Phase Equilibria in Materials (Nature and Properties of Materials - II)
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Lecture - 40
Summary of Course

So, welcome again to this new lecture, lecture number-40 of Phase Equilibria course. So, we are right at the end of the course. So, in this lecture, we will not introduce any new topic, we will just try to have a review of various topics that we have discussed in this lecture. So, what I am going to do is that we are just going to start with, so this basically we started why did we need to learn this course, we needed to learn this course, because as every material has certain phases.

And these that stability of these, what is the type of phase that is present at a given condition of temperature and other thermodynamic variables, what kind of we will determine what kind of properties the material will have. So, that is why knowledge of why do certain phases occur under at a certain condition certain combination of thermodynamic variables. And what kind of a variation do you have as a function of for example, change in temperature or composition as far as metallurgical systems are concerned or even pressure. And what are the various things that you can determine from these phase diagrams, to assist you with processing and product development.

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So, what we did was we started with elements of basic thermodynamics. So, the first topic that we did was essential thermodynamics. So, there is a essential thermodynamics involved knowledge of a concepts of for example, what is the phase, what is the components ok? So, we define that phase is nothing but entity with different physical properties; it means, it may not necessarily have different composition, but it will have different physical characteristics, it will have different properties.

The system is basically an alloy or a compound, whereas components are the one which make up the system. So, a phase you may have two phases of the same component. For example, pure iron will make a delta phase and a gamma phase, but delta and gamma phases have different crystal structures and they have different physical properties. But, they are all they are both made of pure ions. Pure iron is the component pure component. Similarly, if you look at water in case of H_2O H_2O, although it is made up of H and O atoms, we take H_2O as a component, because H_2O is not available as a free H and O are not available as free components, they are available as H_2O molecules.

So, each molecule is a component so, it changes it is phase from solid to liquid to vapour upon application of temperatures. So, these are three essential elements; 1 is system, 2nd is phase, and 3rd is components so, we discussed these things. And then we discussed what do we mean by phase stability? And by phase stability, we meant in terms of thermodynamic terms phase, stability means what is how can we predict which phase so when we talk about water for example, H_2O why is that at 20 degree centigrade liquid phase is stable, but not the solid phase or the vapour phase and that is determined by the thermodynamic considerations, so that is why we needed to understand and correlate it to thermodynamic parameters ok.

So, we defined various terms such as enthalpy, free energy G, so H was enthalpy free energy, Gibbs free energy is G and then internal energy is U and entropy is S and so on and so forth. These are the various terms, which we determine the thermodynamic stability. Then we looked at what is the definition of equilibrium, what is equilibrium? Equilibrium basically means a stable state and no change happens. So, basically in thermodynamic terms, it means that at equilibrium the change in free energy is equal to 0.

And this free energy is related to basically H minus T S enthalpy and entropy in this fashions. In most metallurgical systems, we talked about the Gibbs free energy, there is another free energy, which is called as Helmholtz free energy. But, in our context we generally talk about the Gibbs free energy, which is G is equal to H minus T S, which is enthalpy minus product of temperature and entropy. And it is the combination of enthalpy and entropy and temperature, which determine the phase stability of one phase with respect to another.

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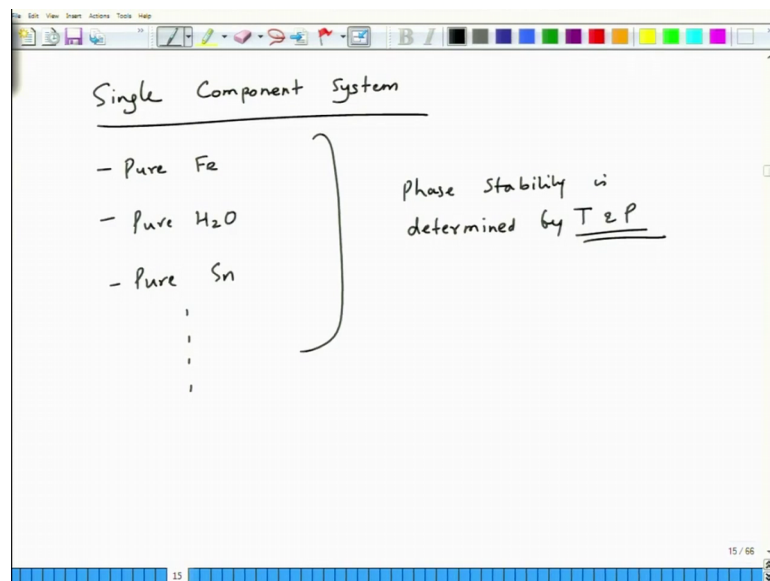
So, and then we looked at the simple phase diagrams. So, some so we looked at the single component system. So, single component system, for example you can have pure iron, you can have pure H 2 O, you can have pure tin and so on and so forth or you can have carbon. So, single component system since they have so they have only one component, the phase stability depends upon two parameters.

So, single component and phase stability is determined by phase stability is determined by temperature and pressure. These are the two thermodynamic variables, which will determine the phase stability. So, when we did that the first thing also in earlier, we looked at the variation of these thermodynamic properties thermodynamic properties with say temperature ok.
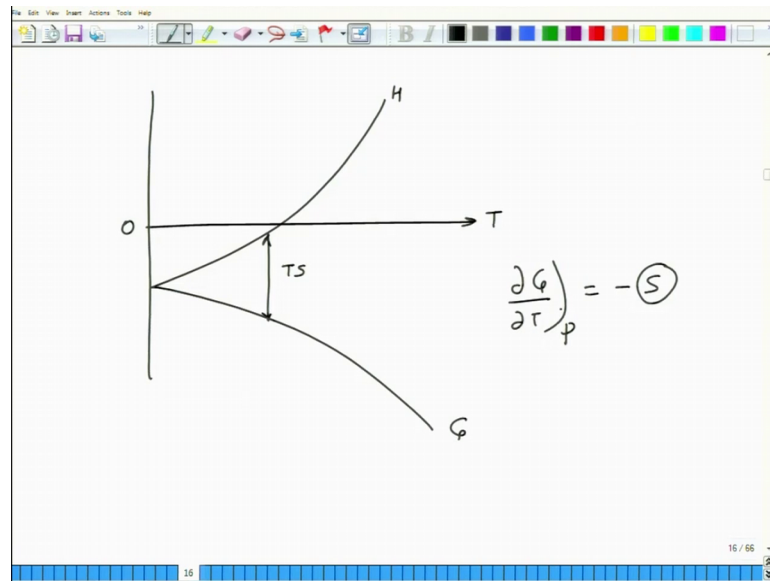
So, we saw that you know how that how the free energy, how so if you look at the variation for instance of free energy versus temperature, so your enthalpy varies like this, this is enthalpy and your free energy varies like this, this is G. And the difference between these two is basically T S term so, this is 0, this is temperature and so that this is how the free energy varies.

And if you look at this slope del G by del T and most of these happens at constant pressure this is equal to minus S. So, basically change in the entropy is always positive as a result del G by del T is negative and that determines that stability of the system, the free energy going towards negative.

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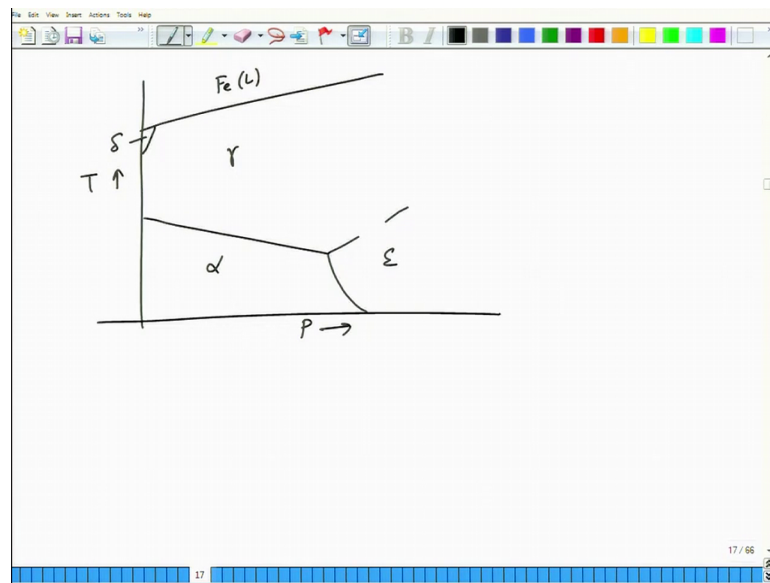
So, if you look so if you look at the phase diagram, for example for pure iron ok. So, pure iron has temperature versus pressure. Phase diagram, so it undergoes, it shows various phases ok so, at high temperature, you have liquid phase. At this temperature, you have delta and then, you have gamma, then you have alpha, then you have epsilon.

So, these various phases of iron are present at different combinations of temperature and pressure. And there are fields in which single phases are stable and these are called as single phase field so phase fields. So, this is temperature versus pressure phase diagram of a single element. Similar phase diagram you will see for basically water as well H_2O system.
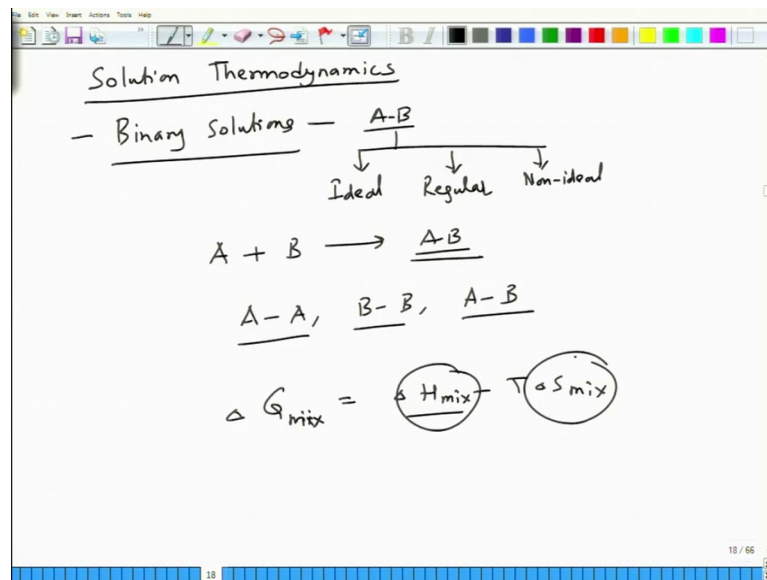
And moving on further, we looked at the effect of we look before we went to phase diagrams further, we looked at the thermodynamics of binary solutions. And this is essential, because no element is pure. Most and most materials are impure in nature. As a result, we started with solution thermodynamics and we looked at first binary solutions.

And binary solutions are basically A-B kind of solutions. And these solutions can be you know the ideal solutions. So, one could be the ideal solution, and then you have regular solution and then you can have non-ideal solutions ok. So, depending upon the level of ideality, you can move away. So, essentially in the solid solution you mix A and B and you hope that, it will give rise to A B and this is determined by the liking of A with respect to B.

So, you will form so when you have A and B present, there is a property of forming A-A bonds, there is a propensity to form B-B bonds and there is a likelihood of A-B bonds. Depending upon the propensity of a material to possess A-B bonds, the material will have corresponding changes in the free energy. So, this change in the free energy upon mixing two elements is called as delta G mixing and this is nothing but delta H mixing minus T delta S mixing.

So, if your delta H mix is higher, if the enthalpy of mixing is higher, then the mixing is not preferred the miscibility of two elements is not preferred. But, if the mixing is lower delta H mix is lower, then the mixing of two elements is preferred, which means A-B

bonds are more preferable as compared to A-A and B-B bonds. So, it is the relative change of delta H mix and delta T, delta S mix that is going to determine whether a solution will be stable or not.

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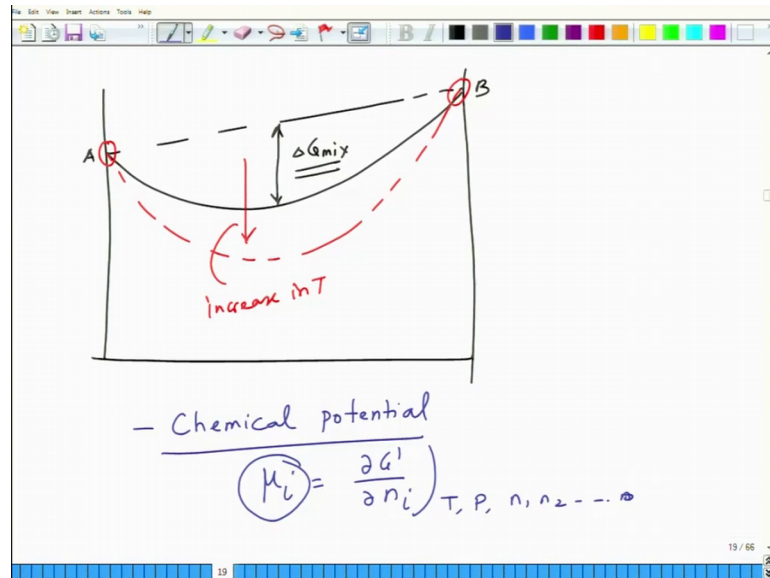
So, we did complete analysis of it so, for instance, the delta H mix if you it also is affected by temperature, because there is a temperature term as well T. So, if you look at the variation for instance, the delta G mix goes like this, so this is delta G mix. This is for example pure A and B and from the rule of mixtures this is delta G mix. So, this delta G mix that is reduction in the free energy is what makes the solution is stable.

So, as you increase the temperature as you increase the temperature, this will further go down to so this will go down to so, I am keeping this as a constant point, but even this point will shift downwards. So, with increasing temperature that mixing is preferred and the free energy of mixing is even lower. And then we introduce a term in the moment you mix things into one other one another they tend to change the at they change they tend to change the you can say the chemical activity of each element.

So, A becomes more active, when you put B, it may become less active, when you put B and so on and so forth. So, this is defined by another term called as chemical potential. So, we determined another term chemical potential, which is mu i which is nothing but change in the free energy upon addition of a component i at constant, temperature, pressure and n 1, n 2, and so on and so forth.

So, change in the incremental change in the free energy upon making incremental change in the composition leads to a property called as chemical potential. So, chemical potential is basically representative of how the free energy will change, when the composition of a system is changed. And this composition change is very incremental, it is not very large.

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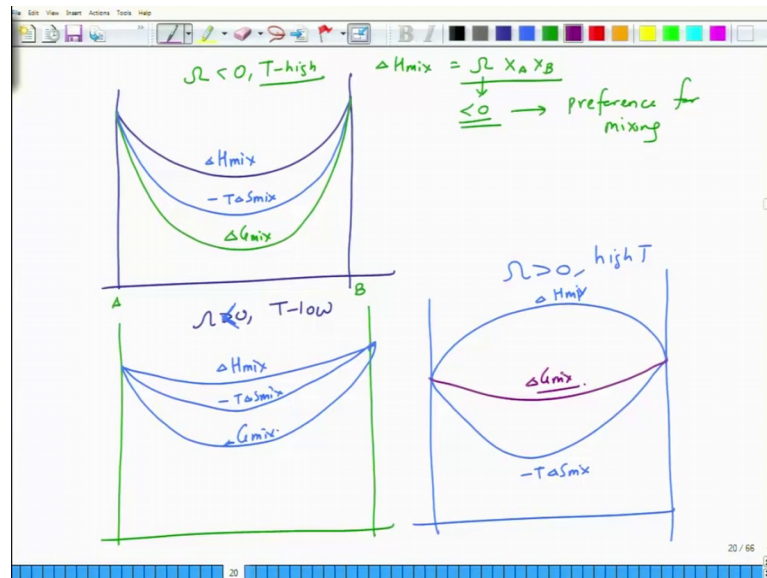
So, then we went through the whole analysis and we saw that depending upon the nature of mixing between two alloys. You can have so your delta H mix could be like this, your minus T delta S mix could be like this. So, this is delta H mix and then delta G could be like this, this is delta G mix, this is A, this is B. So, this is when omega is less than 0 and temperature is high. And what is omega? Omega is essentially a measure of delta H mix, because delta H mix is equal to omega X A, X B.

So, if this term is negative, which means there is a preference for mixing. And when it is positive, there is less preference for mixing. So, when delta omega is less than 0 that is delta H mix is negative that is the behaviour. So, your free energy of mixing is very negative and the alloy formation is preferred.

However, when delta when this is when omega is greater than 0 and temperature is low, then situation may change. So, your delta H mix is like this, minus T delta S mix is like this and there are delta G mixes like this. So, this is delta H mix, minus T delta S mix, and delta G mix and there could be scenario, where delta H mix is positive. So, this in

this case delta omega is not very large, delta H mix is almost flat or sort of becoming to be positive.

You can have scenario when omega is greater than 0 and you have high temperature. So, this is sorry less than 0, low temperature. And now you have delta H mix being positive, which means delta H mix goes like this. The T delta S mix still goes like this so, this is delta H mix, this is minus T delta S mix and delta G is something like this ok.
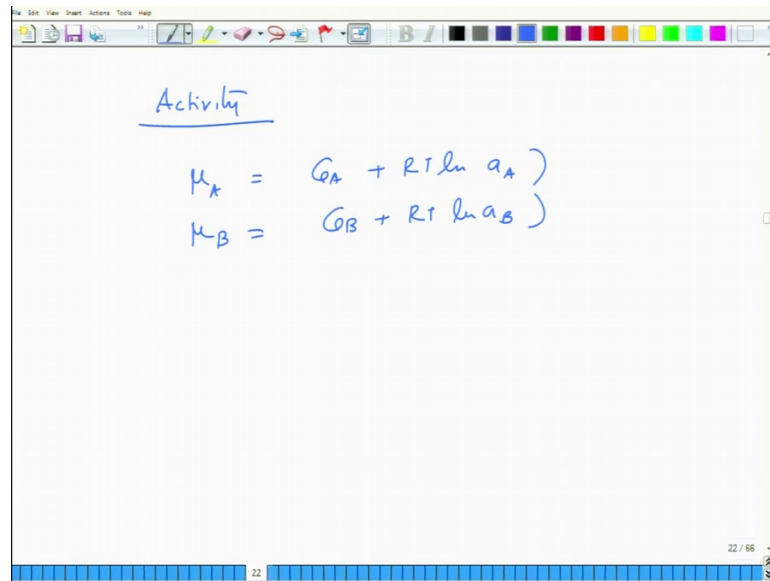
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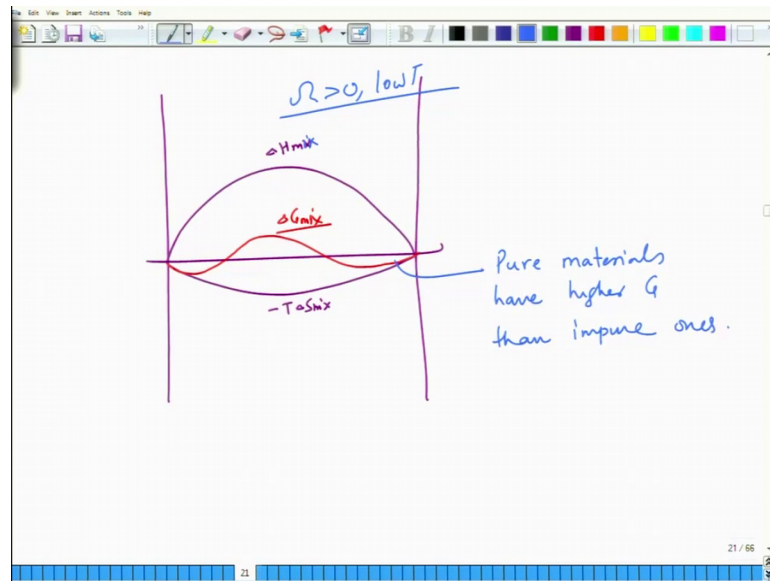
So, you still have some preference for making a solid solution. There can be instances, where delta H mix is extremely positive, and the temperatures are also low. So, this could be delta H mix and your T delta S mix is not massively low. And delta G could show a behaviour like this, this delta G mix. So, even in this situation, where delta G delta H mix is aggressively positive that is and at low temperature, where mixing is not preferred.

Even then, it is delta G mixing is lower for the terminals, which means in pure solid is preferred over the pure solid, even if the mixing is not preferred. So, this still is a very important conclusion that even a slight addition of impurity tends to lower the free energy of pure material.

As a result, otherwise pure material and as a result when pure solid is thermodynamically stable as compared to the pure solid. And this is why and this happens, because this

minus T delta mix contribution prevails at lower impurity levels as compared to that at the higher end impurity levels. So, this basically tells you that pure materials have higher free energy than impure, so slight amount of one's so, slight amount of impurity is thermodynamically step as long as temperature is greater than 0 Kelvin it tends to make an impure phase.

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So, and then we defined another term called as a activity is similar to chemical potential. It basically one it basically tells you that how active how active a element is so basically activity is related to so you can say that activity is nothing but mu A is equal to G A plus R T l n a A and mu B is related to g B plus R T l n a B.

So, higher the activity of element in a ideal material, alloy higher the chemical potential also is. So, then we did the some more thermodynamic analysis, we went to real solutions, we looked at why real solutions can have different phases, they are not exactly miscible. So, miscibility does not take place all the time, they may have miscibility only at the terminals. As a result they end up forming two phases or different phases inter metallic compounds, ordered phases and so on and so forth.

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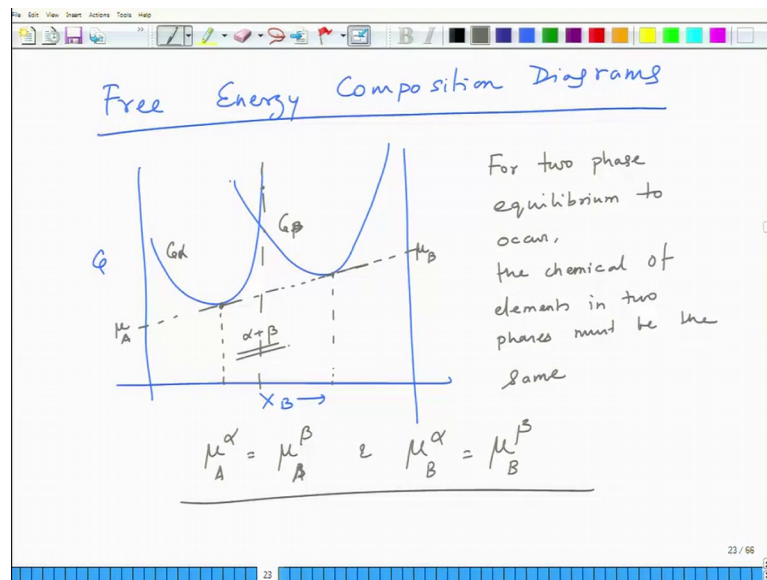
So, we did lot of analysis of this and finally, we stumbled to what we call as free energy composition diagrams, because these free energy compositions free; energy composition diagrams lay the foundation of phase diagrams. And this is they are important, because in the end what you have worried about is a clip and the coexistence of so as long as you have one phase it is all right. But, it is not always like that you when you come from for example from liquid solid state that is a region in which liquid and solid coexist.

So, what is that which makes two phase equilibria possible and the knowledge of that comes from free energy composition diagram. So, for a two phase equilibrium to occur, you have so for example, I have two phases liquid plus let us say this is liquid, this is solid. So, I can see that for certain compositions liquid free energy is lower for certain one for certain places this is G and this is X B and for certain composition solid free energy is lower.

So, for example, if I take this composition of the alloy, what is so I can see that for this composition, here liquid free energy is higher, here solid affinity is lower ok. So, the question is what will happen at this point, so that the way you do is that it is that you determine you draw a common tangent to curve. So, this is G 1, this is G 2, 1st phase, and 2nd phase. So, for this composition what we will have is a two phase mixture, let say this is alpha and beta. So, between this you will have alpha and beta, alpha of this composition, beat of this composition and what is the line tells us this tells us.

So, if you go to, this is mu A, this is mu B. So, basically if the slope of this; slope of this line is nothing but the chemical potential. So, what this tells me is that for two phase equilibrium to occur. The chemical potential of elements in two phases must be the same. What it means is that chemical potential of A?

So, basically what it means is that chemical potential of A and alpha is equal to chemical potential of B A in beta. And it means chemical potential of B in alpha is equal to chemical potential of B in beta. If it was liquid solid, then again it would be the same chemical potential of A in liquid is same as chemical potential of A in solid and chemical potential of B in liquid is same as chemical potential of B in solid. So, this is what we have here as far as two phase equilibrium is concerned, which is done by drawing the common tangent.

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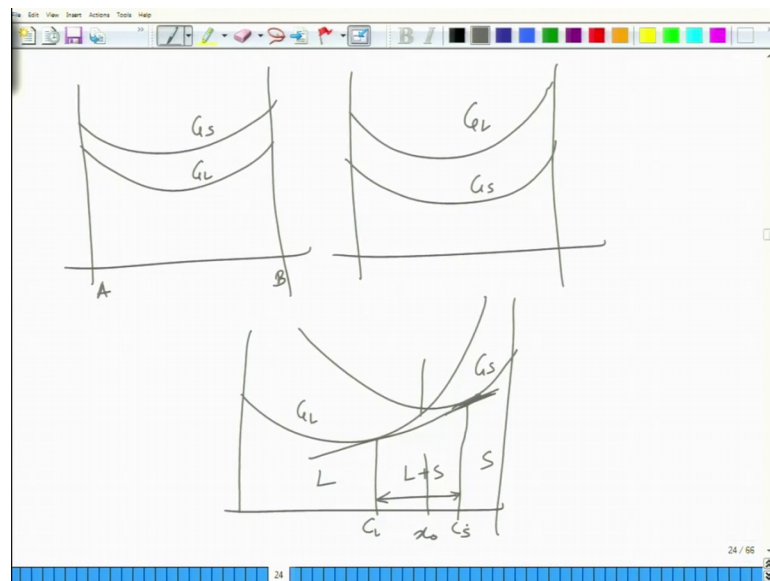
So, this is how you do a phase diagram determinations. So, for example if you have you can draw, energy composition curves for liquid reason your G L will be lower than G S. For solid region in an isomorphous phase diagram for a solid region G L so, this is A, B So, for solid region G L will be less higher than G S.

For two phase region your G L and G S will have behaviour like this, so that you have a two phase region alpha plus beta and this is you just correct this. So, you will have we draw the common tangent. So, this is G L, let us say this is G S, this is liquid, this is liquid plus solid and this is solid either the common tangent.

And this is the composition of liquid in so this is C L, this is C S. So, if your alloy composition is x naught, then composition of liquid in equilibrium with compositions is C naught in equilibrium with solid and solid composition in C S. So, liquid of compression C L is in equilibrium with the solid of composition C S so, this is how you determine phase diagrams.

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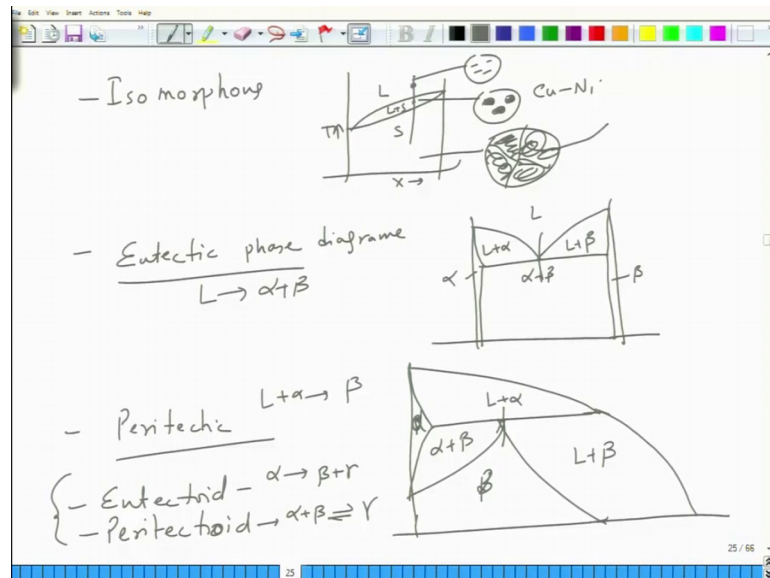
And then we moved down to various kinds of phase diagrams, based on the free energy composition curves, which is also determined by free energy of mixing. So, higher affinity of mixing tend to give rise to isomorphous kind of phase diagrams, sorry lower delta H mix tend to give rise to isomorphic kind of phase diagram, because that is where they are miscible into each other. So, you have isomorphous phase diagrams something like these so, you have temperature, you have composition and this is liquid, liquid plus solid, solid. So, for example copper nickel system has this phase diagram.

Then we have eutectic phase diagram; eutectic phase diagrams are the ones, where delta H mix tend to be slightly higher as compared to isomorphous. And they tend to make, so you have some solid solubility on the terminal ends, but in between they tend to phase separate.

And if the melting point difference is not huge, and you tend to make phase diagram like this, then we have peritectic phase diagram. In case of peritectic phase diagram, delta H mix tends to be high and also as a result also the melting point difference is very high

and hence, what you have is a situation like this. So, for example you can have this kind of behaviour and so on and so forth. So, you can have peritectic reaction, so you can have liquid plus alpha giving rise to you know.

So, this is beta say alpha sorry alpha this is beta, this is alpha plus beta and this vary in liquid plus beta. And peritectic reactions are generally accompanied by other reactions as well. So, you have isomorphous eutectic peritectic and then you can have a eutectoid in solid state. And then you can have peritectoid, which is similar to peritectic, but in the solid state.

So, this is liquid going to alpha plus beta, at this point here liquid plus alpha going to beta, at this point. And then here, alpha going to beta plus gamma solid state reaction and here alpha plus going beta giving rise to gamma in the solid state. So, these are solid state reactions so, they occur in the lower part of the phase diagram, eutectic peritectic are the liquid phase reactions, which are running at all.

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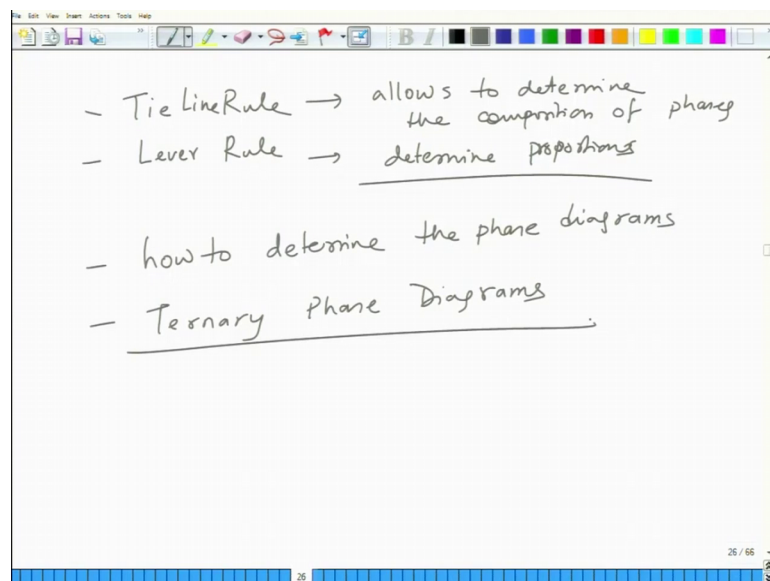
And then we looked at various kinds of phase diagrams the microstructure evolution. But, two important things that we have discussed about tie line rule and lever rule. Tie line rule allows us to determine the composition of phases in equilibrium whereas lever rule allows us to determine the proportions ok. So, we did a few exercises on them as well and these can also be related to the microstructure evolution that takes place.

So, microstructure evolution, for example in this case would be you will have a 100 percent liquid, you will have liquid plus solid. So, this will be 100 percent liquid, here you will have some solid and then you will end up having 100 percent solid. Similarly, you will have microstructure evolution in eutectic and other alloys. And then finally, we did the whole lot of analysis on phase diagrams, we looked at a variety of phase diagrams, we also looked at how to determine the phase diagrams and so on and so forth.

And then finally, we looked at ternary phase diagrams. And their characteristics, which we discussed in a few lectures followed by applications of phase diagrams. So, this is what we have done in this course, we have looked started from basic thermodynamics to build up the background and thermodynamics, looked at how the variation of free energy enthalpy, entropy takes place for various systems looked at regular and non-regular solutions.

And then we looked at solution thermodynamics variation, a gain of thermodynamic entities as a function of composition and temperature and they allows us to determine the construct the phase diagrams that we see in reality. And these phase diagrams are very useful from the perspective of determination of microstructure, determination of solidification temperatures, segregation and so, zone refining, design of alloys and so on and so forth.

So, hopefully you have enjoyed this course, I have tried to give you a reasonably good overview of things. The books that I recommend have been shown in the beginning of the course and also in the intermittently please go through the books and the exercises. I am sure you will benefit, there will be some assignments that you will have to carry out, which will help you to go through the course.

Thank you very much and if you have any questions, please write to me my email is ashishg at iitk dot ac dot in. This is my email ID, please write on it.

Thank you very much.

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