Structure of Materials
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Lecture - 33
Chapter - 07
Phase Diagrams

Let us start by considering a single component phase diagram, which are also called unary phase diagrams.

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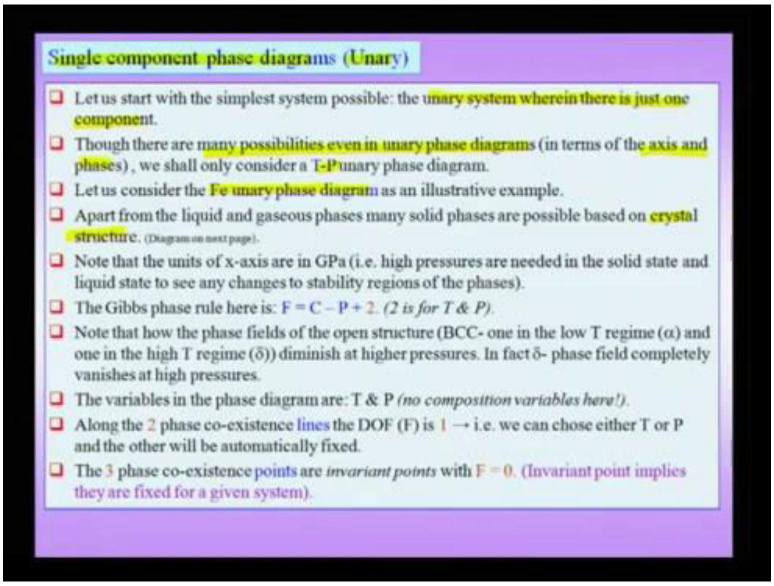

Single component phase diagrams (Unary)

- ☐ Let us start with the simplest system possible: the unary system wherein there is just one component.
- ☐ Though there are many possibilities even in unary phase diagrams (in terms of the axis and phases), we shall only consider a T-P unary phase diagram.
- ☐ Let us consider the Fe unary phase diagram as an illustrative example.
- ☐ Apart from the liquid and gaseous phases many solid phases are possible based on crystal structure. (Diagram on next page).
- ☐ Note that the units of x-axis are in GPa (i.e. high pressures are needed in the solid state and liquid state to see any changes to stability regions of the phases).
- ☐ The Gibbs phase rule here is: $F = C - P + 2$. *(2 is for T & P).*
- ☐ Note that how the phase fields of the open structure (BCC- one in the low T regime (α) and one in the high T regime (δ)) diminish at higher pressures. In fact δ- phase field completely vanishes at high pressures.
- ☐ The variables in the phase diagram are: T & P *(no composition variables here!).*
- ☐ Along the 2 phase co-existence lines the DOF (F) is 1 → i.e. we can chose either T or P and the other will be automatically fixed.
- ☐ The 3 phase co-existence points are *invariant points* with $F = 0$. (Invariant point implies they are fixed for a given system).

The unary system is such a system, in which there is just one component, in other words composition cannot be a variable in a unary phase diagram. But, still there are many possibilities, even in unary phase diagram in terms of the axis and the phases, which form. For an illustrative example, let us consider the iron unary phase diagram, in which we have temperature and pressure acts the variables, the thermodynamic variables which are varying.

Now, we have already noted that, apart from in the liquid and solid state, there are many phases possible and in the solid state, we can differentiate many phases based on the crystal structure.

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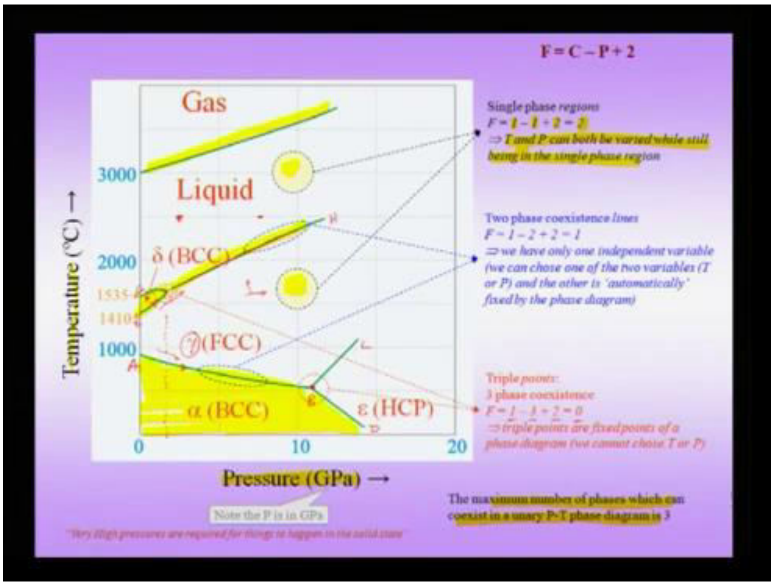

$F = C - P + 2$

Single phase regions
$F = 1 - 1 + 2 = 2$
⇒ T and P can both be varied while still being in the single phase region

Two phase coexistence lines
$F = 1 - 2 + 2 = 1$
⇒ we have only one independent variable (we can chose one of the two variables (T or P) and the other is 'automatically' fixed by the phase diagram)

Triple points:
3 phase coexistence
$F = 1 - 3 + 2 = 0$
⇒ triple points are fixed points of a phase diagram (we cannot chose T or P)

The maximum number of phases which can coexist in a unary P-T phase diagram is 3

"Very High pressures are required for things to happen in the solid state"

And so, let us have a peak into what the unary phase diagram we talking about, so we are talking about a unary phase diagram of iron, where pressure is one of the variables along the X axis and temperature is the other variable along the Y axis. Therefore, there is just one component, which is iron and we are varying these two variables to find out, what happens to the phases as we change the temperature and pressure.

The important thing to note is that, the units along the X axis are in Giga Pascal and the reason is that, because high pressures are needed in the solid state and liquid state to see any changes in the stability regimes of the phases. Because, we are talking about say for instance, alpha n which is the BCC form of iron. If I want to see any changes with respect to the stability regime or the change in phase, I need to apply very high pressures and these pressures of the order of Giga Pascal.

Now, in this case, because temperature and pressure are two variables, therefore the Gibbs phase rule is the extended phase rule, wherein F equal to C minus P plus 2. That means, the variable now is not 1 as in the reduced phase rule, but the complete one with C minus P plus 2 and component is just 1. Because, we are only considering iron, an important thing which we will know we will note when we see the diagram is that, the open structure BCC in the low temperature regime, which is been labeled alpha. And the another BCC structure, which occurs in the high temperature regime, which has been labeled delta these diminish at high pressures.

So, when we go to this phase diagram, so you have the phase stability regime of BCC here, the phase stability regime of delta here and this BCC. So, this is the entire phase stability, regime of BCC form of iron, the low temperature form is called alpha, the high temperature form is called delta. But, both these phase fields diminish as you go to higher pressures and this is not surprising, because we know BCC is a open form of packing and therefore, the packing fraction is not good.

And therefore, we would expect that, the closed pack form which is now for instance, gamma in the case of which is labeled as gamma in the case of iron, it is phase field will expand. So, you can see that, the phase field lines are all going upward and this line goes downward so that, you will see that, there is an expansion of the phase field for the gamma form of iron. Along the two phase coexistence lines, the degree of freedom is 1 and along wherever three phases coexist, the degree of freedom is 0.

That means, all the three phase coexistence points are all invariants of the phase diagram and which are these three phase coexistent regimes, there is one here which is now an invariant of the phase diagram. Because, the degrees of freedom if you calculate at these triple points is F equal to one component minus three phases, plus 2 for temperature and pressure, the net is 0 that means, this is an invariant of the phase diagram. That means, the place where the gamma form the alpha form and the epsilon form coexist, that point is an variant of the phase diagram.

Similarly, if you calculate the number of degrees of freedom for the coexistent point, wherein delta phase, the liquid phase and the FCC phase coexist, which is right here Again you would note that the degrees of freedom is 0, which implies that this is also an invariant of the phase diagram, which means it occurs at a very fixed pressure, if you draw down the line and it occurs at a fixed temperature. So, it is a invariant of the phase diagram.

Now, let us notice a few things about this, if you look at a single phase field then you can calculate the degrees of freedom like for instance, this is a single phase field here where pure liquid coexists or pure liquid exists, this is the single phase field of FCC iron already we have labeled the or colored the single phase field of the BCC to be yellow. Similarly, we have a single phase field for the HCP form of iron, which is known as the epsilon form.

The FCC form and the HCP form are the close packed forms, while the two BCC forms are the open forms. And if I now calculate my degrees of freedom, in these two single phase regions, the liquid and the FCC forms, I can see that f becomes one component two for temperature and pressure. And there is single phase therefore, 1 minus 1 plus 2, which is 2 that means, temperature and pressure can both be varied still being in the single phase region that means, not only is this point in the single phase region for, which say for instance the pressure is 2500, approximately here the temperature is 2500 degree Celsius and the pressure is say 2 point 5 GPa.

But, also such a point here for which the temperature is 2500 degree Celsius, but the pressure is approximately 7 point 5 GPa that means, that in these regions, I can vary my temperature and pressure. And still continue to be in the single phase field, of course till I hit the boundaries, where the single phase no longer, now as I pointed before that suppose I am looking at the coexistence lines between two phases.

And there are many of these for instance, this part of the phase diagram for instance suppose I am looking at a line a b c d, the a b part is the coexistence between alpha and gamma phases, along the b d curve you would notice that the alpha and the epsilon forms the h c p form of the iron coexist, along the b c line, it is the FCC and the HCP forms coexisted.

Similarly, you can label, the other parts also like e f g h and suppose I take my f h part of the curve, which is along this line I would know, that the liquid and the FCC forms of iron coexist. Similarly, you have a coexistence line here I right at the top, where in the gaseous and liquid forms of iron coexists, though for my material science perspective this very high temperatures, where the gaseous form forms is not a much of not a much technological importance.

But, it is important to note that, what we already know that if we heat the solid becomes liquid and higher temperature, it becomes gas what is surprising however, is that normally you expect, that the low temperature form is a close packed form. And the high temperature form is the open form, but in the case of iron, at low this is true however, beyond 1000 degree, Celsius at one atmosphere pressure or the pressure which is shown here.

But, that implies that, here you do find that there is an close pack form, open form, liquid gas kind of a phase transformation. But, at even lower temperature you find the closed pack form, which is rather surprising, so and the manner in which, these lines are sloping is important to note. Because, you notice that the coexistence lines, which demarcates the gamma form from the BCC form is sloping, upward and similarly the FCC and alpha form is sloping downward here.

So, this slope is downward this slope is upward, such that the gamma phase field, the close packed phase field, expands on increasing the pressure which is not surprising that means, at a higher pressure you would rather prefer to have a lower volume, which is what is provided by the gamma form of iron. Similarly, compared to the liquid state, the solid state has a higher density and therefore, at higher pressures you would find the liquid state, phase field is line the liquid solid gamma line is actually sloping upwards.

And the important point to note is that the maximum number of phases, which can coexist in a unary pressure temperature diagram is 3 and as we have noted, before this happens in points like B and F, where in three phases coexist.

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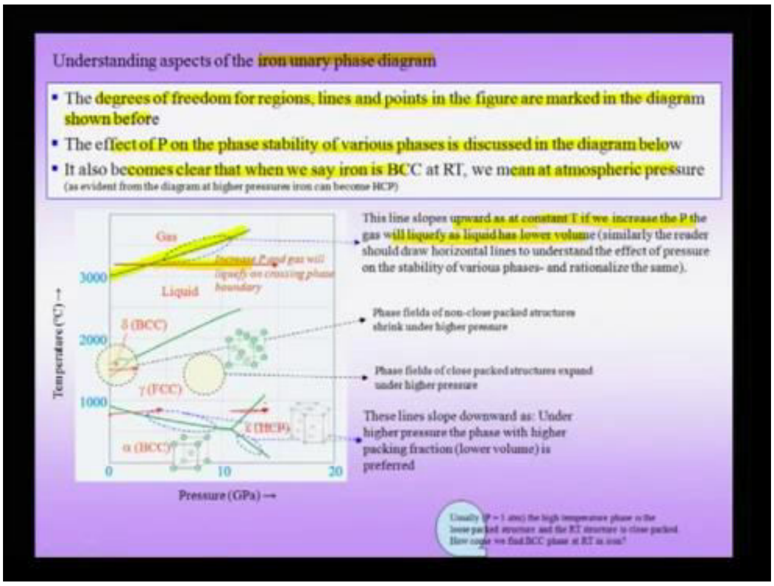

Understanding aspects of the iron unary phase diagram

- The degrees of freedom for regions, lines and points in the figure are marked in the diagram shown before
- The effect of P on the phase stability of various phases is discussed in the diagram below
- It also becomes clear that when we say iron is BCC at RT, we mean at atmospheric pressure (as evident from the diagram at higher pressures iron can become HCP)

This line slopes upward as at constant T if we increase the P the gas will liquefy as liquid has lower volume (similarly the reader should draw horizontal lines to understand the effect of pressure on the stability of various phases- and rationalize the same).

Phase fields of non-close packed structures shrink under higher pressure

Phase fields of close packed structures expand under higher pressure

These lines slope downward as: Under higher pressure the phase with higher packing fraction (lower volume) is preferred

Usually (P = 1 atm) the high temperature phase is the loose packed structure and the RT structure is close packed. How come we find BCC phase at RT in iron?

So, let us dwell a little more and try to understand, some of the points we already make and try to introduce, some more concepts in understanding of the iron unary phase diagram. The degrees of freedom for regions lines and points, in the figures are marked in the diagram as shown before, so these are the various regions in the phase diagram, the effect of pressure on the phase stability is also discussed in the diagram below.

And it also becomes clear that, when we say iron is BCC at room temperature, we usually imply atmospheric pressure. And we have noted here, that when you increase the pressure then you will see a phase transformation taking place that means, you would go from suppose I am at such an high temperature, where delta form is stable. And I increase the pressure, then I will see a phase transformation from the delta form to the gamma form.

Similarly, suppose I am in a phase field here, where I see the alpha form a stable, which is BCC and I increase the pressure, then I would notice that there is a phase transformation, from the alpha to the gamma form. So, and the one line which we did not discussed, before why is the gaseous line going upward, the rational is very similar this line slope upward as at constant temperature, If we increase the pressure the gas will liquefy as the liquid has the lower volume.

And this implies, suppose I am at a constant temperature and increase the pressure along this line, then the gas will liquefy and we will cross the gas liquid boundary and the system, will from the gases state will become a liquid. So, to summarize what we have learnt about the unary phase diagram of iron in the unary phase diagram, we have the Gibbs phase rule where in I have to keep the extended form of the phase rule, where in F equal to C minus P plus 2. Since, already I have told that the phase diagram is the unary phase diagram, I can safely substitute for the components the value one and the maximum number of phases, which can coexist.

In such a system is 3 and the minimum degrees of freedom for which of course, you will notice that, when the three phases coexist is 2 plus 1, which is 3 minus 3, which is 0 which means, that when 3 phases coexist that point will be an invariant of the phase diagram. It is important to note the other important point, which I told you is that when I want any changes in the solid state, then I have to use high pressures of the order of GIGA Pascal, only them will there be any change to the phase, which is stable we have to note that along the two phase or single phase regions.

The degrees of freedom is 2, that means pressure and temperature can both be varied in two phase coexistence regimes like the gas liquid line, which is here the liquid its gamma line or the delta liquid line, which is curving like this. And among all these two phase coexistence lines, the degrees of freedom is 1 that means, if I choose my temperature then automatically the pressure will be chosen, like suppose I choose my temperature to be here then, automatically along the two phase coexistence lines the pressure is chosen.

So, I have no choice over pressure similarly of course, I can choose the pressure and the temperature will automatically be chosen, by the phase diagram as dictated by the phase diagram. And we have also noted, that there are three phase coexistence points which are invariants of the phase diagram, so it is a nice to understand ah this illustrative example which is the unary phase diagram.

But, often as I pointed out in material science and metallurgical engineering you would actually encounter, what are known as phase diagram, which will actually be either a binary or ternary phase diagram, where in the whole phase diagram is drawn at one atmosphere pressure. And the important variables are composition along one or two axis and temperature along the other axis.

So, we will encounter many more of these phase diagrams, but we started with the simple example wherein you have unary iron, which we know exists in isomorphism forms like the alpha form and the BCC form. And the gamma form which is the close packed form and we also, additionally encountered the fact that, when you increase the pressure then even the gamma form transforms to an alternate close pack, form the epsilon form.

So, normally when you are dealing with iron nobody discusses this epsilon form, but at high pressures, you can note that the gamma form actually transforms to the hexagonal close packed form, which is the stable form under high pressures.

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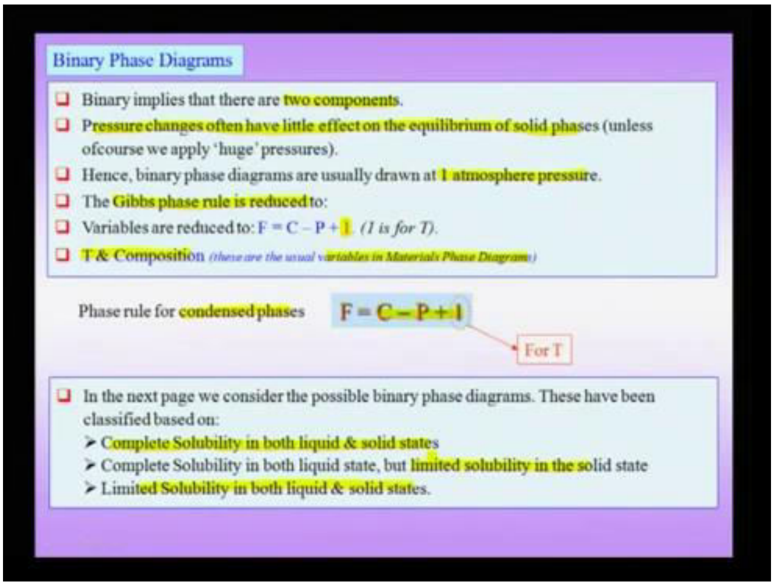

Binary Phase Diagrams

- ❑ Binary implies that there are two components.
- ❑ Pressure changes often have little effect on the equilibrium of solid phases (unless ofcourse we apply 'huge' pressures).
- ❑ Hence, binary phase diagrams are usually drawn at 1 atmosphere pressure.
- ❑ The Gibbs phase rule is reduced to:
- ❑ Variables are reduced to: $F = C - P + 1$. *(1 is for T).*
- ❑ T & Composition *(these are the usual variables in Materials Phase Diagrams)*

Phase rule for condensed phases $F = C - P + 1$

For T

- ❑ In the next page we consider the possible binary phase diagrams. These have been classified based on:
  - ➢ Complete Solubility in both liquid & solid states
  - ➢ Complete Solubility in both liquid state, but limited solubility in the solid state
  - ➢ Limited Solubility in both liquid & solid states.

Now, let us proceed further and try to understand what are called binary phase diagrams, the fact that the word binary is used implies, that there are two components. And these two components, as we have already noted can be elements like copper and nickel, they could be even compounds like alumina and chromium. So, we will take up some examples to understand these kind of phase diagrams and we have already noted that pressure changes, often have very little effect on the equilibrium of phases.

Unless of course, we are talking about very high pressures which normally we do not encounter in normal technological processing, therefore we will usually tend to draw all these, binary phase diagrams at one atmospheric pressure. And since we are drawing it at one atmosphere pressure, the Gibbs phase rule reduces to F equal to C minus P plus 1, this one is for temperature.

Because, pressure has already been chosen to be one atmosphere and typically temperature and composition are the usual variables in a materials phase diagram. And this composition of course, could be atom percent could be in weight percent or equivalently could be expressed in mole fractions . So, therefore, the phase rule for condensed phases where we keep the pressure constant is c minus p plus 1.

Now, we will try to classify possible binary phase diagrams and this classification is based on, the fact that is there complete solid solubility in both the liquid and solid states, is there solid solubility only in the liquid state. But, limited solid solubility in the solid state or is there limited solubility in both liquid and the solid state, so this is the one way of classifying and understanding, binary phase diagrams that is based on the solubility in the liquid state and the solubility in the solid state.

Typically when you find that there is complete solubility in the solid state, which is where as we have noted, before they can be many phases based on crystal structure and composition. If you find complete solid solubility in, which case you would know that you are actually satisfying, what we already encountered before the Hume Rothery's rules therefore, if Hume Rothery's rules are satisfied.

And you find complete solid solubility, then you would expect that the liquid state there is complete solubility. But, on the other hand just because the liquid state there is complete liquid solid solubility, it does not imply that the solid state you will find complete solubility. And we will see examples of these kind of variations to the phase diagram.

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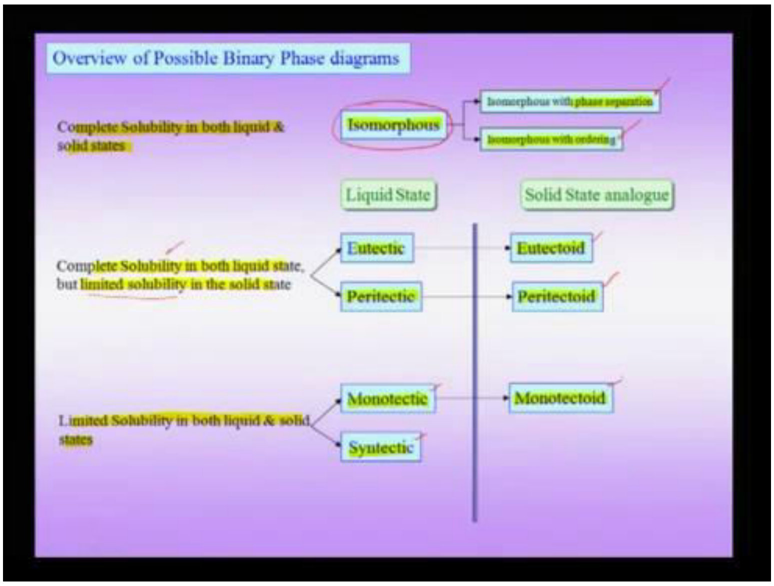

Overview of Possible Binary Phase diagrams

Complete Solubility in both liquid & solid states

Isomorphous

Isomorphous with phase separation

Isomorphous with ordering

Liquid State

Solid State analogue

Complete Solubility in both liquid state, but limited solubility in the solid state

Eutectic

Peritectic

Eutectoid

Peritectoid

Limited Solubility in both liquid & solid states

Monotectic

Syntectic

Monotectoid

So, we will consider an overview of possible, binary phase diagrams based on the solubility criteria. So, the complete the first case is of course, there is complete solubility both in liquid and solid states and these are called isomorphous phase diagrams. And even within isomorphous phase diagrams, there are cases where even though there is solid solubility.

But, at lower temperatures this solid solubility is sort of broken up and you may have phase segregation, there are eight other cases in variations of isomorphous phase diagram, where you would notice that there is isomorphous phase diagram with ordering at low temperatures, though that implies we are talking about complete solid solubility, this is not completely extending up to the lowest temperatures then we consider cases wherein there is complete solubility in the liquid state.

But, limited solubility in the solid state and that implies, you can see what we call we will understand later to be eutectic reactions and peritectic reactions that means, there are eutectic systems, like lead tin and there are peritectic systems. And we also have reactions, which are the solid state analogs of this eutectic and peritectic, which are the eutectoid and peritectoid reactions, which also we will consider examples of, there are eight other systems, where in you will find limited solubility both in the liquid and solid states, these are labeled the monotectic system and the syntactic system.

And the solid state analog of the monotectic reaction is called the monotectoid reaction and though, we are considering it for completeness here some of these monotectic syntactic and monotectoid reactions, we will not deal in any detail further in this course. So, to summarize this slide we can classify binary phase diagrams based on liquid and solid solubility.

An isomorphous phase diagrams is one, where in you have complete liquid and solid solubility, but there are variations to the isomorphous phase diagram, where in the solid solubility does not extend, all the way down to low temperature. And at low temperature you may actually observe phase segregation or ordering and actually, you will find signatures of these even in the way, the liquid or the solid is stabilized and we will see examples of these.

There are eight other phase diagrams, where in there is complete solubility in the liquid state, but limited solubility in the solid state and these kind of reactions are labeled as eutectic and peritectic. And there are solid state analogs of these, which are known as eutectoid and peritectoid, there are other phase diagrams or other systems, where in there is limited solid solubility both in the liquid state and in the solid state and these are called the monotectic.

And the syntactic systems and the of course, you can have a reaction which is the solid state analog of the Monotectic, which is the monotectoid reaction. So, at this point of course, much of this may not be clear, but we actually take up examples. And draw the phase stability lines, it will become clear that what we mean by this Isomorphous eutectic and Peritectic and their solid state analogs.

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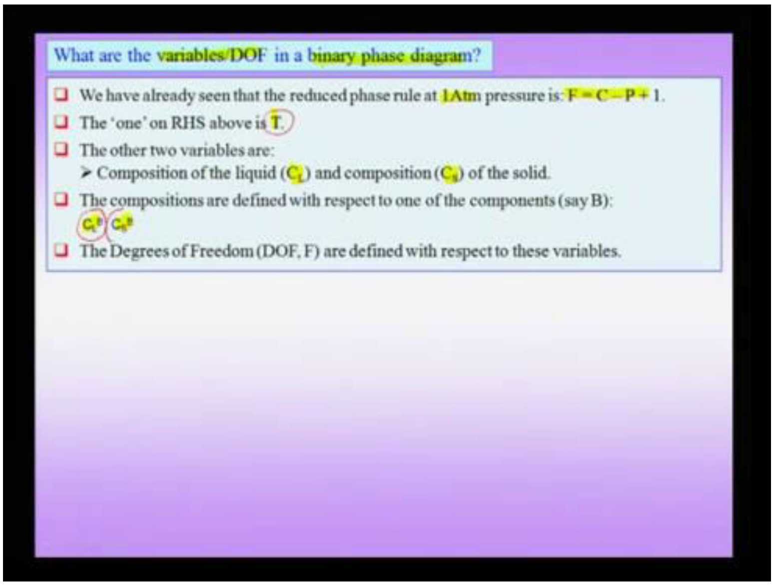

What are the variables/DOF in a binary phase diagram?

- ❑ We have already seen that the reduced phase rule at 1Atm pressure is: $F = C - P + 1$.
- ❑ The 'one' on RHS above is T.
- ❑ The other two variables are:
  - ➢ Composition of the liquid (C_L) and composition (C_S) of the solid.
- ❑ The compositions are defined with respect to one of the components (say B): C_L^B C_S^B
- ❑ The Degrees of Freedom (DOF, F) are defined with respect to these variables.

So, before we proceed further we have seen that, when we talked about the unary phase diagram the only variables possible where pressure and temperature. And there were no further variables to be considered. Because, the component was just one and therefore, there was no need to talk about composition variables, but in a binary phase diagram, we need to understand, what are the variables and degree.

Hence, some of these variables will play the role of the degrees of freedom of the system and therefore, I need to know what are the variables and degrees of freedom in a binary phase diagram. Now, obviously we are considering the reduced phase rule at one atmosphere, to be f equal to c minus p plus 1 and the 1 on the right hand side is temperature.

Now, that means automatically in a binary phase diagram, one of the variables is going to be temperature, the other two variables can be the composition of the liquid or the composition, of the solid this is very important to note, that the variables here are not composition of any of the other things. But, it is actually the composition of the liquid and the composition of the solid.

And these compositions of the liquid or the solid can be defined with respect to any one of the components, for instance I can talk about the composition of the liquid to be say for instance 10 percent of B or of course, if b happens to be copper, I can talk about the composition of the liquid being 10 percent copper. I could alternately talk about the composition in terms of a tie a component.

But, it is of no difference and therefore, I will stick to the fact that composition is typically referred to the 1, which is on the right hand side which is the b component therefore, the two variables composition variables the composition of the liquid and the composition of the solid. And these are specified based on composition of the liquid in terms of these percentage or atom percent of B and the composition, of the solid in terms of b.

And obviously, the degrees of freedom therefore, can be any one of these the degrees of freedom can be temperature, the composition of the liquid as specified with respect to B and the or the composition of the solid.

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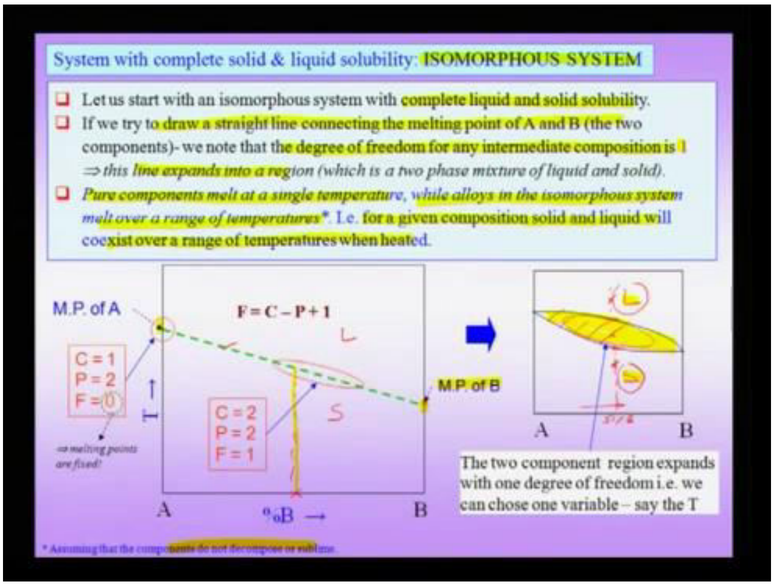

System with complete solid & liquid solubility: ISOMORPHOUS SYSTEM

- Let us start with an isomorphous system with complete liquid and solid solubility.
- If we try to draw a straight line connecting the melting point of A and B (the two components)- we note that the degree of freedom for any intermediate composition is 1 ⇒ *this line expands into a region (which is a two phase mixture of liquid and solid).*
- *Pure components melt at a single temperature, while alloys in the isomorphous system melt over a range of temperatures**. I.e. for a given composition solid and liquid will coexist over a range of temperatures when heated.

The two component region expands with one degree of freedom i.e. we can chose one variable – say the T

* Assuming that the components do not decompose or sublime.

So, let us start my understanding what are isomorphous phase diagrams or an isomorphous system, as we have pointed out an isomorphous system is one where in there is complete liquid and complete solid solubility. And we have also pointed out this is possible only when Hume Rothery's rules are satisfied and that means, the A and B components, which want to find the boundary have the same crystal structure, they have similar kind of electro-negativities that means, there is no tendency for them to form a compound.

And they have very similar in other words A and B are very similar in terms of sizes electro-negativity etcetera, such that and crystal structure that means, the radius is very similar the radius difference is not more, than above 12 percent the crystal structure is same. And also the electro-negativity difference between the A and B components is small.

So, that the tendency to from compounds is small and this implies, that you could have what you might call an isomorphous phase diagram, where in there is complete solid solubility. Now, there is one way of understanding this aspect, that if we try to draw a straight line connecting the melting points of A and B the two components, we note that the degree of freedom for any intermediate composition is 1, that implies that this line expands into a region.

Therefore, if I have a melting point of A and I have the melting point of e and I form any composition for instance I, it take my for instance a composition is 50 percent of B. And if I note, that at this point there are two phases which have to coexist, because this is the for instance the solid state and this is a liquid state, then automatically given the fact that there is one degree of freedom, this will actually expand into a region as shown in the right hand side of the figure that means, between the single phase regions, the liquid region and the single phase region.

Which is a solid region and both are defined with respect to A and B that means, A composition changing B is increasing along this direction, then this between the liquid and the solid regions. Actually, you will obtain a two phase region which is a mandatory, this is based on the fact that the degrees of freedom has to be one and therefore, you will have a two phase region, always between two single phase regions.

In a binary phase diagram, this implies that pure components melt at single temperatures this is something, we know while alloys in the isomorphous system melt over a range of temperature, this is very important note. And of course, we are assuming that these components do not decompose or sublime, when you are heating them and therefore, they will actually melt.

And that also implies that for a given composition the solid and liquid, will coexist over a range of temperature, this is something very important note point number one being that if I have a pure substance A, it will melt at a single temperature. Similarly, if I have A pure substance B, it will melt at a single temperature known as the melting point of B, but if I take any composition in between, for instance I take 50 percent B, then such a composition will not melt at a single temperature, if heated it will melt over a range of temperatures.

In other words, if I hold such a substance at somewhere here suppose this is my 50 percent B line and I hold it here I will have a pure solid with 50 percent B, if I hold it here I will have a combination of liquid and solid coexisting, if I heat it even further actually I will have pure liquid. And this is something very different from a pure substance where in you would find that it actually melts at a single temperature, that means an alloy does not melt at a single temperature, at least for this isomorphous system.

As you see here we will of course, which are identify special compositions which will tent to melt like a single component or a pure element, which we call congruent melting compositions. But, in general you would note that such compositions do not melt at a single temperature and they actually melt over a range of temperatures, so for this composition for instance this range of temperatures is from here to here, that the composition with 50 percent, B say suppose I will take 50 percent B that composition will melt over a range of temperatures.

And, so this is an very important thing to be noted and which is very different from that for a pure substance, so for a pure substance you have a very fixed melting point. But, for a alloy the melting point, is over a range of temperatures and is not a single temperature. Additionally of course, it is important note that if I have the melting point of a and the melting point of B.

And I choose an alloy anywhere in between say 50 percent B, I cannot interpolate the melting points, I cannot find the melting point of any alloy by drawing, a straight line between the two and taking a dotted line, like the green line and interpolating to find the melting point. So, melting point is not one of those things which you could find by interpolating the melting points of A and B.

So, this is the very important point to be noted and we have noted that therefore, between any two single phase regions for instance the liquid and solid, you will have actually A two phase region and for instance in this diagram, we have marked this two phase region in the shade yellow.

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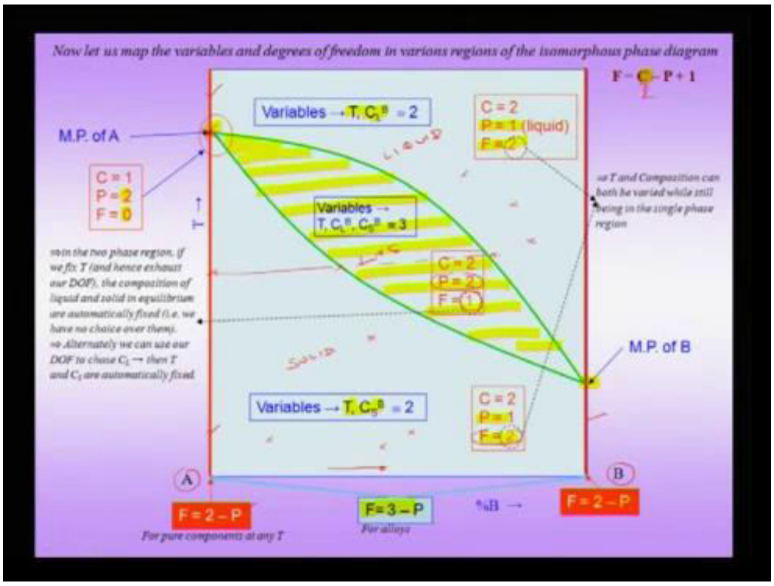


Now let us map the variables and degrees of freedom in various regions of the isomorphous phase diagram

⇒ In the two phase region, if we fix T (and hence exhaust our DOF), the composition of liquid and solid in equilibrium are automatically fixed (i.e. we have no choice over them).
⇒ Alternately we can use our DOF to chose C_L → then T and C_S are automatically fixed

⇒ T and Composition can both be varied while still being in the single phase region

So, let us go ahead and map the degrees of freedom in various regions of the isomorphous phase diagram. So, in the binary phase diagram we have of course, the two pure components, which is a on the left hand side and b on the right hand side for the pure components. Of course, C is equal to 1 and therefore, you can write down the phase rule as two minus P.

And therefore, if you go along the temperature axis you will find for instance at low temperature, there is the solid phase at high temperature, there is the liquid phase. And between the solid and the liquid phases, you have liquid plus solid it is important note of course, that any given solid between A and B that means, excluding the red lines drawn on the right hand side and the left hand side, these two red lines actually both the liquid and the solid will have both the components A and B in various percentages that means, with increasing percentage of B.

As you go from the left hand side to the right hand side, now along this pure two phases I pointed out that the degrees of freedom is 2 minus P for both these terminal ends. And whenever there is pure solid that means, there is a single phase the phase rule tells you it is 2 minus 1 that means, the degrees of freedom is 1 that and that degree of freedom, we know is temperature. As you go even above here for instance again, here you have the single liquid phase and the degree of freedom is 1 which is temperature.

But, suppose I am in the two phase coexistence, regime here at this point here, which is the melting point of A at this melting point of A which is been encircled, you would notice, that the two phases coexist and therefore, the degrees of freedom is 0. And we all know that the melting point is an invariant of an for an element that means, every elements melts at a very specified temperature given the fact that the pressure is fixed.

Similarly, the melting point of B on the right hand side the degrees of freedom is 0 and that means, the melting point of B is also fixed based on the reduced phase rule for a single unary component, for any composition in between the phase rule is can be, now written as since there are two components, I can write down c is equal to 2 for any composition below.

And that means, the phase rule becomes f equal to 2 plus 1 3 minus p and that is what has been written in the middle of the phase diagram here, that implies that for all compositions binary composition, which have both A and B, the phase rule is 3 minus P and therefore, if I am in the pure solid state or the pure liquid state the number of phases is 1.

And which you can be seen here, so therefore, your phase is equal to 1 in the pure liquid state and the phase is equal to 1 in the pure solid state, that tells you if you substitute into 3 minus p that the degrees of freedom is 2 for both these single phase regions. And these 2 degrees of freedom have to be either the temperature or the composition of the liquid, because you have three variables, here to consider as we talked about in a binary phase diagram, the temperature, the composition of the liquid or the composition of the solid.

But, we know in the liquid state we have only liquid therefore, the only composition variable, automatically has to be the composition of the liquid. Similarly in the solid state though we have three variables for, the entire phase diagram only two variables are applicable to the solid state, which is temperature and the composition of the solid.

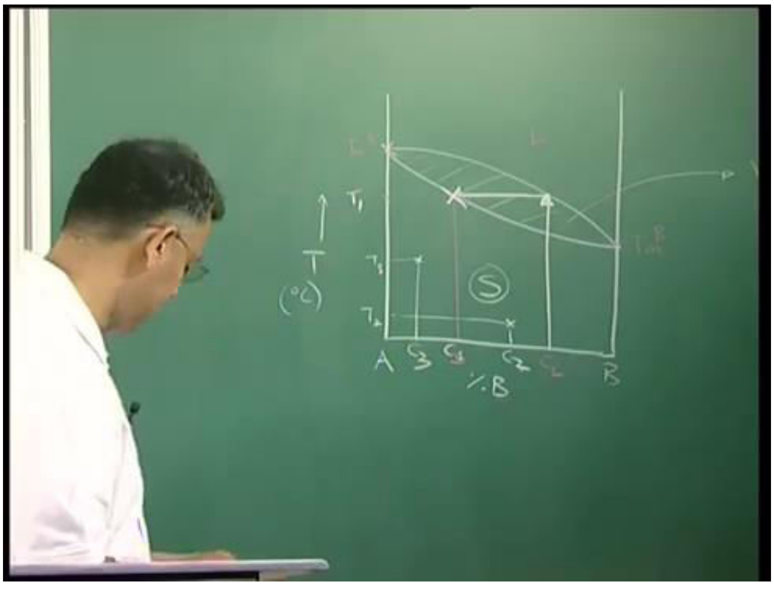
Therefore, I can change the temperature and composition of the solid, which are the two variables both of these are degrees of freedom because f is equal to 2.

So, I can be here somewhere else here in the phase diagram or somewhere here and still that means, I can change my temperature and the composition of the solid and still be in the single phase solid regime. So, it is equally true for the single phase liquid region, I could be here or somewhere else in the single phase liquid region that means, I could change my composition of the liquid or I could change the temperature and still be in the single phase liquid regime.

Now, suppose I am talking about the two phase coexistence regime, which is between the solid state and the liquid state which I am shading with yellow color here. And here two phases coexist as shown here that implies that, now f equal to 3 minus P that since two phases coexist the degrees of freedom reduces to 1. And since I have three variables the three variables being temperature, the composition of the liquid or the composition of the solid, I can only choose any one of these three and the other two will be automatically determined.

For example, suppose I end up choosing temperature say suppose, what I am working at this temperature, then the composition of the solid and the composition of the liquid are automatically determined. Just to avoid clattering, this diagram further I will go to the board and explain this concept.

(Refer Slide Time: 33:08)



So, I have an isomorphous phase diagram, where in my percentage B and this could be in weight percent or in atom percent and temperature as the axis. And typically you can choose temperature to be in degrees, Celsius or in Kelvin, I have the melting point of A which is an invariant of the phase diagram and the melting point of b which is another invariant of the phase diagram and between, the two I have an isomorphous system which is typically drawn like this.

So, now, suppose I fix my temperature to be a certain temperature which I choose, so I have 3 degrees of three variables here in this region, in the shaded region, I have three variables. And these three variables happen to be temperature, the composition of the liquid and the composition of solid and both these could be specified, in terms of the percentage of B.

So, I my isomorphous phase diagram with three variables, now as I pointed out the since the degrees of freedom f for this region is just 1 that means, out of these three variables I can only choose one at a time, the other two will automatically be determined by the phase diagram. Suppose I end up choosing my temperature and I call this temperature T1 and of course, I have to choose my temperature, between these two extremes where I have my two phase region that means, it has to between the melting point of B and the melting point of A, where I have a two phase region.

And I choose my T 1 and I draw a horizontal line and once I do that, since T 1 is chosen the composition of the liquid, which is here sorry this is the composition of the solid. And since the liquid is above and the composition of solid, which is in equilibrium with this are both automatically determined by the isomorphous phase diagram. So, to repeat again if I choose a temperature T 1 in the two phase region, which lies in the two phase region between T M of A and T M of B, then I would notice that the composition of the solid and the composition of the liquid, are automatically determined by the phase diagram.

Similarly of course, I could do a reverse experiment I can choose my composition of this liquid and ((Refer Time: 35:38)). Now, I will choose the same composition which I choose before I choose my composition of liquid to be like this, then automatically the phase diagram will tell you that the composition of the solid, which will be in equilibrium will be this number here, which is the composition of the solid and both these liquid and solid will be in equilibrium at a temperature T 1 therefore, in the two phase region, the degrees of freedom is 1.

And this degree of freedom could be 1 of these 3 temperature composition of liquid or composition of solid. And once I choose any one of the three like the temperature, the composition of the liquid and the composition of the solid, which is in equilibrium with this liquid both automatically determined by the isomorphous phase diagram. So, this is an important point to note that, I have only one choice in the two phase region, why in the single phase region like for instance.

Suppose I am talking about the single phase field where the solid exists, then I can choose my composition for instance, I could choose this composition and I could choose this temperature or I could choose an alternate temperature, say this is T 2 this is 3 T and I can choose an alternate composition for instance, say this is c 2 and this is c 3, I can or this can be C 3 and this can be C 2. And I can choose the T 3, C 3, T 2, C 2 combinations.

And still continue to be in the single solid phase regime, that implies that I have got an higher degree of freedom, which is two in the single phase region while I have a lower degree of freedom, which is 1 in the two phase coexistence regime which is the solid plus liquid mixture.