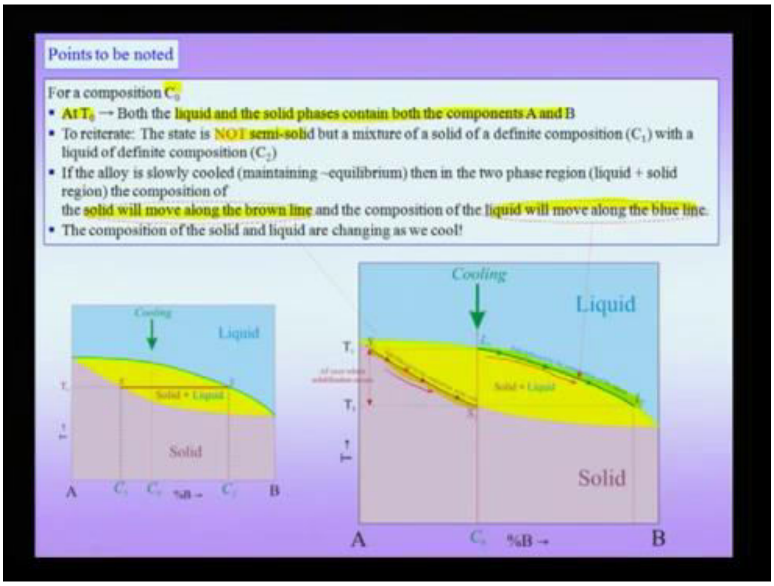

Points to be noted

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- If the alloy is slowly cooled (maintaining ~equilibrium) then in the two phase region (liquid + solid region) the composition of the solid will move along the brown line and the composition of the liquid will move along the blue line.
- The composition of the solid and liquid are changing as we cool!

So, i would like to know how the composition of the liquid and the composition of the solid is changing as we cool from a temperature which in which we had only an uniform liquid. Now, a few points to be noted for a composition C 0 at T 0 which is a two phase mixture liquid and solid phases, both contain elements a and b and this liquid plus solid mixture is not a semi solid, but it solid of definite composition in equilibrium with a liquid of very definite composition.

An important point to note is that as we have seen before in the previous slide that the composition of the solid is constantly changing and it is changing along the what we may call the solidus line and the composition of the liquid is constantly changing along the liquidus line and this is an very important point to note that the composition of the solid. Will move along the brown line which is a solidus line and the composition of the liquid will move along the blue line which is the what we may call the liquidus line.

So, we have the path as we cool followed by the solid and there is an alternate path followed by the liquid. ,so since this is slightly sometime difficult to understand and important to note.

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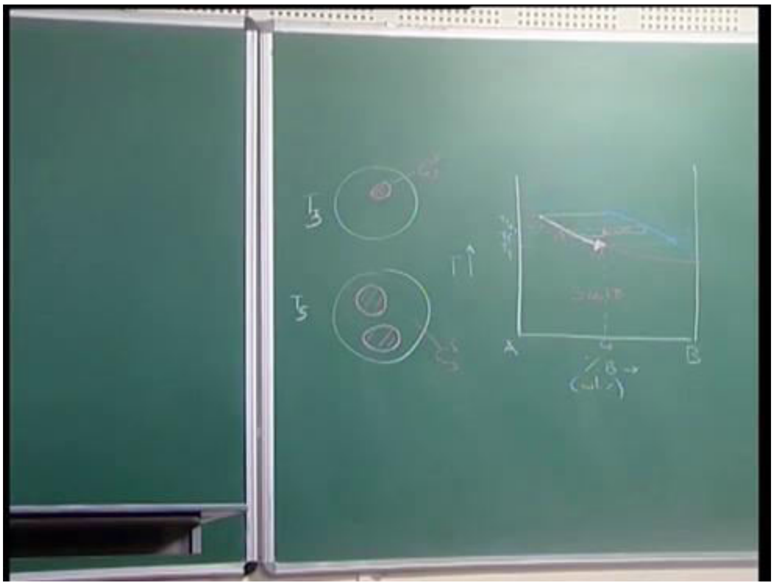

I will go to the board and explain a little more about this. ,so I have my isomorphous system and in the isomorphous system I draw the two lines the above line which is called the liquidus line and the bottom line which is my solidus line and for instance now, I will take assume that this is weight percent of b this is my temperature axis along and now, I am choosing a composition which is C 0 and my components are A and B. For instance, as we have noted before they could be pure elements or they could even be compounds.

Now, as I cool from this temperature the first solid appears and I make my tie line here at a temperature T one and I assume that the last solid which comes out I draw a tie line here is at say some T 9. So, I can draw a series of temperatures below this and I would note that the first very first solid which comes out the fraction of it is practically 0, but I go down to say an intermediate temperature say I call this T 5 or one of this intermediate temperature this is now, my fraction of the proportional to the fraction of my solid and this length is proportional to the fraction of my liquid.

But the point I was trying to make here is that the solid which came out first had this composition the solid which came which is in equilibrium or at this temperature T 5 has this composition and the final solid which comes out of, the liquid has this composition correspondingly, the if you note the liquid . So therefore, I have these 3 composition ,so I call this C solid 1 C solid 2 or C solid 5 and C solid 9.

Correspondingly, if you note the composition of the liquid which first started precipitating my solid that composition of the... So, as I am cooling the composition of the solid is changing which means that, suppose I pick up my very first temperature T 1 and I draw a schematic I practically have liquid and I just assume that an infinitesimal amount of solid forms. Now, when I am at temperature T 5 there is or I can even choose an intermediate temperature. Before that, if you want say a temperature T 3 and at temperature T 3 you would notice that there is a solid and the composition of the solid would be C solid.

So, I will mark this solid in red C solid 3 now, at a lower temperature say for instance as I noted for T 5 not only is the amount of solid increasing. ,so I will have more of solid and this amount will be dictated by the lever rule as I draw in the two phase region using the tie line and for that I will use the fulcrum like this in the middle now, so this is my composition of the solid at temperature 5.

So, from T 3 to T 5 my amount of solid is increased not only my has my amount of solid increased, but also the composition of the solid is changing that means, if equilibrium has to be maintained this original solid which formed has to diffuse in it more of B. So, that it becomes richer in B and therefore, the composition is constantly changing to maintain what we call equilibrium that means, to be in accordance with the phase diagram.

Now therefore, I note that my composition of their solid is changing along this line the bottom part of the curve and the composition of the liquid is changing along this line which is the two part of the curve. So, composition of the liquid changes along the liquidus line of the phase diagram the composition of the solid changes along the solidus line of the phase diagram and therefore, my composition is constantly changing as I am slowly cooling from a single phase liquid to a completely solid state.

So, this is important point to note that when I try to over lay cooling curves on a equilibrium phase diagram I have to note that still I assume that equilibrium is maintained that means, the compositions have to change in accordance with the phase diagram and these compositions change along the two phase coexistence lines. So, coming back to our slide, we note that once again that my composition of the liquid is changing along this line as I slowly cool and the composition of the solid is changing along the solidus line as I slowly cool.

So, this is very important to note and therefore, I bring to focus the utility of the tie line construction and the lever rule for computing the fractions and also knowing the composition of the solid and liquid which are in equilibrium.

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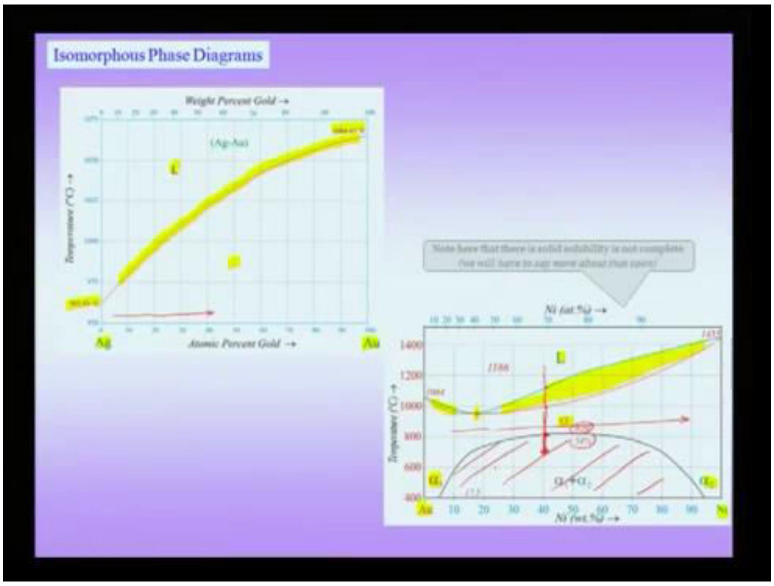

Isomorphous Phase Diagrams

Now, let us take up some examples of phase diagrams some common examples which especially ,so isomorphous kind of a system and we have already noted that isomorphous systems imply complete solid solubility and also complete liquid solubility. Additionally we had make a remark that though complete solid solubility is expected, but we may not expect this at all temperatures and at some low temperatures you may have something known as phase segregation or what you might call compound formation.

So, let us start with the gold silver system which is a nice illustrative system and as you are aware gold is a noble metal and silver is also a noble metal and these are both are precious metals and if you notice this that gold melts at a higher temperature of 1064 degree celsius, silver melts at a 961 degrees celsius. But the overall structure of both is cubic close packed and they are, so similar that the isomorphous phase diagram practically is a very thin kind of a region, which I am highlighting here, wherein the two phase region coexist such a very thin region of two phase coexistence.

And you may already have noticed one non reality that previously when we do our phase diagram. The way we had drawn it we have drawn it as if it is a double convex kind of a lens, so you see that the top line and the bottom line form a double convex lens, but this you can clearly see it is not like that it is almost like a what we may call a lens of a different type wherein both sides are convex or one concavo convex lens.

So, and their lens is very thin here ,so we have the liquid region and the liquid is comprising of atoms of silver and gold and then there is a solid region which is a solid solution gold and silver and as you go from the left hand side to the right hand side. You notice the amount of gold is increasing in the solid solution, but it remains an what you might call a completely disordered solid solution as we for any percentage of gold and any percentage of silver would mix in the solid solution and you will get a disordered solid solution.

Now the diagram on the right is slightly different diagram this is a good nickel diagram like in the case before both gold and nickel are cubic close packed structures, but there is an important variation with respect to the previous diagram or there are two important variations which we need to note. Number one is that in this diagram you notice again there is a non-ideality with respect to this double convex kind of a system which we had noted for the case of a what you might call a illustrative example.

So, we had noted there is a double convex kind of a situation, but you go down here you do not see that double convex kind of a system. In fact, the double convex has split into two double convex lenses around a point which we note here as a composition of about 17.5 percent of nickel therefore, this is one non-ideality which we note here and we will have a little more to say about this in the coming slides.

But we have liquid above and we have the solid solution alpha and the solid solution has both gold and nickel and if you are to this left of this composition 17.5 percent. You have a lens wherein the solid plus liquid would coexist again you would have another convex lens wherein again convex double convex kind of a construction wherein you find the liquid and alpha would coexist.

Now, if you go down to a lower temperature there is something very interesting happening here and we will as I pointed out we will say a few more things about it in the coming slide. What we notice is that this uniforms disordered solid solution alpha splits into what we may call alpha one which is again comprising of gold and nickel, but it is a gold rich solid solution and alpha 2 which is a nickel rich solid solution both of them have; obviously, a cubic close pack crystal structure that is why we are able to go from this end of the phase diagram to that end by constantly increasing the percentage of nickel.

But between the two alpha 1 and alpha 2, if you notice here carefully you find that there is a 2 phase mixture region below a temperature of about 820 degree celsius and the maximum of this curve lies at 44 percent of nickel. ,so if I am below this maxima and I intersect this that means, suppose i am cooling an alloy with forty percent nickel I will first start off being a liquid then I will go into the two phase region where I will have a liquid plus alpha coexisting.

Then I would notice that if you go down to lower temperatures here at this temperature your alpha will start slitting into alpha 1 plus alpha 2. That means, you will have two solid solutions both of them are f C both of them, contain gold and nickel one of them has a higher percentage of gold and other one has a higher percentage of nickel and this will land up with the two phase mixture at room temperature ,so you just emphasize this aspect once more.

So, suppose I am cooling this solution and as usual this is percentage of nickel here in this case and this is my temperature and this is a schematic here. ,so you have to be little careful that at low temperatures I can draw some kind of a what we might call a dome and suppose I am cooling an alloy here I would have an uniform alpha at high temperatures, but at low temperatures you would have a mixture of alpha one and alpha 2 suppose I mark alpha 1 in red and alpha 2 in blue, I know this is my tie line now, this X Y is my tie line and the amount of alpha 2 is proportional to this arm of the lever.

So, I am a fulcrum here at C 0 and my amount of alpha one is proportional to this arm of the lever and therefore, when I cool below this temperature which is now, my say some temperature T 1 I would have a mixture of alpha one plus alpha 2. ,so in other words an uniform homogenous solid solution alpha which contains gold and nickel splits into two solutions again both alpha one and alpha 2 have gold and nickel, but the percentages of gold and nickel are dictated by these ends of the tie line.

So, this will tell me how much of nickel is present in alpha 1 and this will tell me how much of nickel is present in alpha 2 therefore, I notice that this there is a small or a important variation to the isomorphous phase diagram at low temperatures where there is phase segregation. Now, we will say a few more things about what kind of an enthalpy would lead to this typically, systems showing a positive enthalpy of mixing would show phase segregation.

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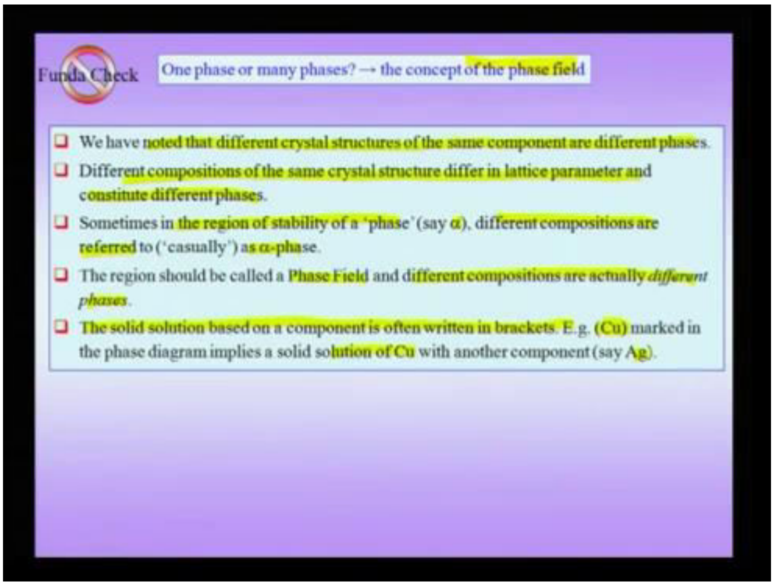

Funda Check

One phase or many phases? → the concept of the phase field

- ☐ We have noted that different crystal structures of the same component are different phases.
- ☐ Different compositions of the same crystal structure differ in lattice parameter and constitute different phases.
- ☐ Sometimes in the region of stability of a 'phase' (say α), different compositions are referred to ('casually') as α-phase.
- ☐ The region should be called a Phase Field and different compositions are actually *different phases*.
- ☐ The solid solution based on a component is often written in brackets. E.g. (Cu) marked in the phase diagram implies a solid solution of Cu with another component (say Ag).

Before we take up additional kind of phase diagrams let us make a small check of what we have learned. ,so for first is the concept of what is called the phase field often we may say in looking at a phase diagram like this that this is my alpha phase, but you we have already noted suppose i take up my composition like this here which has a this is a different phase as compared to a phase which is here as compared to a phase which is here which is a different composition also.

If I take a same composition heated up the lattice parameter changes and therefore, very technically or being a purist I will have to classify even say p one has to be different from p 2 in terms of the phases. So, what is this alpha which I am labeling here ,so truly speaking this alpha is what is called the phase field and not a phase ,so this is a combination of many phases and that is called a phase field and we label these phase fields with two ways either, we call them the alpha or sometimes we may put this phase field for instance copper and enclose it in brackets which means it is a solid solution of copper.

So, to summarize we have noted the different crystal structures of the same component are different phases different compositions of the same crystal structure which differ in lattice parameter constitute different phases sometimes, in the region of stability of a phase say alpha different compositions are referred to casually as the alpha phase. So, this casual reference implies that truly we are speaking we are calling it a phase field.

I mean it should be called a phase field and different compositions actually are different phases within the phase field and often that the solid solution based on a component is often written in brackets. for instance example copper is put within brackets and this implies that this is a solid solution of copper say with a some other component like for instance silver.

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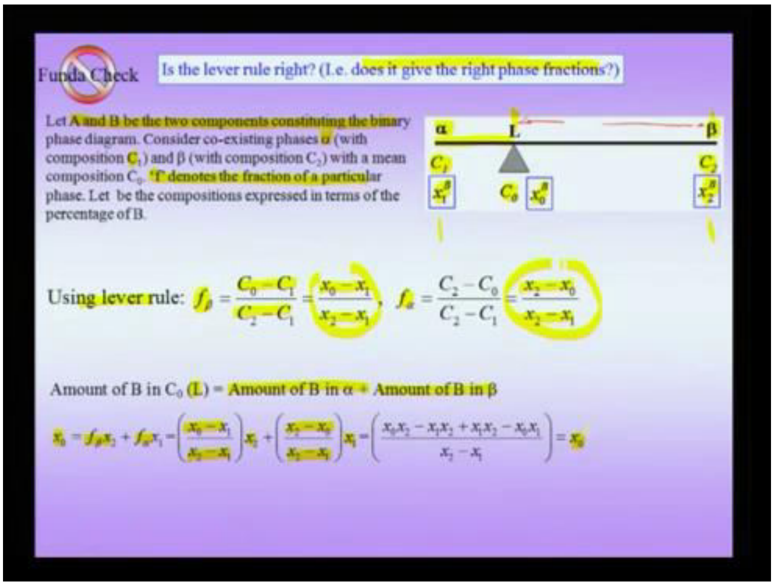

Funda Check

Is the lever rule right? (I.e. does it give the right phase fractions?)

Let A and B be the two components constituting the binary phase diagram. Consider co-existing phases α (with composition C_1) and β (with composition C_2) with a mean composition C_0. 'f' denotes the fraction of a particular phase. Let be the compositions expressed in terms of the percentage of B.

Using lever rule: $f_\beta = \frac{C_0 - C_1}{C_2 - C_1} = \frac{x_0 - x_1}{x_2 - x_1}$, $f_\alpha = \frac{C_2 - C_0}{C_2 - C_1} = \frac{x_2 - x_0}{x_2 - x_1}$

Amount of B in C_0 (L) = Amount of B in α + Amount of B in β

$$x_0 = f_\beta x_2 + f_\alpha x_1 = \left(\frac{x_0 - x_1}{x_2 - x_1}\right)x_2 + \left(\frac{x_2 - x_0}{x_2 - x_1}\right)x_1 = \left(\frac{x_0x_2 - x_1x_2 + x_1x_2 - x_0x_1}{x_2 - x_1}\right) = x_0$$

Next thing of course, we note that we have used the lever rule we have and we know how to compute now, using the lever rule the fractions of say for instance the solid and liquid in coexistence. But you would like to know if the lever rule is right that is does it give the right fraction of the phases present in a two phase mixture ,so let us assume that a and b are the two component constituting the binary phase diagram let us consider a phase alpha which is in with composition C 1.

So, this is phase alpha of composition C one which is coexisting with a phase beta of composition C 2 now, the initial starting composition is C 0 on which is say of instance was originally in a single phase liquid field, but later on split into the alpha and beta phases. Now, f here denotes the fraction of a particular phase and we are expressing all our compositions in terms of beta that means, suppose the composition of alpha can be written as X subscript one in terms of b.

Of course, you could have called it X subscript alpha in terms of b also which is equivalent and the amount the composition of b beta phase is X subscript 2 in terms of B and the composition of the starting liquid is X 0. Now, we know the fraction of using the lever rule that the fraction of beta can be written as C 0 minus C 1 which is this arm of the lever divided by C 2 minus C 1 which is the terminal ends of the lever now, in terms of the composition variable X 0, we can write this as X 2 minus X 1 divided by X 0 minus X 1 divided by X 2 minus X 1.

Correspondingly, we can write down the fraction of the alpha which is now, proportional to the other arm of the lever here, so m proportional to this arm of the lever and I can write down the fraction of alpha as X 2 minus X 0 by X 2 minus X 1. Now, if I want to calculate the amount of b in the whole 2 phase mixture I know that in the original liquid for instance it is proportional it is equal to the amount of b in alpha plus the amount of b in beta and i know that the amount of b in l at l is the nominal composition is X 0.

Therefore, but on the right hand side we have the amount of b in alpha which can be written as f beta into X 2 that is the fraction of beta into the composition of beta X 2 here and fraction of, alpha into the composition of alpha which is X 1 and both of these are in terms of percentage of b for instance. Therefore, I can substitute from above and I can write this as from here I can write X 0 minus X 1 by X 2 minus X 1 into of course, X 2 which is the composition of the beta amount b in alpha.

And similarly, I can write for amount of b in beta to be the fraction of alpha which is X 2 minus X 0 by X 2 minus X 1 as taken from here multiplied by X 1 and simplifying, we note that this becomes equal to X 0. That implies left hand side is equal to right hand side which also implies that the lever rule is the correct rule to determine the fractions of the alpha present and the beta present in a two phase mixture, with a starting composition which is C 0.

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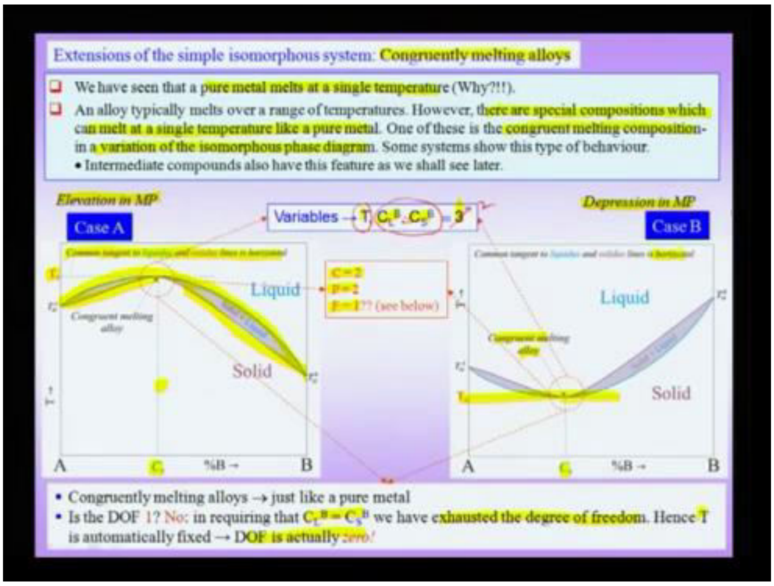

Extensions of the simple isomorphous system: Congruently melting alloys

- ❑ We have seen that a pure metal melts at a single temperature (Why?!!).
- ❑ An alloy typically melts over a range of temperatures. However, there are special compositions which can melt at a single temperature like a pure metal. One of these is the congruent melting composition- in a variation of the isomorphous phase diagram. Some systems show this type of behaviour.
  - Intermediate compounds also have this feature as we shall see later.

- Congruently melting alloys → just like a pure metal
- Is the DOF 1? No: in requiring that $C_L^B = C_S^B$ we have exhausted the degree of freedom. Hence T is automatically fixed → DOF is actually *zero!*

So, that implies that the lever rule is and we are valid in using the lever rule for calculations of phase fractions now, let us consider what we may call variations to the simple isomorphous system and we introduce the concept of what is known as congruently melting alloys. ,so if you go back we had noted that when we have an isomorphous system it does not look like the real isomorphous system for instance we talked about the silver gold system or the gold nickel system it does not look as ideal as the double lengths.

Which you were we had drawn schematically for an isomorphous phase diagram that means, real phase diagrams have variations and one of those, variations we saw was the case of the gold nickel. I shown below wherein there was a phase segregation, below a temperature of about 820 degree celsius for a composition with 44 percent of nickel now, if we note there are two systematic variations or extensions of the isomorphous system.

Which are possible and these are what we might call elevation in melting point and depression in melting point the elevation of melting point is shown in the diagram on the left hand side, and the depression in melting point is shown in the diagram in the right hand side. Before we consider these diagrams we I have previously noted that a pure melts at a single pure metal melts at the single temperature that we and we have noted that compositions having two elements for instance copper and nickel melt over a range of temperatures.

However, we will note that there are special compositions which can melt at a single temperature like a pure metal and these are called congruent melting compositions of course, these occur only in specific alloy systems. It may not occur in all alloy systems and the first two of them, we consider here the two congruent melting types in this current slide and these are variations to the isomorphous phase diagram and we will note later that actual some actual systems show these type of behaviors and if you note that intermediate compounds may also melt at a single temperature.

Which is like you know a pure metal or a congruent melting alloy composition and when we refer to alloy here we are talking about a disordered solid solution, so we have two variations to their congruent melting alloys, one is elevation in melting point on the left hand side another is depression in melting point which is labeled as case b. So, in case a we note that you have the liquidus line goes above up compared to the normal and the solidus line has two parts to it.

The part to the left which forms the lens with the liquidus line and again a right part which again forms another lens with the liquidus line and between the top and bottom the liquidus and solidus lines. We have what we might call a two phase mixture of liquid and solid now, for a composition C 0 which is exactly at the what you might call the tangent which is drawn at temperature T 0 and we should note that if you draw a tangent at horizontal line at T 0 then the both these curves will be tangent tangential to this line we draw at T 0.

That means, the common tangent to liquidus and solidus line is horizontal this is an important point to note and I will repeat it again the common tangent drawn to the liquidus line and the solidus line has to be horizontal and that is the temperature and that tangent if you extrapolate to the temperature axis will be the temperature at which this congruent melting alloy will melt. So, we have already noted and we have seen how to calculate the degrees of freedom in these solidus liquidus and the two phase regions.

I mean the solid region the liquid region and the two phase region, but let us try to do this now, for a congruent melting alloy for a congruent melting alloy we know that the number of components is 2, the number of phases is 2. Because now, we have the solid and liquid phases coexisting and suppose you substitute it in the phase rule which is at constant pressure you will land up with the degrees of freedom is equal to one, but from it is as obvious from this phase diagram that there should be no degrees of freedom.

Because, this is like a melting point for the alloy with composition C 0 that means, it should be an invariant of the phase diagram, so where is the paradox, the paradox can be resolved by understanding that we have 3 variables here the temperature the composition of the liquid and the composition of the solid, so there are totally 3 variables, but then when I am talking about a congruent melting composition what I am doing is that I am insisting that the composition of the liquid has to be same as the composition of the solid.

Because, that is it is not any different because, that is where the common tangent is the solidus line touches the liquidus line which touches the horizontal line drawn at temperature T 0. So, insisting that the composition of the liquid and the composition of the solid have to be the same we have exhausted that one degree of freedom which we had and that implies that the temperature is automatically fixes and the degree of freedom is in effect equal to 0.

So, this is an important point to note that a congruent melting alloy of composition C 0 melts at a temperature T 0 like a pure metal and because, at this melting point the composition of the liquid and the composition of the solid is same though. We may use a lever rule to calculate one degree of freedom that one degree of freedom is exhausted in putting this additional constraint on the compositions which implies that actually we do not have 3 variables we have only two variables, temperature and the composition of liquid which becomes equals to the composition of the solid.

And therefore, in effect we have only two variables and therefore, the degrees of freedom drops down to 0 similarly for the case of a depression in melting point which is shown on the right hand side we note that we can have a common tangent construction at T 0 and we have the degrees of freedom at this for this composition C 0 at T 0 to b 0. That means, it is an invariant of the phase diagram that means, it can the temperature and composition cannot be changed at which this alloy would melt.

So, that is an called an congruent melting alloy now, the difference of course, from the diagram case a ad case b is that in case b the liquid sort of exists to even lower temperatures. As compared to the case a and the common tangent T 0 to both these curves lies entirely below both these liquidus and solidus lines. On the other hand, in the case a the tangent lies completely above the solidus and liquidus line. And as for case A, now this tangent is the tangent to both the liquidus and the solidus lines and it has to be horizontal.

So, this is a point we need to not, so we have two cases the what we may call the elevation in melting point case and the depression in malting point case and in one case we can think in case a we can think as if the solid has been stabilized to higher temperatures. The other case we can think as if the liquid has been stabilized to lower temperatures as we cool now typically when you observe these two variations.

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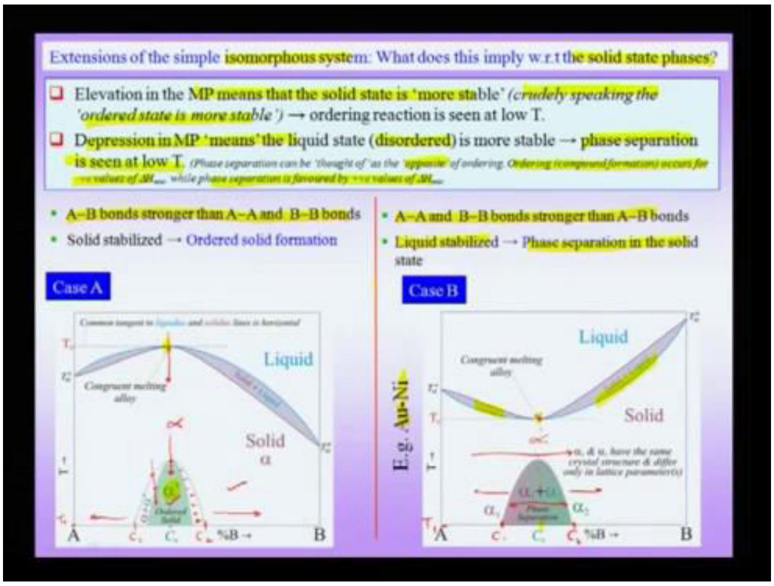

Extensions of the simple isomorphous system: What does this imply w.r.t the solid state phases?

- ☐ Elevation in the MP means that the solid state is 'more stable' *(crudely speaking the 'ordered state is more stable')* → ordering reaction is seen at low T.
- ☐ Depression in MP 'means' the liquid state (disordered) is more stable → phase separation is seen at low T. *(Phase separation can be 'thought of' as the 'opposite' of ordering. Ordering (compound formation) occurs for –ve values of ΔH_{mix} while phase separation is favoured by +ve values of ΔH_{mix})*

- A–B bonds stronger than A–A and B–B bonds
- Solid stabilized → Ordered solid formation

Case A

- A–A and B–B bonds stronger than A–B bonds
- Liquid stabilized → Phase separation in the solid state

Case B

There are typical signatures of these for the solid state and these are important to note that is when we have an isomorphous system of these two kinds that is elevation in melting point or depression in phasing point that there are important changes. Which may take place to the solid phases and if you talking about a elevation in melting point this somewhat means that the solid state is more stable or crudely speaking the ordered state is more stable and this sometimes shows up a signature that if your solid has been stabilized.

The ordered state has been stabilized typically at lower temperatures you would observe what is known as an ordering reaction that implies suppose I take a composition and this ordering reaction. Of course, does not take as you can see from the diagram below does not occur for an entire range of compositions it occurs for a typically for a limited set of compositions for a given temperature say for instance I am talking about a temperature T 1 here, so for this temperature T 1.

If I choose the composition to the left of say I call this C one and I call this T 2 if I choose the composition to the left of C one there will be no ordering transformation if I choose the composition to the right of C one there will be no ordering transformation, but if i choose any composition in between say for instance the composition C 0. Which is marked here then this alpha solid solution which is now, a disordered solid solution will get ordered at low temperature that means, it will show an ordering transformation.

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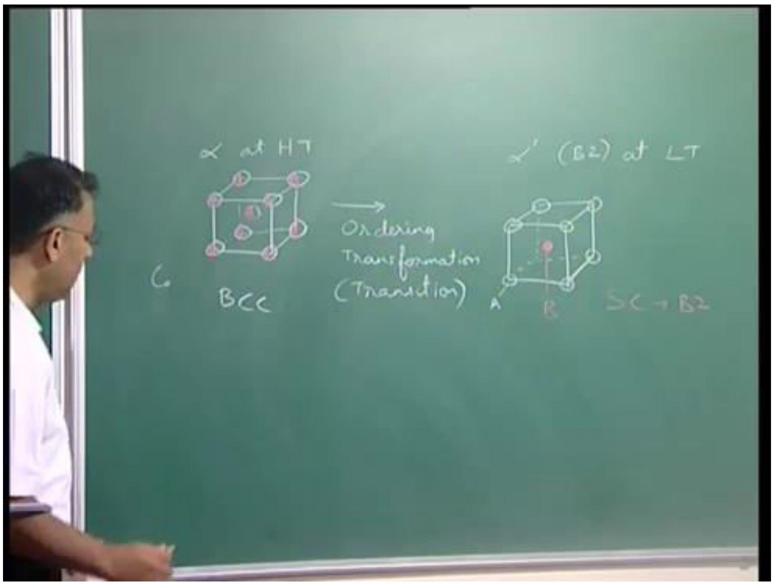

And I label this ordered structure as alpha prime say for instance we have talked about this before, but we will briefly state for instance what we mean by this ordering transformation. This is of course, I am just giving one example of, an ordering transformation and there could be various different kind of ordering transformations as we shall see in a coming slide. So, for instance, at high temperatures now, I am talking about a composition C 0 which lies in the ordering region.

And for simplicity, I can assume that, in that C 0 lies in a 50 50 mixture to make like simple. So, my disordered solid solution which I this as high temperature could be a BCC structure. So, I go have an ordering transformation and since the composition does not change I can call it an ordering transition as well. So, I have a disordered solid solution here which is BCC here and this is just an example and here I have an ordered compound which is simple cubic which is a which is also called a B 2 structure.

Therefore, the composition has not changed when I go from for instance the alpha to alpha prime here when the ordering transformation takes place, but I note that the crystal structure has changed this is now, a BCC while on ordering. It becomes a B 2 and this is just one example of an ordering transformation or a ordered structure and I label my ordered structure typically with the prime and I would call it an alpha prime which is or a beta prime or one of those primes which means that, I am talking about an ordered structure.

Now of course, if I choose a composition not at the peak like I did here I choose something to the left and slowly cool then I would notice that I will go through a two phase region from here to here, wherein I would observe that the alpha phase which is the disordered phase coexist with the alpha prime phase and as usual I can use a tie line construction to determine the compositions.

In other words suppose I am entering a two phase field not at the peak of that, but I am having a composition like this and I am slowly cooling a composition which is down here say I call this C 3 or something and suppose I am at a temperature which is in the two phase region here.

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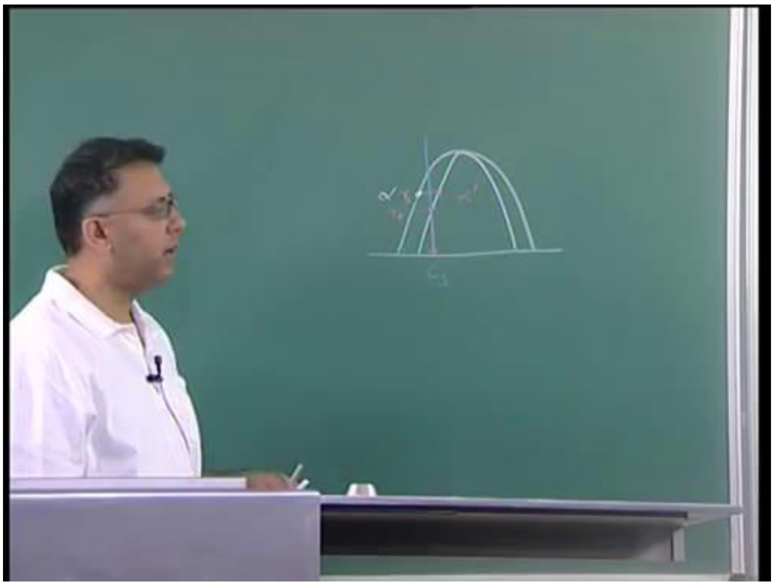

Then, I know that here is my alpha prime which is the ordered structure and here is my alpha which is disordered and here at this temperature say T 3 I will have a mixture of alpha of this composition in equilibrium with alpha prime of this composition in equilibrium with alpha of this composition. Of course the phase fraction of alpha will be proportional to this arm of the lever the phase fraction of alpha prime will be proportional to this arm of the lever and through from temperature starting from here to here.

I would have a two phase mixture of alpha and alpha prime, but below this temperature which I can call T 5 I would have a completely ordered structure alpha prime that means, the ordering reaction would occur over a range of temperatures and what is meant by ordering reaction is the fact that slowly you have. Of course, here there is no sub lattice concept it is a disordered solid solution slowly regions would form wherein you would have an ordered structure and you would have two sub lattices forming and therefore, slowly the whole system will get ordered and finally, below temperatures T 5 you will have an ordered structure.

So, this is a nice example of how an ordering reaction takes place when you cool a system, so at high temperatures we have the liquid at slightly lower temperatures when you cool. You have the alpha phase and then even at lower temperatures then you could have the alpha prime phase which is the ordered version of the alpha phase now, the opposite of that and of course, we can rationalize this kind of an ordering and we can understand that this takes place when the a b bonds are stronger than the A A or B B bonds.

That means, that my system wants to order that means, the a wants to have b coordination around it the b wants to have an a coordination around it which is what you typically observe here in this case there is no preferred ordering. Of course, this what we mean by this symbol as we have noted before is probabilistic ordering of a lattice site either by a or by b, but in this circumstance you could have one unit cell in which you could have a here and b here and in other case, you would have an A here and A A here.

So, there is randomness, but in this case you would notice that every b is surrounded by a is and every A is surrounded by B. That means, that unlike neighbors are preferred and that is why the ordering reaction takes place and we already seen a typical signature of this is this elevation in melting point at high temperatures which tells you that, there is a possibility of ordering at low temperatures.

Of course, as I again to emphasize the fact that ordering does not occur for all compositions it is usually centered around the composition which is the congruent melting composition. Now, on the other hand, the other example is what we call depression in melting point that means, that the liquid state which can be thought of as a disordered state is stabilized and whenever this happen there is a possibility that phase separation takes place at low temperatures.

Now, this phase separation can be thought of as an opposite of ordering in some sense because ordering or compound formation occurs for negative values of enthalpy delta h mixing is negative while phase separation takes place by for positive values of enthalpy. Of course, when we mean negative or positive what typically happens is that if you have close that means, values close to 0 mixing enthalpy preferred disordered solid solution that means, A A and B B bonds do not have any preference to form.

If you have large positive values of enthalpy that means, that you are going away from where the disordered solid solutions preferred then you would have a tendency of phase separation at low temperatures. But, on the other hand, if you have large negative value of enthalpy of mixing in that case it is directly implies that a b bonds are preferred over a a or b b bonds and this implies that an ordering reaction may take place at low temperatures.

So, let us consider now, the phase separation system which means there is a depression in the melting point and depressing in the freezing point and this is seen typically for a system like the gold nickel system whose actual phase diagram we will take up in one of the coming slides and you notice that as before there is a two convex lenses here. There is a congruent melting composition at C 0 somewhere, here or on those compositions and you notice that as you cool a composition here at low temperatures you have phase separation initially.

Of course, you have liquid then you have alpha then this alpha splits into alpha one plus alpha 2 at lower temperatures now, alpha one and alpha 2 since, we have a continuous phase field going from this direction to this direction it implies that alpha one and alpha 2 are nothing but, of similar crystal structure or of the same crystal structure. But, only differ in lattice parameter, therefore you have at low temperatures a dome forming like this and within this dome you have a two phase mixture unlike the case of ordering you had a single phase region here and two phase region was between the two here.

There is a single phase region to the left and there is a single phase region to the right and the two region is between these two limits that implies if I take a composition between say for instance C one and C 2. At now, I am at a temperature T one the n for T one between C one and C 2 I would notice that there is a phase separation when I cool an alloy of composition C 0 which is between C one and C 2. So, for this case I can think that the A A and B B bonds are stronger than the a b bonds.

That means, people would like to have like neighbors rather than unlike neighbors and this implies that the liquid state this happens when the liquid state is stabilized and this shows up as a phase separation at low temperatures. Like for instance, typically alloys containing copper as a positive enthalpy mixing with many elements would tend to segregate at low temperatures and would from a separate phase. And suppose, you took an for instance aluminum nickel system then this would tend to rather form a compound rather than phase segregating at low temperatures.