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# Lecture No. #15

# Errors in drawing phase diagrams, Fe-C vs Fe-Fe 3 C phase

So, let us try to this time today try to address some of the questions, we have recently come across in the quiz one. We will start with the last question, the last question is basically to identify what are the errors in the phase diagram.

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And I thought that should be easier, because you must have gone through such phase diagrams before it goes something like this, let me see the phase diagram once again for you and then. (No Audio From: 00:45 to 00:58) This is what is the phase diagram that is given to you and people have been asked to identify what are the errors? Some of the errors are very very obvious, because most of the errors that you see here, can be easily addressed using one single principle called the phase rule.

All of you know, the phase rule says P plus F is equal to C plus 1 this is the condensed phase rule and we deal with only condensed phase rule in the whole of solid state phase transformations or solid to liquid phase transformations. As a result, you can see that if this is the phase rule that, we are talking about this phase rules tells us that whenever you

have a transformation taking place at the pure metal end where the number of components is equal to 1. Then, the phase transformation should deal with 0 degrees of freedom, because if components is equal to 1. And if there is a phase transformation where, one phase is transforming to another phase, P becomes equal to 2 and the moment C is 1 and P is 2 automatically F is to be equal to 0. So that what that particular phase rule tells you.

So, if C equal to 1 and p equal to 2 obviously, F equal to 1, F equal to 0. So that means, the degrees of freedom for any phase transformation for a pure metal, were 1 phase changes to another phase, whether it is a solid state phase transformation, solid to liquid or liquid to gas whatever. And only thing is when you are talking of liquid to gas cases, we usually use not the condense phase rule, we use the generalized phase rule, were people have F is equal to C plus 2 and bring in the effect of pressure. Whereas, all these phase diagram that, we talk about pressure is always kept constant, because pressure is kept constant, we use the condensed phase rule.

And once, we use the condensed phase rule, for any pure component it is like for a pure metal, this has to holds good and if it holds good then, automatically you will see that this is one of the major error there. You see that here, solid to liquid transformation is taking place over a range of temperature, it cannot occur over a range of temperature. Because solid to liquid phase transformation again, there is a solid involve there is a liquid involve, there are 2 phases that are involved.

And when we are talking of a pure metal there is number of components is one and if number of components is one, obviously, F has to be 0; that means, solid to liquid transformation for any pure metal should occur at a fixed temperature, it cannot occur over a range of temperature. But it can occur over a range of temperature for an alloy, that is what we see in a isomorphism, that is what we see even for an alloy of this composition let us say. Any alloy of that composition you will see there is something called a liquid us, there is something called as solid us. And there is a temperature range between the two and this temperature range between the two basically means, that there is 1 degree of freedom.

And that 1 degree of freedom comes, because C equal to 2 the moment C equal to 2 and p equal to 2 then, F has to be 1. So, if you put C as 2 and p as 2 then F equal to 1 and that

is what you see here. So, here you cannot, because we are talking of pure component A and one side pure component, B on other side here, you need to see that this actually has to join each other. (No Audio From: 04:55 to 05:03)

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This is first, the second thing that you see that the eutectic horizontal that you see here. Were a liquid is given alpha plus beta, you see that it is an incline eutectic whenever you see incline means, that eutectic for various compositions in this alloy is occurring as the function of temperature. So that again is against the phase rule, again phase rule tells that whenever you have three phases involved in a reaction, eutectic is a one such a reaction were liquid is given alpha plus beta. So, there are three phases are involved. So, whenever liquid gives alpha plus beta the P equal to 3 and the number of component C, C is how many, we are talking of a binary alloy. So, C has to be 2 then, F has to be 0, F 0 basically needs that is associated with that reaction is invariant aspect. That means, temperature is fixed the composition of liquid that undergoes the eutectic reaction is fixed and the composition of two solids that are coming out of the liquid are also fixed.

Here you see, that the composition of the solid, two solids is fixed, but the compositions of the liquid which is undergoing the eutectic reaction is not fixed. You see that, the eutectic reaction appears to be occurring over a range of composition, as if any composition that you choose, that all of those liquids are going to give you alpha plus beta and that again differs this phase rule. Were you see that the degrees of freedom are 0

when I say difference of freedom are 0 only one single composition of the liquid can undergo a eutectic reaction. You cannot have any composition liquid and think that it will undergo eutectic reaction and that is the reason why I told you earlier also.



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For example, if you have a eutectic reaction, if you ask me what would it happen if I choose a hypo eutectic composition. Whether this hypo eutectic composition, the liquid the alloy composition that I am starting with is this composition, which is different from the eutectic composition. Then, how do you say, this alloy also there is a eutectic reaction taking place in this alloy, how do you say that liquid can have only one single composition. In principle I can choose any alloy here, alloy

Even if you all choose this composition called C 1 by that time this liquid reaches the eutectic temperature that liquid will have only this composition, it will not have the compositions with which you have started with. You are starting with your alloy composition as that, the moment alpha comes out of this, the liquid composition changes. To such an extent that, by the time you reach the eutectic temperature the liquid that is left out, after some alpha has precipitated out that liquid will have this composition and it

is that liquid which undergoes the eutectic reaction. So, which ever composition, we choose between that eutectic horizontal, in all the cases whether it is a hypo eutectic or a hyper eutectic the liquid that undergoes eutectic reaction is always this liquid only and that is the reason, reason for that is that the eutectic is invariant.

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So, that is the reason why this is the, if you think this is the second error in this, this is the first error, the third error is this. And both of them are related to only one single phase rule related to the eutectic, the phase rule for the eutectic, when you apply the phase rule to eutectic it tells you that any binary system. That is why we always talk about binary eutectic in a binary system, what sorry turnery eutectic in a binary system when I say a turnery eutectic. Basically, it means one liquid giving you two phases there are three phases that are involved. So, you can say simply a eutectic in a binary system is invariant, but a eutectic in a turnery system need not be invariant, but there are special eutectics in a turnery systems.

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Were one liquid gives you three solids there are eutectics like that available in turnery phase diagram. Such eutectic again would be invariant, because there the P will be equal to how many? 4 not 3 there are 4 phases involved and the number of components see is 3 if C is 3 and p is 4 then, F has to be 0 again. That means that particular eutectic reaction will happen at a fixed temperature and all the 4 phases will have fixed compositions they cannot have any compositions of their choice. The liquid of a particular composition containing, so much of A, so much of B, so much of C will give you alpha plus beta plus gamma and each of them will have certain fixed amounts of A B C inside them and that is what is a turnery eutectic in a turnery phase diagram. So, this is something which one has to remember.

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So, that is the third one then, there is a forth issue which comes with respect to this, this is a miscibility gap there, the miscibility gap basically means that a 1 phase is splitting into 2 phases isn't it. A 1 plus splitting into phases means a miscibility gap should always be enclosed in a single phase domain only. You cannot talk about a miscibility gap in a 2 phase domain, what you see here is a 2 phase domain alpha plus beta in a 2 phase domain you cannot have a miscibility gap, because miscibility gap basically means alpha 1 plus alpha 2. You can have a miscibility gap here, possible inside the alpha, inside the beta if you want to you can have a miscibility gap, but not inside a 2 phase p. Because that defines the whole concept of miscibility gap, miscibility gap basically means one single phase which is the single phase that high temperature.

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When I bring it to lower temperature there it is splitting into 2 phases basically, because the delta H is positive. And at low temperatures the delta H dominates the T delta H terms and as a result, the free energy curve will have a tendency like that. And this if I take it to higher temperature, at higher temperature T delta H dominates and as a result the free energy curve will not be like this. But the free energy curve will become something like this and the moment you become, you get a free energy curve like that then it becomes a single phase. So that is why at higher temperature in any 2 phase field, in any miscibility gap at high temperature you get a single phase.

And this single case phase at low temperature, because T delta S term being smaller plus T itself is smaller. So, delta H dominates and this you will get only when delta H is positive. Delta H for the solid should be positive to be able to get a miscibility gap and it should be sufficiently positive to be able to overcome the T delta A. That is why in some cases, you may have what is called miscibility gap at sub 0 temperatures? At up to room temperature you may see everything is solid solution, but if you take it to further lower temperatures were, actually the T delta H term is much smaller, because T is very smaller. And the delta H is though positive is not highly positive, the amount of the actual absolute value of delta H is going to decide how big is the miscibility gap. The this temperature that you are going to see, were the miscibility gap closes.

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The miscibility gap close can close here or there it can close here, below the room temperature depends on the particular system and it can happen when the delta H is very small. And if it is very close to 0, you may not have any miscibility gap at all. So, that is what you see that. So, the moment you see the miscibility gap it has to be there inside a single phase, because the meaning of closure of miscibility gap means, once I cross that I have a single phase and in this phase diagram I do not have a single phase.

So, that is why that is the 4th error in this. The fifth error is a little more difficult for you to see, I do not know how many of you have come across this is the. We always say a 2 phase boundary between boundary between any 2 phases should enter into a single into a 2 phase field rather than, entering into the single phase field what does that mean. Let us try to look at it from the free energy concept. In fact, this is one of the ways to understand, why an iron carbon diagram is different from iron cementite diagram? If I draw 2 phase region at a given temperature, let us now, draw at this temperature the free energy composition diagram.

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If I draw the free energy composition diagram at that temperature, what you see is that, you have an alpha, you have a beta. So, if you look at this, this common tangent that I am going to draw is going to decide that this is the composition of alpha in equilibrium with beta which is the composition of beta in equilibrium with alpha. Now, if you look at this, if you extrapolate this to a higher temperature, if this is the type of, we will erase some of these so that it becomes more clear to you. So, we will draw it everything perfectly now, excepting this particular problem.

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So, we have now a phase diagram, were we have a horizontal, the eutectic reaction is horizontal then, the second thing is you have the eutectic composition is also a fixed composition then, we have a situation that the melting of the pure a happens at a fixed temperature. So, that is also taken care then, we do not have a miscibility gap here, accepting that, we have a situation like this that is the last error, that we are talking about. And this if we extrapolate this and what is this line? What is that line, can tell me? Solid us of alpha, very good, what does that give you? What is this? What does that tell you I will draw with a color. What does this tell us? Tell us you common tangent between liquid and solid and anything beyond that fine.

So that is the definition of solid us, solid us anything else? Composition of alpha in equilibrium with liquid at all temperatures that various temperatures, it gives to the composition to alpha whatever you have said is right I do not say wrong. The other attribute of that line is that it gives you the composition of alpha at any given temperature in equilibrium with liquid. So, now if I look at a particular temperature draw a temperature, something like this, we are looking at this temperature, at that temperature if I am looking at I draw a free energy composition diagram. In principle if I draw it, at that temperature what is cable? Alpha up to this composition, alpha plus liquid at and if you go further you will get a beta.

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So, in such a case now, let me draw that this we know. So, if I draw this is an alpha phase, you have a liquid and you have a beta phase and alpha plus beta is not stable at that temperature. So, as a result the liquid curve should be below the alpha and beta that has to be understood. So, if I draw beta here. So, this is the alpha curve, this is the liquid curve, this is the beta curve. The way I draw will be in such a way that, stable states alpha and liquid and liquid and beta not the alpha plus beta, if this is above than this two curves that means, that I am at a temperature were the liquid is actually not stable both alpha plus beta are stable. So, now if this is the case now, if I draw a common tangent between alpha and this and another common tangent between these two now, I get these compositions the 1 2 3 4. Each of this compositions we have already talked about it earlier I will still just for the sake of completion I will say this is composition of alpha in equilibrium with liquid, this is composition of liquid in equilibrium with alpha, this is composition of liquid in equilibrium with beta, this is composition of beta in equilibrium with liquid, am I right clear Raj Kumar. So, if that is the case now, at the same temperature if I am extrapolating this curve, what does this curve tell me now, tell me, we have said already what does this curve tell us.

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Now, if I take this curve, what does this give us? With, can you repeat what you said? In equilibrium with beta, it cannot be in equilibrium with alpha plus beta what is the meaning of that, composition of alpha in equilibrium with beta am I right. So, this line always that is what we call it as Slovus line, Slovus line always gives you this, on the left

Slovus line gives you composition of alpha in equilibrium with beta, the right Slovus line will give you composition with beta in equilibrium with alpha. So, now if I am extrapolating this to a higher temperature such that I come to this temperature of my interest, at that temperature this point is composition of alpha in equilibrium with beta. Now, let us see at that free energy composition diagram, what is the composition of alpha in equilibrium with beta? If I want to do know that, what should I do if draw a common tangent between alpha and beta draw it let us draw that.

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So, let us draw a common tangent between alpha and beta. And see where these two touch each other, when I see that, you will see that this the common tangent which is drawn from beta to alpha will touch the alpha at some compositions like this. And that I would call it as C alpha in equilibrium with beta and the geometry of these curves is such that, this common tangent point where which is C alpha beta will always be higher in B content than C alpha liquid, why? Because beta is a at a higher level, beta curve is at higher level than, the liquid curve, liquid is at a lower level than the beta, why? Because at that temperature liquid is more stable. Because of that temperature liquid being more stable, liquid curve has to be lower than the beta curve. And because one curve is lower and another curve is higher now, when I am drawing common tangents, it is not possible for the common tangent between beta and alpha to have a composition to the left of the alpha and liquid it has to be always to the right of the alpha liquid. So that means what C alpha beta is higher than, C alpha liquid in terms of percentage B.

It has to be that way, looking at the free energy diagram and this you will know only if you look at the free energy composition diagram. Now, so that means, that this what is what does; what do you call this composition? This means, the composition of alpha in equilibrium with a Metastable phase, because beta is the Metastable phase at that temperature the composition of alpha in equilibrium with the Metastable phase is always higher than the composition of alpha in equilibrium with the equilibrium phase. So, this is true for any type of phase diagrams, the composition of any one single phase in equilibrium with the stable phase is always lower. In terms of the solute content when compared to the composition in equilibrium with the Metastable phase state this we are going to immediately see with an example of iron carbon diagram. So, now if that is the case this composition what does this tell you.

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If I extrapolate this composition, it is telling that C alpha beta is for me this is C alpha liquid at that temperature. At that temperature this is the C alpha liquid, this is the C alpha beta. So, this tells you that C alpha beta is lower than C alpha liquid in terms of solute which is wrong. Whereas, if I draw the salvos line like this and if I extrapolate the Slovus line, I can clearly see that this particular composition now, which is nothing but the extrapolation of the alpha Slovus; that means, this is the composition of alpha in equilibrium with beta. So, the composition of alpha in equilibrium with beta now is higher than the composition of alpha in equilibrium with liquid and that satisfies the free energy composition diagram for that particular temperature.

As a result this kind of curve is not possible. So, you cannot draw a Solvus line like this, you have to draw a Solvus line like this, so that the extrapolation should always. That is why in other easy fashion, what people say is that, the extrapolation of the Solvus line to higher temperature, should always end up into a 2 phase field rather the ending up into a single phase field, you get into a problem. So, the extrapolation should always lead into a 2 phase field, this is a 2 phase field liquid plus alpha field. So that is what, you will see from this and for that you need to understand this (( )) computational diagram. And now, if you look at this I draw use the same concept two iron carbon diagram, we are all aware of iron cementite phase diagram.

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Let us say lets draw the iron cementite phase diagram. Any; how many of you remember, can somebody come and draw cementite phase diagram. Suppose, to be that bread and butter of metallurgies, draw it.

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My dear friend, you are right in the diagram, but can you look at the scale and give me some idea, what is this composition in a iron carbon diagram?

2 percent.

What is this composition in iron carbon diagram?

0.5.

0.5 not 0.35, 0.5.

So, you have put 0.2 percent very close to 0.5 that is wrong, that is the only mistake that I see in this phase diagram. And second mistake that I also see is what is this composition?

0.8.

0.8 and you are 0.5 is greater than 0.8. So, always you have to whenever though you are drawing a schematic diagrams, you have to have some idea of the scale, it need not be exactly to scale, but you should have some feeling for it. That is fine, why do not you; do not shrink it, draw along (No Audio From: 29:30 to 29:38) in that anyway.

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You are not using engineering drawing, forget it I understand that you know, but you are not able to draw it to scale, I will try to I will try to that.



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This is horizontal if it does not look like please forgive me. Another important thing that, you should also remember is, when you drew this, this segment is equal to the segment in your diagram, you are not and this is 0.1, this is 0.18, this is 0.5 so that also has to be kept in mind. So, simply just do not draw anyway you want after that so, I am you know

one has to be careful in drawings. So, the comeback 2.8 again is the problem here. So, something like this. So, we draw it something like this, fine to some extent we have tried, we cannot really try to great extent. So, this is what is the diagram that you are talking about and we have here, again F e 3 c phase we call it. So, this is liquid, this is liquid plus gamma, this is gamma, this is liquid plus F e 3 c and this is gamma plus F e c 3 and this is alpha plus F e 3 c this is alpha and this is delta and this is liquid plus delta, this is delta plus gamma. So that is what is the phase.

Now, if I look at iron carbon diagram should look like, it also up to this, why we should bother about this? We should bother about it, because we know certain grey casterines when I solidify, I get carbon, I get graphite instead of F e 3 c is it not. So that means, I need to understand, what is the equilibrium between this liquid which is giving you the graphite? The graphite that is coming out should be equilibrium with the liquid so that means, some equilibrium between the graphite and liquid also should be understood and that will it affect the phase diagram. So, for example, if I take a eutectic were liquid is giving you gamma plus F e 3 c and look at the other eutectic were this is liquid is giving you gamma plus graphite. Will these two eutectics have the same temperature, will these two eutectics have the same temperature, will these it depend on? That depends on exactly the free energy composition diagram.

If I look at some temperature were for example, if I am talking about at a temperature, let us look at this temperature for that case, if I am looking at that temperature, were I have a gamma plus F e 3 c. And liquid is giving you gamma plus F e 3 c, I have brought the liquid to this temperature I am looking at that or I am looking at this temperature. For example, were liquid plus F e 3 c is there, any temperature you can consider, let us look at this temperature let us say, if I am looking at that temperature I will see what would happen. Now, let us look at this temperature, this I call it as T 1 temperature, at T 1 temperature I have what is the equilibrium; what do I have I have gamma plus F e 3 c, but F e 3 c is not a stable phase. So, in principle what is the equilibrium phase mixture at that temperature, it should be gamma plus graphite.

Actually it should be gamma plus graphite instead of that I have gamma plus F e 3 c. Now, let us look at the equilibrium between gamma F e 3 c and graphite and if I look at that what I see is that I have three phases. So, I should be able to draw free energy curve with the three phases.

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If I draw that, one is gamma, this is gamma. Now, what about F e 3 c? F e 3 c is a inter metallic compound, line compound. Line compound with 6.3 percent carbon so, and the other end I will put it as carbon, pure carbon let us say, that is my graphite, this is my pure iron, this is pure carbon 100 percent carbon that means, graphite. Whereas, F e 3 c is somewhere here, let us call F e 3 c somewhere here let us say, though it is not exactly to scale let us look at that. If that is the case then, if I am looking at the free energy curve of F e 3 c, how should it be? It should be narrow free energy curve; that means, so, it should be a narrow free energy curve which should look like this at that composition of 6.67.

Now, (()) are result to the F e 3 c there should be the free energy for graphite, it should be layer, because graphite is more stable than cemented and where will it be? It will be on the right extreme where carbon is, this is the pure carbon. So, the free energy of graphite will be simply nothing but one point somewhere on this, like whenever we are talking about free energy of pure metals it is nothing but this; what is this point? This is nothing but free energy of pure iron in the gamma from at that temperature. Similarly, free energy of graphite at that temperature pure carbon is some point here, if I take that now, if I draw common tangents I will see that, there is a common tangent between gamma and F e 3 c, there is also a common tangent between gamma and graphite. And if I look at this I will see that this common tangent and this common tangent will not be the same. That means, the composition of gamma in equilibrium with F e 3 c is different from the composition of gamma in equilibrium with graphite and it is always the composition of gamma in equilibrium with graphite will have a lower solute content. Lower carbon content when compared to the composition of gamma in equilibrium with Cementite, because Cementite is the metastable phase.

So, the composition of gamma in equilibrium with the stable graphite will have a lower carbon content when compared to the gamma in equilibrium with the metastable F e 3 c. That means, at that temperature if I find out, if I want to find out, what is this composition? What is this point at that temperature? What is this point? Yes, not in F e 3 c in equilibrium with F e 3 c gamma is not inside F e 3 c. So, this line tells me the composition of gamma in equilibrium with F e 3 c. So that means, this point is what this point according to me is this point, according to the free energy composition diagram it is this point is that point at that temperature, because we are drawing it at that temperature. Now, if I want to see locate the composition of gamma in equilibrium with graphite, it will be somewhere on the left side somewhere here.

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And if I do it for various temperatures, you will see that at all temperatures it will be to the left only. So that means, if I find out for various temperature these points and join them as a line, you will see that this is what happens. This is what is iron, this is what is gamma, is it a Solves line or a solid us line? Solves

This is a gamma solves in equilibrium with graphite, this is the gamma solves in equilibrium with cementite so, you have a different solves now. And similarly, if I do the same thing here, for the liquid and F e 3 c and instead of F r 3 c I want to consider liquid plus graphite let us say. If I consider liquid plus graphite I exactly get the same thing accepting that this gamma curve is replaced with liquid curve, cementite will be there and graphite will be there. And graphite will be always be at any given temperature, graphite will always have a lower free energy than a cementite at any given temperature, because graphite is more stable than F e 3 c.

So, this curves, this common tangents are not going to really get affected, the exact positions will get affected, but the relative positions is never going to be affected. The relative positions always sales that the composition of any phase liquid or gamma or alpha in equilibrium with graphite will always have a lower carbon content when compare to an equilibrium with the cementite, if that is the case then I will see that this will be the liquid, liquid us in equilibrium with the graphite. If this is the liquid us in equilibrium with cementite, this is the liquid us in equilibrium with graphite. And now, if I now, look at what is and similarly, if I can also draw I will have this and I will also have this, all the pink curves that you are seeing for all either the solves lines or the liquid us line in equilibrium with graphite, all the yellow lines that you see here are all in equilibrium with cementite.

Now, let us look at what about the reaction temperature eutectic reaction, if I look at this reaction and if I look at this reaction which reaction should be lower temperature? which reaction should be higher temperature? Which one? Graphite. Because the when I am thinking of the reverse reaction of this, cementite plus gamma giving you liquid, because cementite is a Metastable phase, it wants to convert into a stable state at a lower temperature.

So, the melting point of the cementite gamma eutectic is lower than the melting point of the graphite gamma eutectic. So, graphite gamma eutectic will have a higher eutectic temperature, cementite gamma eutectic will have a lower eutectic temperature, because it is a Metastable eutectic this is the stable eutectic this is the Metastable eutectic and that is the reason why you would see this. So, basically this curve get us connected sorry, I would not draw it that way. Wherever this curve, wherever this pink touches this point, this curve the gamma, gamma solidus with the liquid, there you will see and this one will remain and this which is like this now, would get shifted to this, it should get shifted to this point.

So, you will see that the eutectic composition also, will shift to the left because of that and this curve will come and touch. So, the eutectic composition because of this curve been left side. So, you will see that sorry all pink I should draw, this is the iron carbon diagram now, this will be the iron cementite diagram were, you will see the eutectic composition will be there and this one the eutectic composition will be this. And similarly, you would also see that, the composition of maximum composition of carbon soluble in gamma and carbon soluble in graphite both of them will be different. And the same thing holds good here also, we will see that the eutectoid also will shift, you will see that eutectoid composition will be like this and whereas, this will be the eutectoid.

So, both the eutectoids will change and what does not change is these lines, these lines will not change, can you tell me why and this whole portion does not change, because there is no cementite involve there, there is no graphite, there is no cementite there. Wherever cementite and graphite coming to picture that portion alone get us modified, in this it is only liquid giving gamma plus delta so, there is no other reaction. So, the; that means, the eutectic reaction get us modified the eutectoid reaction does not. So, this is how you can understand that thermodynamics particularly p a G composition in diagrams can help us to understand this. So that, you know the whether the eutectic reaction in a iron graphite occurs at a lower temperature or it higher temperature and the eutectic composition also.

What is the composition that is should choose, if I want to get 100 percent eutectic mixture in a iron graphite system are in a iron cementite system. Obviously, that will be different and unless, you really calculate this thermodynamically and get this compositions, you will not be able to get a 100 percent eutectic mixture if you are interested in it. So, this is something which is; what is the; one of the points that we have it in that. The second thing that the first question asked you is about nano, what happens if I take a nano particle and melt it? I think most of you know that the melting point will not be the same as a normal metal.

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And that can be easily seen from a G verses T diagram, if I draw it. If I draw a G verses T diagram for a solid and a liquid, the moment I say instead of a bulk solid I am taking a nano particle of a solid, we thought that nano particle of a solid, we know that nano particle of a solid has a higher surface energy. And the moment I add this surface energy to the bulk volume free energy, the free energy overall free energy of this solid is higher with respect to the bulk solid. So that means, I will have a free energy curve of the solid shifted to higher temperature now, a higher value of free energy the. So, solid; bulk solid will have a free energy decided by this and the nano crystalline solid will have a higher free energy, the moment I put a higher free energy, you would automatically see that the intersection.

Is now, liquid is not changing liquid, there is they are not talking of a nano liquid here. So, liquid free energy curve will not change, the moment you change the solid free energy you would see that it intersect certain lower temperature and that is the reason why you will see a nano particle melts at a lower temperature. But there can be a different situation which is what, is the second part of that question that you see. If this nano particle is embedded in a matrix, which has a higher melting point, is the matrix is let us say imagine a situation, I have a lead particle inside an iron matrix or an aluminum matrix. And now I am hating this and this lead is a nano particle, nano particle of a lead embedded in a aluminum lot of people are doing research on this what happens? What is called super heating? Once, you start heating this, when will this lead melted 321 degrees

which is the suppose to be it is normal melting point or some other temperature. When you look at r will it melt at lower temperature than it is normal melting point or will it melt at a higher temperature than it is normal melting point.

That is where you see that, the moment I start heating it both this solid and this solid as a function of temperature there is an expansion is it not. Every solid expands as you heat it, there is something called coefficient of thermal expansion and this coefficient of thermal expansion when you look at it, a material which has a higher melting point will have a lower coefficient of thermal expansion. As a result it apply certain pressure on the solid, on the nano particle, the moment a pressure is applied you see that the under high pressure, if you look at Claudius chaperon. Whenever you apply a pressure, whenever the delta v between solid to liquid, when a solid is going to liquid if there is a volume expansion under that conditions whenever a pressure they applied you see a solid is more stable, because solid occupies less volume than the liquid. So, you will see the stability becomes actually this.

Once that happens you will see that the melting point goes up, always you see this happening. Whenever you take an embedded part nano particle, an embedded nano particle at a higher temperature than it is normal melting point, it is because of the pressure effects. And in principle people can actually calculate, what are the pressure effects? How does the free energy change as a function of pressure.

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Basically, we all remember G is a function of temperature, pressure, concentration is it not. In a normal free energy expression that we talk about, we do not talk about this, because we are fixing it. If you do not fix it will change and once, you do that you will actually see this happening and that is an explanation for that particular question. Yes, anything, any metal inside another higher temperature metal, if the outside metal matrix is the lower meting point when this problem does not come, by the time you reach the melting point of this that has melted already. So, there no problem the problem comes that you have reached the melting point of that, but the outside he has not melted that is still solid and that applies pressure on this and that pressure influences the free energy and once it influences the free energy the melting point get us influenced.