Phase Transformation in Materials

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Lecture - 04
Gibbs Free Energy of Binary Solution

In the last lecture I discussed about the stability of the phases for pure component system, I took examples of ice and water mixture. As you know, ice water both consisting of H2O molecules. Therefore, we consider as a pure component. There are many examples, such that pure like carbon can exist in diamond and graphite and many other things, but we know diamond is not stable graphite is more stable.

That is mainly because of delta G of both diamond and graphite. If you calculate at normal room temperature and pressure graphite will have lower value of G a free energy than the diamond. So, this formula is in as helped to explain different kinds of stability, different stability of different kinds of phases across the different branches of engineering even stability of steam as function of water as composite water can be explained.

Now, question is this metallurgical oil is full of alloys, we are dealing with alloys everyday starting with steels aluminum alloy to copper alloys ceramics. They are also alloys. So, we must have a good knowledge of how do we modify this stability conditions for alloys. The real question is that as I told you in the last class, we cannot use the same way whatever I presented in the last lecture for the alloys. So, we have to change.

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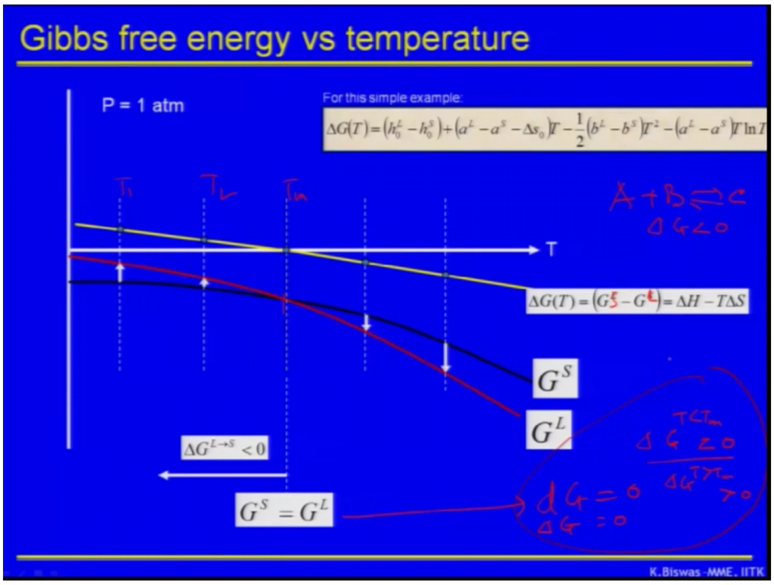

So, to give an idea this condition is going to be remaining same this condition will remaining same for universally same for all systems, that the directional phase transformation depends on the sign of delta G. Delta G is 0 at the transformation temperature whether it is melting solidification or in a solid state transformations, but delta G is negative then transformation will happened in the preferred directions, if delta is positive transformation will not happened in the preferred direction. So, sign of delta G dictates the direction of phase transformation. And I will explain you in terms of water ice analogy.

So, now let us see what happens for the alloys. Alloy means you have more than one component. And I give you an example of if I add salt into water. You know that if I add salt into water the melting temperature of ice will increase. We know that that is why in in the cold countries when the snow actually covered the roads to melt it down they sprinkle salt, because salt will increase the melting temperature of ice. So, there is some change because of addition of salt that is why it happens. And in fact, the changes basically happening because of free energy change free energy is getting altered by addition of the salt.

So, free energy of the systems can be altered a change by addition of the second or third components, whether we add carbon into iron to make a steel or whether we add copper into aluminum to make dural aluminum, we are changing the free energy of the system.

How it is done? First thing you have to understand the difference between mechanical mixture and the alloy, because I find myself while teaching in lectures in IIT that this concept is not clear for many of the students. As you know mechanical mixture means what if I take sand and add salt into it, whatever we grind it they will not mix together that is a mechanical mixture, but suppose if I take milk add coffee into it or sugar into it they will all completely mix nicely.

In fact, the mixing will happen such a nicely that you cannot differentiate between salt sorry between the sugar and the coffee with a milk, in fact because we add coffee milk and sugar together to will get a test different test. That is also answer my question that they are atomically mixed. So, mechanical mixture means that I add something into something else and they remained separated, but mechanically get mixed.

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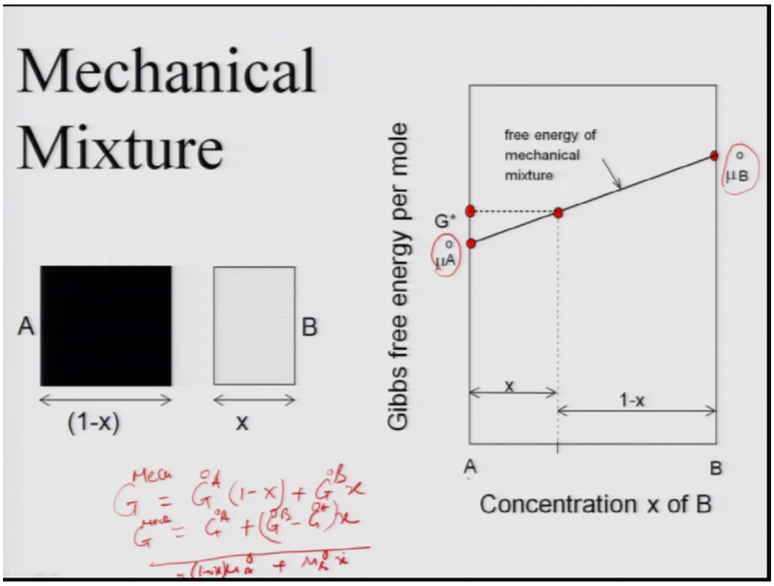

So, suppose if I add A and B together. And amount of B in A is given by the ratio of between B and A is given by x. We will come to know what is x very soon there is a way of representing x and 1 minus x is; obviously, equal to x A because x, x is a fraction. So, therefore, 1 minus x is equal to A. Now, if I mix A and B and form a form a mechanical mixture sorry form a mechanical mixture like that, and then what will happen if I plot the free energy G. Again G is what is important if I plot G as a function of concentration at the particular temperature the G of the mixture will be given by the straight line why very simple G of A multiplied by 1 minus x plus G of B multiplied by 1 minus x what is a G of the system. So, if I write down like this G of A multiplied by 1 minus x plus G of B multiplied by x sorry. So, that is what is actually this is the equation of straight line.

How it is the equation of straight line? Write let us write down G of A; so G of B minus G of A into x. So, this is the G mechanical mixture. That means this is y equal to mx plus c that is a straight line equation. So, this straight line has a fixed slope that is GA minus GA and it is a fixed intercept and many times for the pure component we to separate it out of the mixture we always write a super script 0. And that 0 is tells you that this is pure it is not been contaminated by something else. So, the G a 0 is what is given here shown as a mu A 0. This is just a symbol we will explain it very soon what is the meaning of the symbol that is given by this point.

Similarly, on the B side, B is a pure 100 percent B here. A is 100 percent B here. And we are adding then together (Refer Time: 07:01) is given by mu B 0 that is again nothing, but GA. 0 I have written here because pure components to separate out. We will put superscript 0, whether we write in terms of mu or in terms of G that is not going to change these are only conventions; mu was used by some scientist. And it has been accepted across a world all that is why we use mu naught is you can use G 0 also there is nothing wrong about it and this is the functions this is the plot of the function which is given here the straight line you can see here correct.

So, at a particular composition x of A, x of B actually and 1 minus x of B; A yes this equation is followed. So, I can actually calculate G of that mixture simply we are following this line, but you know alloys are not mixture alloys are all atomically mixed solution what is the meaning of solution is very simple, if I take water add salt and sugar stir it nicely for about 2 3 minutes it will be solid solution right. And if I add a more amount of a sugar there is a limit of saturation beyond that sugar will not be mix in a water. These all we know from a school phase, there is no need of explaining.

So, this same thing can be translated in solid. In solid same features can happen I can add carbon into iron, I can add manganese into iron and make a solid solution. So, physically speaking I am making mixture. Now the difference between the mechanical mixture and the alloy is bought about by the entropy function. That is what the changes happens and to be frankly speaking, I want to show you this picture this is a thumb stone Boltzmann Ludwig Boltzmann.

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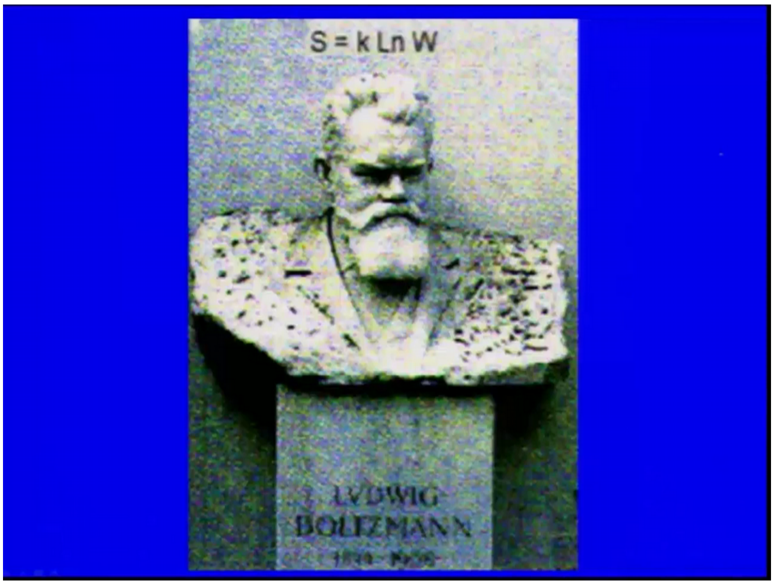

He lived 1849 to 18 something 86 very (Refer Time: 08:51) person. He discovered this entropy s equal to klnw. You can clearly see it is written on his thumb stone it is so famous function just to give an idea that this is so important for a solution things are completely different.

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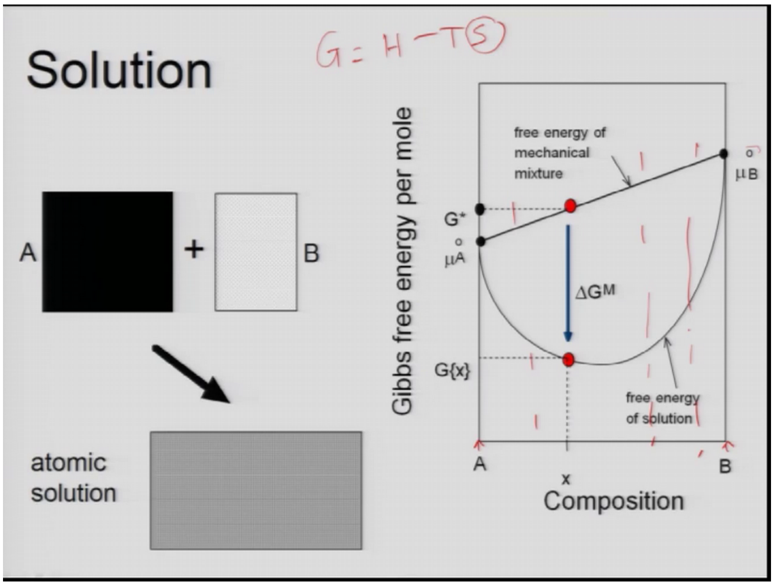

So, that next 10 15 minutes we are going to spend time how to explain solution. What are the stability conditions for that solution means like this? Suppose we have A and B like carbon iron and carbon in steel mix them together. They form a atomic solution, this is written atomic; that means, they are mixed atomically they are cannot you can separate one atom from the from the mixture they are so nicely mixed. So, what actually happens if I do mixing that, if I mix that the things which is change in the G function G is equal to h minus ts the important changes happen is the s entropy gets change completely?

In a mechanical mixture they are lying separately. There is no mixture between the 2 components. They are basically sitting side by side like the students sitting in the class they did not like each other they will never mix each other same thing happens. So, they are not mixed together. So, if they are not mixed together there is no change of entropy. Because you cannot change the configuration of the system entropy has 2 components one is the configurational entropy other one is the vibrational entropy. I am talking about configurational entropy which is the major part of the entropy change whenever you mix 2 things together.

So, that change will not happen if they are mechanical mixture, but that change will be very seriously affecting the phase stability the movement you atomically mix them together. Now, we can actually will go into equation part very soon, but before I do that plots are always helpful to memorize you to understand you to keep it in mind. Remember equations you have to remind close your eyes and remind no forget it. And then you can get it back, but plots it will remain all throughout your life that is why plots are better.

So, here what I have done. I have again using the same plot free energy versus compositions here A and B are 2 pure components. And this straight line tells you mechanical mixture free energy. And this curve which you see here is looks like a parabola, is what is for the atomic mixture or the solution. How does it come like this? It will clear to you with soon from the function, but first initially you accept that this functionally like this. Because sometime many of your teacher will tell you this is like this only plus you please accept it now you.

So, clearly see this is like a parabola inverted parabola. It is starts from pure A ends at pure B. If this 2 points both are mechanical mixture and the free energy of this solution are same at this 2 point, they are matching the values actually, but they deviate slowly. As you increase the concentrations reaching a maximum value or you can say minimum value depends on what is the sign and then it again should stop, but it is basically a inverted parabola.

Now, question is this at a particular composition x, the physical mixture has a free energy equal to G star written here you see here I can simply put a dotted line and find it out, but the, but the atomic mixture has a free energy given by G within curly bracket within x. So, there is huge change of free energy delta G m what is written here is a difference of free energy between a solution here and a mechanical mixture. That is why a solution is more stable than mechanical mixture always. That is why alloys are more stable than mechanical mixture. That is why it is easy to make alloys. Because it is the free energy which stabilize them thermodynamically something stabilized means that this is basically a more stable structure, because thermodynamics tells you in in terms of energy perceptive.

But I can have both mu A 0 and mu B 0 on the both sides, I am not changed because they are the free energy of the pure components pure A here there is no B into it because B here. There is no a into it correct and you can actually similarly calculate any from any value of x these values, that will also tell you the relative values of the G, but at any compositions other than pure A and pure B, you can clearly see this solution atomic solution is more stable than the mechanical mixture. Then you may ask this question sir why sand and salt never mix there are some other reason for it, they do not like each other that is why they do not mix each other.

Now, how do I actually get into mathematically?

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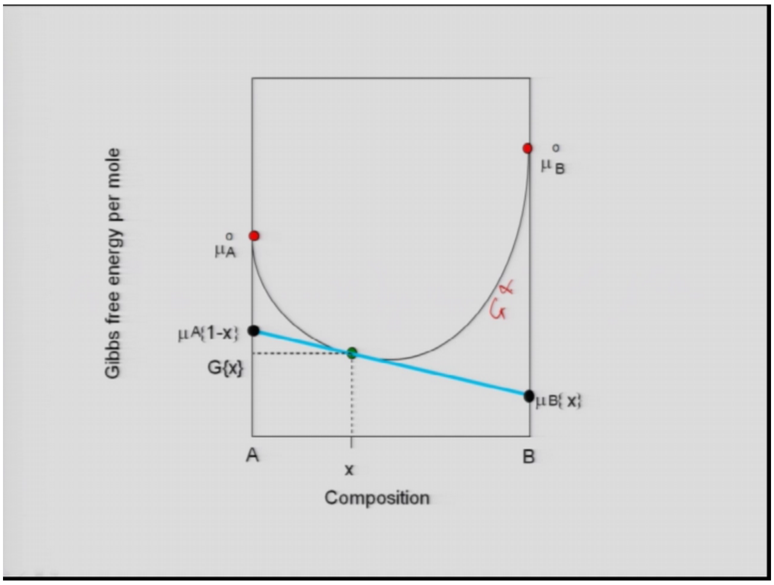

Let us get into the stability in terms of that. And will explain; what is the meaning of this mu here. Again I have plotted free energy versus compositions inverted parabola I did not plot the mechanical mixture of free energy functions. What I do here? This construction we are doing it without doing mathematics. Please remember this construction has more far reaching consequences than the mathematics in metallurgy, that is why we are prove in mathematics, but anyway it will come let you better we will do mathematics very nicely and show you how this things come.

So, what I have done I had a composition x, I marked a block. So, you see here this is a block. And then I passed a straight line through this point; that means, I make a tangent to the curve add this point. Go back to your class to mathematics, I do not know whether you studied, but I studied myself that tangent to the curves can be easily obtained at a particular point just taking the slope correct. I can by knowing the slope and I if I know 2 end points I can easily formulate the equation of the tangent. So, now, the tangent actually meets both pure A end and pure B end. That is why it is written mu A within curly bracket 1 minus x mu B within curly bracket x. Because it contain x whatever fraction of B and x 1 minus x fraction of a that is why this curly brackets are given like this.

So, what is the meaning of this this mu are actually known in the literature as a chemical potential. Chemical potential is really very difficult concept for a student to grasp. In fact, it is also very difficult for me, before I came know much more about it this equation which you see here can be mathematically written by these G.

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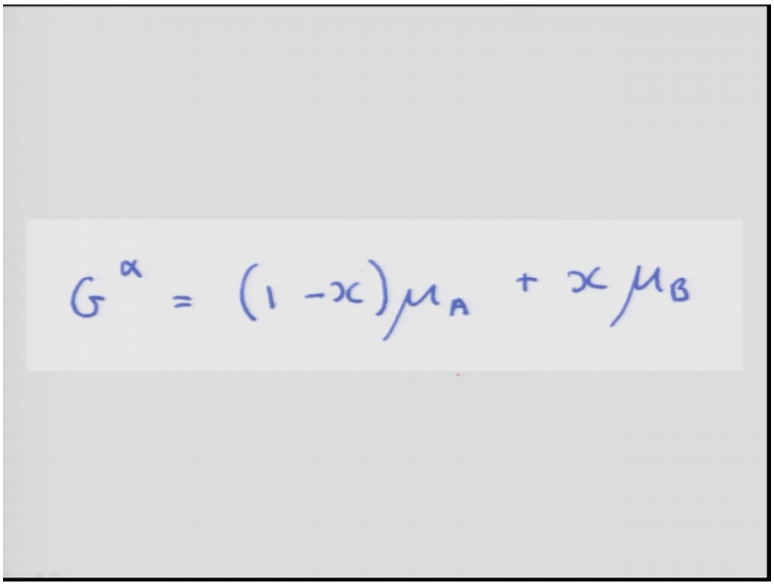

Suppose this is alpha phase, this is alpha. Let us suppose alpha is alpha iron or something. So, G of alpha is equal to 1 minus x of mu A plus x mu B. This equation is same as what I have written here you see here, this same I can easily write mu A 0 plus 1 minus x whatever 1 minus x. So, mu x or this is 1 minus x this top one, plus mu B 0 x this is what exactly same sorry exactly same.

So, this mu A and mu B, they are not we are not put zeroes super scale because they are not pure anymore because we are talking about a alloy of composition x of fraction of x B and fraction of 1 minus x of A. So, you cannot put superscript any more so; that means, the straight line or tangent which I have drawn they have the equation of this is given by this. Correct? That is what is what you should know. The straight line equation which is shown here is given by that. Now what does it tells you it does not tell you anything it tells you that at this composition, chemical potential of a in this alloy is given by mu A, which is determined by this way chemical potential of B, which is given by this point at A composition of A alloy x is marked by this block that is how we can measure chemical potential.

But before I go back go into details of that, let me explain what is chemical potential. Chemical potential will be given in large definitions many definitions in thermodynamics books, but try to understand one thing clearly. What is the meaning of the word potential? Potential means suppose if I say you have bigger potential become a professor; that means, you have all the qualities to become a professor or all the qualities to become suppose prime minister of this country that is what the potential means. So, in physical science potential in a alloy or potential in a atomically mixed solution means of a particular component means, it has the ability to react ability to react, in the system if I add something else in the system it will react that is the meaning of potential

So, this chemical potential tells the chemical reaction ability of the component in the alloy that is what it tells you so; that means, it tells you that free energy is available to do work for that particular component in the system. It has the free energy available to do work; that means, for change over it has change of free energy is negative for this component in the alloy. So, it can react and then make phase transformation possible. That is the way we can define potential otherwise you can mathematically define it is nothing, but change of free energy when you have a big solution add a small quantity of component B at a constant temperature pressure. And all other conditions the change of free energy basically given by chemical potential.

But these definitions are always misleading and these gives you only you know very difficult way of representing things. The easiest of thinking is that the ability to react in in a particular system therefore, stability of a system can be easily obtained when you have multiple phases, then only we can obtain stability of system which phase is stable which phase is non stable.

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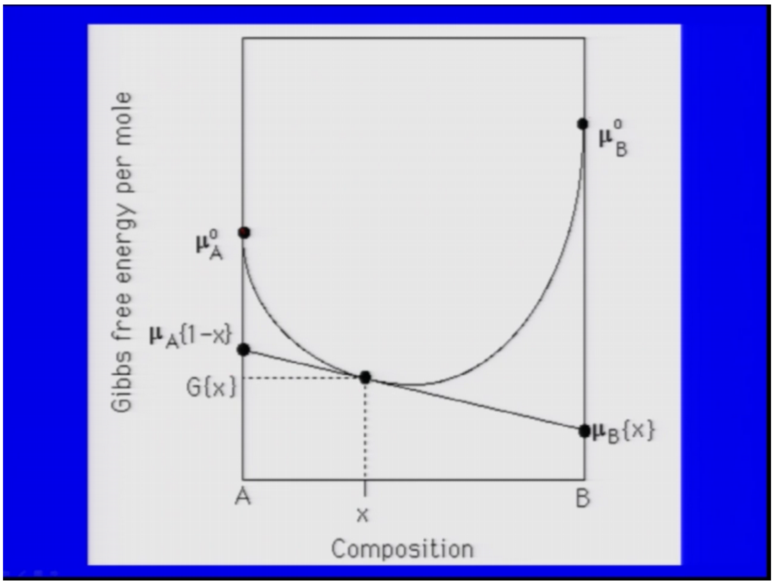

So, let us next 5 6 minutes, let us do that. So, now, let us suppose again I have drawn here free energy as a function of compositions for a alloy with A and B, where you can see x, x amount x fraction of B and 1 minus x fraction of x and again free energies are shown here. For the pure these are the pure A and the pure B because there is you cannot draw it you can draw tangent even a here, but the tangent will again pass through this point only. So, mu A 0 and mu B 0 is for the pure. And these are actually for the component A and B in the alloy consisting of x fraction of B or 1 minus x fraction of a and if the G is again G curly bracket x.

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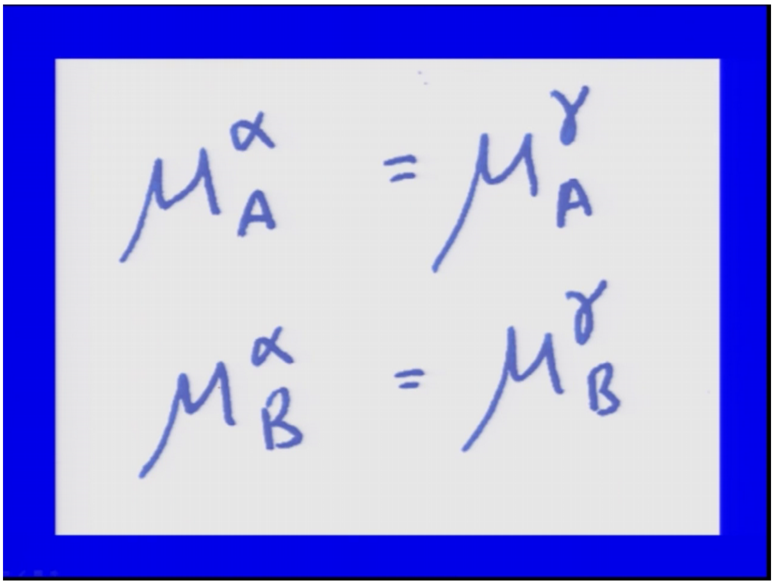

So, the condition of equilibrium or stability is given by these this is again transformed Gibbs, it tells you if I have 2 phases alpha and gamma. Again I will show by plots, but just tell you if I have 2 phases alpha and gamma the potential chemical potential of a component a in alpha, that is why a subscript alpha superscript. Remember this you cannot interchange this thing alpha will be in superscript a will be in subscripts. So, chemical potential of A in alpha must be equal to chemical potential of A in gamma similarly chemical potential of B. Because it is an alloy or is a mixture solution there will be 2 components chemical potential of B in alpha equal to chemical potential of B in gamma what it say chemical potential of any component all the phases will be equal that is what it says.

So, that is the basically stability conditions, this can be proved I do not have time and you know classes to prove that, because this is 30 lecture course lot of things to be taught it is there in thermodynamics books, but if you want we can actually help you in getting the answers in discussion forum, that is that can be done. So, how can I make it a very nicely elegant in plots?

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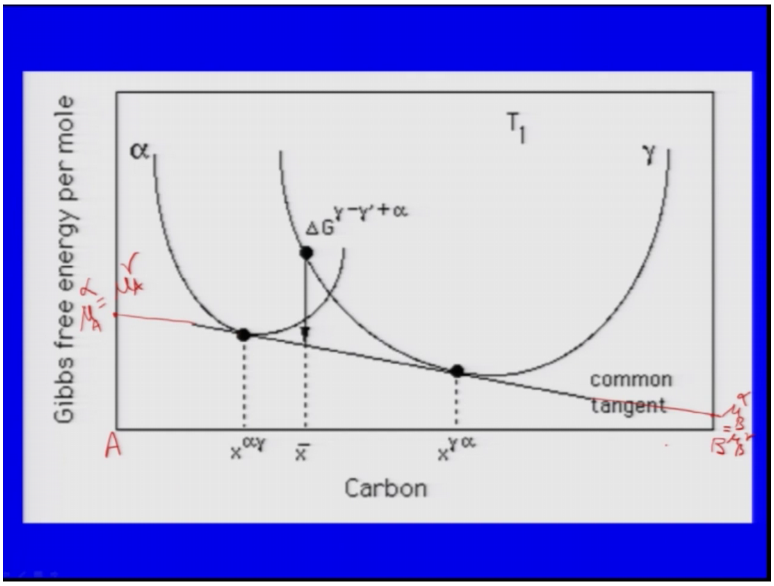

Suppose I have G, the free energy of these alpha is given by these G alpha. You can see this is written alpha black both are black actually one is alpha other one is gamma. So, there are 2 free energy curves, which I can which I can easily obtained from cp values that I have shown you. In the last class now what I do I do a common tangent between them, at this temperature t 1. Very clearly you see this is common tangent will pass through these 2 points. You cannot draw a common tangent other than these 2 points. Because is a common tangent common tangent means slopes here equal to slopes there. That is the mathematical condition.

So, this is a composition given by x alpha gamma. This is the composition given by x gamma alpha. Now what does it tell you? If I extend these 2 lines you can clearly see this is these are the mu values, the chemical potential vales. So, this is A this is B right this is actually steel. So, carbon is written that is why. So, therefore, it will be iron and carbon does not matter A and B. Let us consider. So, this is mu A alpha correct this is also mu B alpha because this is passing through alpha.

Similarly, it is also passing through gamma common tangent. So, I should write mu A gamma and they are equal, because they are hitting this y axis on the same point. So, this is also mu B alpha is equal to mu B gamma. So, you can clearly see this condition, what I have shown you earlier this condition is graphically shown. Therefore, this is the condition of stability of phases in a multi component system or in a more than 2 component one component system.

Now, at any composition x bar shown here. The free energy difference between these 2 is given by these arrow; these 2 means what free energy of the gamma which is higher value here you can see here. And free energy of the mixture of alpha and gamma is given by this point because this is; what is the common tangent line. So, this is the difference this is free driving force available for the transformation from gamma to alpha plus gamma; that is what is this will all discussed in details how to calculate free energy differences. So, in a very simple term you have got an message that for systems having more than one components, we must look for chemical potential equality for the stability. The moment this equality will not be satisfied, there will be phase transformation that is what happens in the systems.

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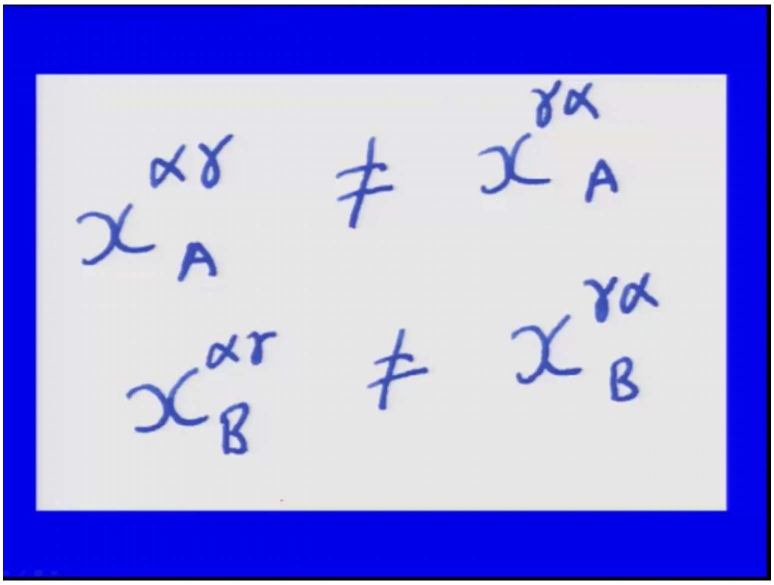

To give an example you know this is what is not satisfied written. When a alpha gamma interface, let me explain that also this alpha gamma means suppose composition equilibrium compositions of the alpha phase in contact with gamma. In equilibrium concentration of the gamma phase in contact with the alpha, correct? They will remain in touch each other, but their composition will be different one composition here other composition there. That is why we have to mark alpha gamma here gamma alpha there.

Otherwise it will be confusing if I put both alpha gamma both side it will confusing gamma alpha confusing. This is composition of alpha phase in contact with gamma because they are touching each other, they has to be touching each other otherwise there will be no phase transformation. So, between gamma in contact with alpha. So, these are the equilibrium compositions or when system is at a temperature t 1 atmospheric pressure temperature t 1 sorry.

So, now when this condition is not satisfied what will happen? Then this equality will not happen this where equality in compositions therefore, you understand this this composition equality is not the condition for stability. This this is the chemical potential must be equal across the interface. When this condition will not be satisfied you will have ice berg in sea. Water sea water is a live source of heat, but still ice bergs will sail in sea water. Why does it happen because chemical potentials are modified by the presence of salt? That is what I told you answer I gave you.

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So, because of the chemical potential modification because of presence of different salts, this chemical potential equality satisfied, across the interface between the iceberg and the water. And this is the reason although water temperature higher than 0 degree Celsius you will have iceberg present in the water. An iceberg is dangerous because you know the titanic right. That is why so, these icebergs are present in across the northern hemisphere or the southern hemispheres and at the poles also remain with water.

So, we can actually explain the stability of this iceberg using chemical potential equality. This is possible and this has been done by the many scientists. So, in a nutshell I in this 2 lectures I have you given you an idea, how to obtain the information regarding stability of the phases, thermodynamically.

This is very important, but these only tell you which were the reaction will happen, transformation will take place. It does not tell you how fast how slow the reaction or the transformation will happen. This can be obtained only by understanding definition or the movement of the atomic pcs across the interfaces. That is basically not done by thermodynamics that comes from the ides of diffusion. So, slowly after may be one or two more lectures we will get into diffusion. And we need to discuss about the interfaces when we talk about diffusion.