Phase Equilibria in Materials (Nature and Properties of Materials - II)

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Lecture - 11
Free Energy Curves & Various Systems

Welcome to you all this is lecture number 11 of Phase Equilibriam module. So, we will just recap the contents of the last lecture before we move on to the next one.

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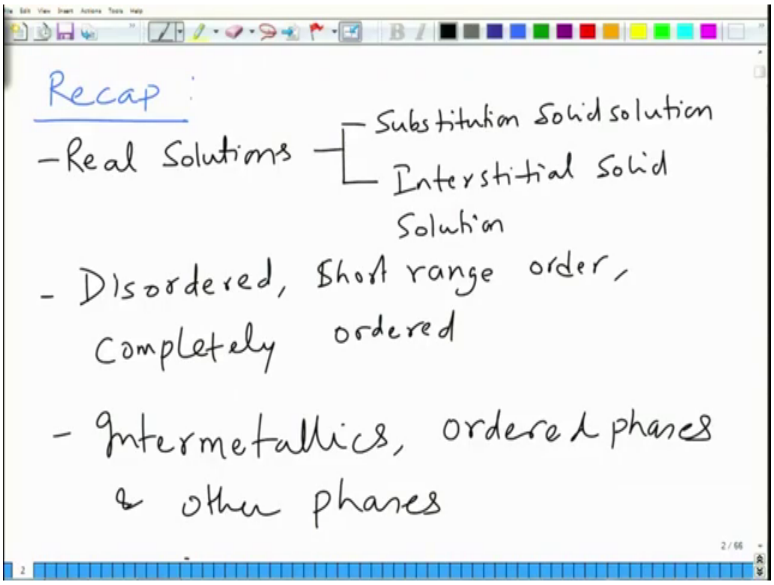

Recap :

- Real Solutions
  - Substitution Solid solution
  - Interstitial Solid Solution
- Disordered, Short range order, Completely ordered
- Intermetallics, ordered phases & other phases

So, in this last lecture number 10 we started our discussion on real solutions.

Now, real solutions are those which do not obey the constraints such as you know size differences are not there, in reality atoms are different in sizes as a result you have different strain fields which affect their mixing. And they are basically the enthalpy of mixing and then they have structural dissimilarity. So, one might be FCC and other might be BCC and so on and so forth there may be differences in electronic behaviour.

For example they may have different valances then have different electro negativities and electronic configurations. So, all these things lead to formation of solid solutions which are imperfect solid solution they are not i resolution which means there is not complete randomization as we expect. And also the entropy changes in that case are different as compared to real solutions at different temperatures.

So, what you may form is substitutional solid solution or interstitial solid solution. And these may be disordered short then something the short range order or completely ordered ok.

So, depending upon factor various factors, solutions may be disordered they may be short range order they may be long range ordered. So, and they may form various phases; these phases could be you know Intermetallics this they could be ordered phases and variety of other phases and we also described a parameter called as s.

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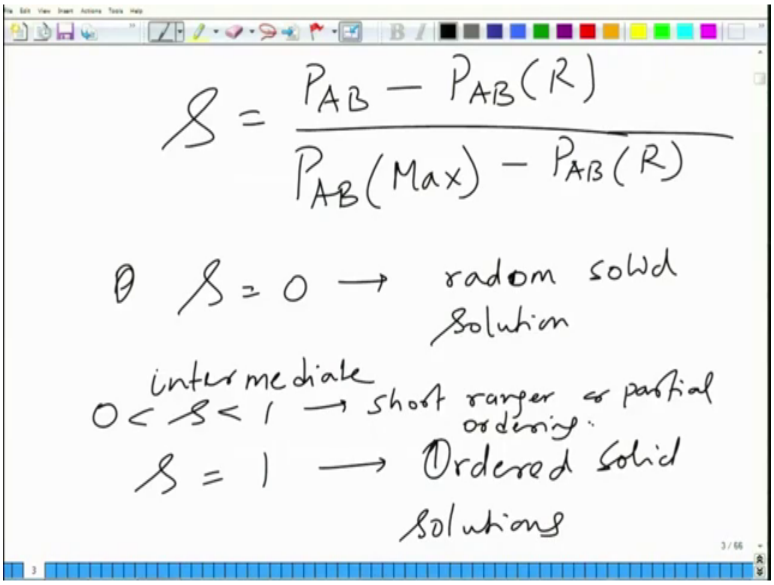

$$s = \frac{P_{AB} - P_{AB}(R)}{P_{AB}(Max) - P_{AB}(R)}$$

θ $s = 0 \rightarrow$ radom solid solution

intermediate

$0 < s < 1 \rightarrow$ short ranger or partial ordering.

$s = 1 \rightarrow$ Ordered Solid solutions

In which was basically the difference of observed number of A B bonds minus PAB random then what is the maximum number of PAB bonds if it was completely ordered and then again in a random solution.

So, basically if you had s being equal to 0 that means, A B was equal to A B random in that case number of bonds are same as in the random solid solution which means there is a tendency for randomness. So, you can have s to be equal to 0 which is completely random solid solution very close to real scenario.

But that does not happen in most cases or you can have other scenario which is s is equal to 1 where number of AV bonds is same as the maximum number of AV bonds that you can have in an ordered solution solid solution in that case it will become equal to 1.

So, this is completely ordered and this is possible this is found in various example in various material systems. And then you can have intermediate s; that is s less than 1 greater than 0. This may say short range or partial ordering and this is seen in this is possible in variety of solid solutions which are although disordered, but they may be partially ordered.

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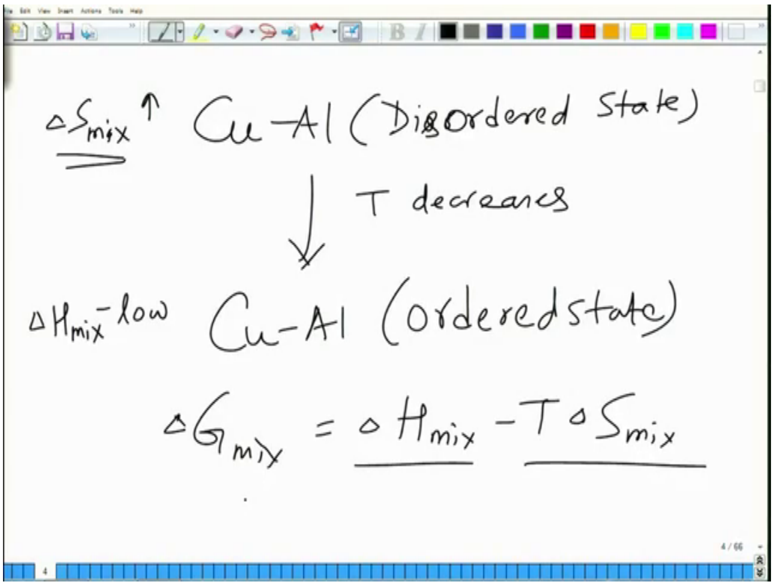

$\underline{\Delta S_{mix}}$ ↑ Cu-Al (Disordered State)

↓ T decreases

ΔH_{mix} - low Cu-Al (ordered state)

$$\Delta G_{mix} = \underline{\Delta H_{mix}} - \underline{T\Delta S_{mix}}$$

So, we took example of for example, in copper aluminium system; copper aluminium system goes from disordered state to Cu Al ordered state as the temperature decreases. So, temperature decreases. So, across a below a certain temperature it becomes a ordered solid solution above a certain temperature it becomes disordered solid. You can see that when its disordered then delta S mix which is driven by configuration entropy is high whereas, in this case when you have an ordered solid solution state in this case delta H mix is low.

So, it is. So, if you look at delta G mix delta G mix this is the delta H mix minus T delta S mix. So, it is the competition of these two terms which determines which phase will be stable at which temperature and it turns out at high temperature the minus T delta S mixed terms term wins over the delta H mix term as a result disordered phase is more stable whereas, at lower temperature the delta H mix term is dominates over minus T delta S mix.

So, decrease in delta H mix is higher than increase in then the lowering of this term as a result of reduced entropy. As a result delta G mix is lower for ordered systems. So, this is what happens in case of real solutions? You can have complete ordering you can have incomplete ordering you can have partial ordering.

So, now let us begin this lecture with discussion on what are these other phases.

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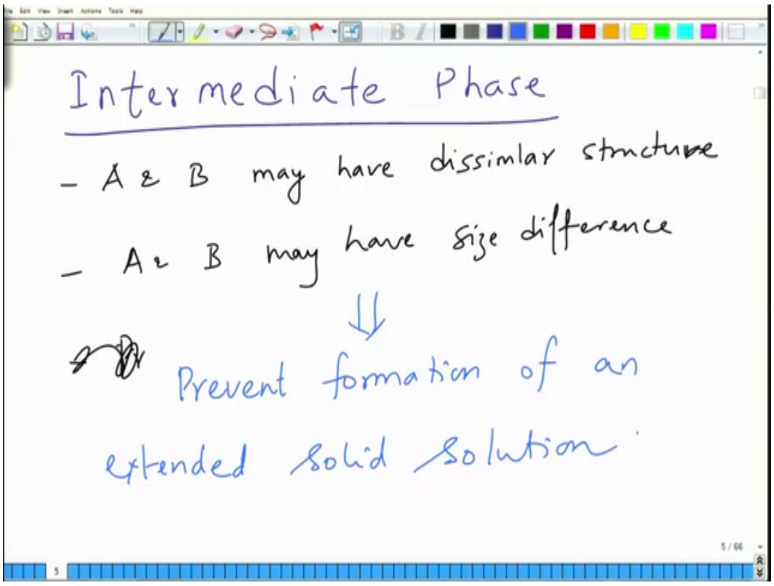

Intermediate Phase

- A & B may have dissimilar structure
- A & B may have size difference

$\Downarrow$

Prevent formation of an extended solid solution

So, let us first begin with lets define as sorry intermediate phase. So, as a name itself suggests the intermediate phase is the phase which form somewhere in between at the composition range when they are not able to form solid solution all throughout.

So, for instance A and B may have dissimilar structure or they may have. So, you may have to recall the module one structure of materials where we discussed the formation of solid solutions or they may have size difference beyond what is predicted by (Refer Time: 07:17) to form a solid solution or they may have excessive differences in the electro negativities.

So, these differences may lead to formation of. So, these will prevent formation of an extended solid solution across the composition range as a result they form phases in between. So, if you consider pure A and pure B.

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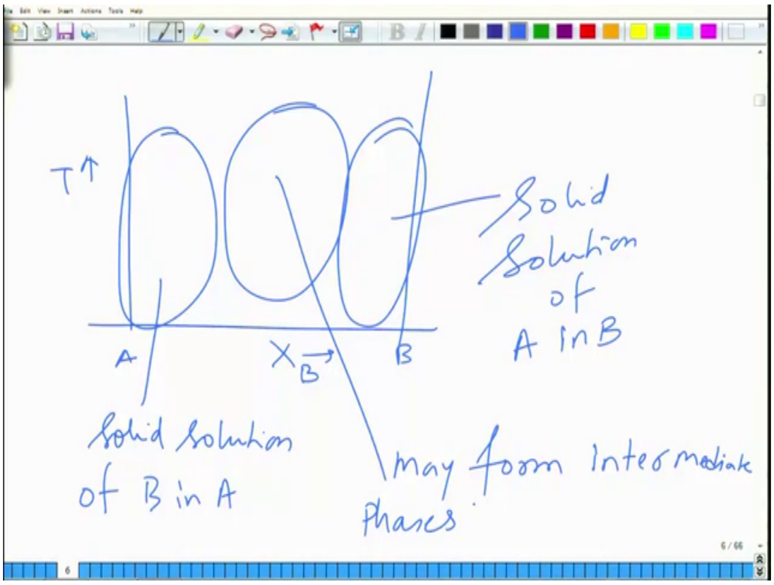

So, let us say this is the composition space this is A this is B and this is let us say temperature. So, on this side they may form solid solution of B in A on this side they may form solid solution of A and B somewhere in between they may form either these two solid solutions may coexist or they may form intermediate phases which are different to solid solutions. So, that is a possibility that may occur in material systems.

So, some of these phases intermediate phases may have. So, there are various kinds of intermediate phases that can form.

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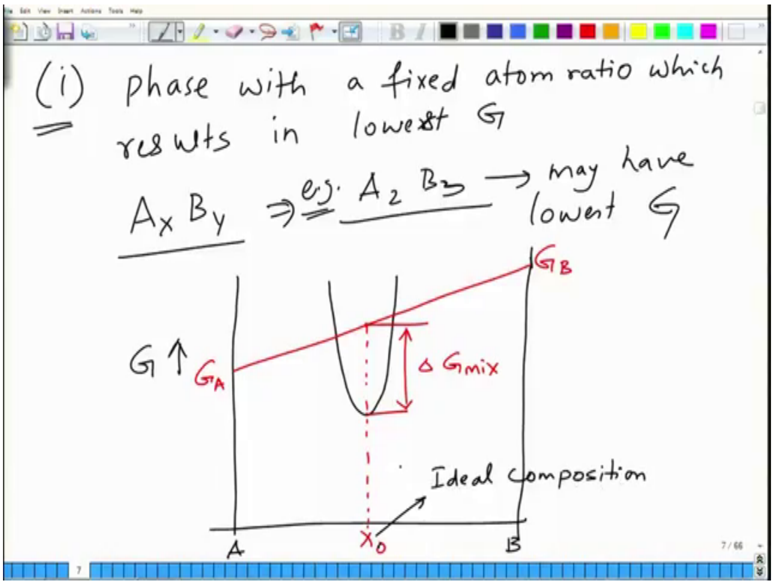
(i) phase with a fixed atom ratio which results in lowest G

$A_xB_y \Rightarrow$ e.g. $A_2B_3 \rightarrow$ may have lowest G

For example, there could be a phase with a fixed atom ratio which results in lowest G. So, for example, you can have a formula A x B y. So, A x B y for instance it might be you know A 2 B 3; A 2 B 3 might have lowest energy as compared to A 2 O or you know A B or A A B 2 and so on and so forth. So, this is. So, For example, A 2 B 3 may have lowest G.

So, basically what happens is that and if these the phases if these if such phases which have fixed atomic ratio which means they will have their free energy curve is also very narrow.

So, when you plot their free energy as a function of composition. So, this is A this is B this is G. So, these phases have relatively narrow free energy composition profiling and if you plot for instance this would be the free energy that is predicted by for instance.

So, this is the let us say composition this is where they have minima. So, this is what is the delta G mixing and this is nothing, but G A partial mole energy of mole energy of A and B and this is what is basically the you can say this X naught is nothing, but an sort of ideal composition and given the narrowness of the free energy curve it tends to have very little compositional tolerance as far as its own existence is concerned. So, A X B Y literally means A X B Y it does not have any tolerance for extra A or extra B.

On the other hand you have a scenario if the in which the phase has.

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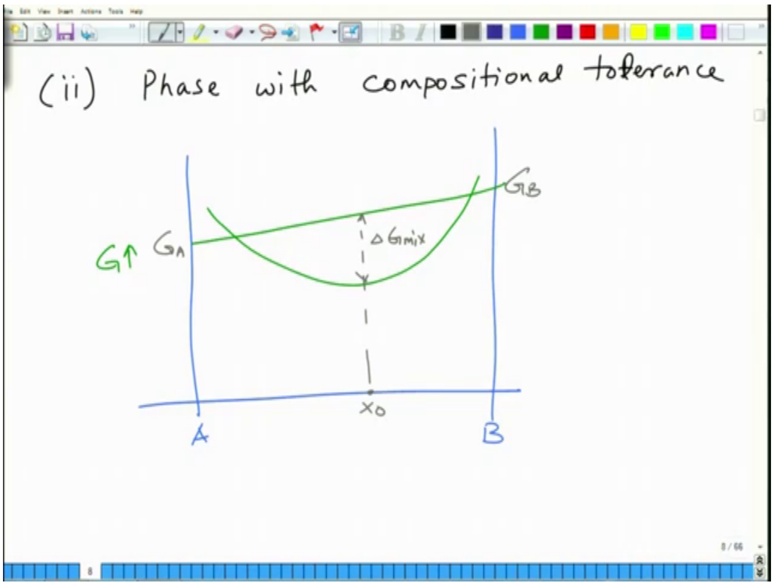

(ii) Phase with compositional tolerance

So, you can have the scenario phase with compositional tolerance. So, in such a case the curve may be shallow like this. So, again if you apply this is let us say X naught this is delta G mixing, this is G A this is G B and this is the phase O, but this is shallow as a result it can have wider compositional tolerance.

So, generally the shallowness of curve is determined by.

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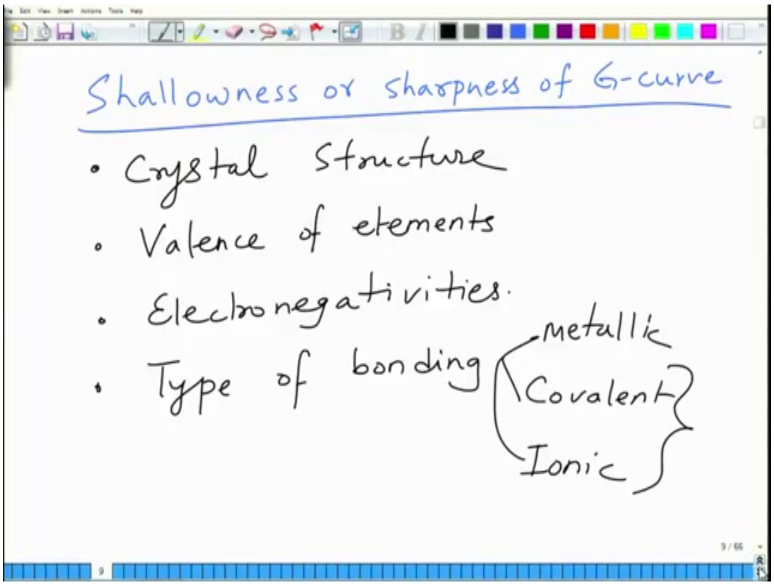

Shallowness or sharpness of G-curve

- Crystal Structure
- Valence of elements
- Electronegativities.
- Type of bonding
  - metallic
  - Covalent
  - Ionic

So, what makes this shallowness or let us say sharpness of G curve what does it depend upon? It depends upon factor such as crystal structure. It also depends upon valence it depends upon electro negativities. And it depends upon type of bonding between the elements whether they have metallic or they have covalent or they have ionic.

So, in general compounds of metallic bonding will have more tolerance for compositional fluctuations as compared to compounds with covalent in ionic bonding they are more stiff bonds with the higher energy and the structures are far more stiff as well and they do not allow too many composition fluctuations instead when you change the composition they tend to crystallize in different other forms.

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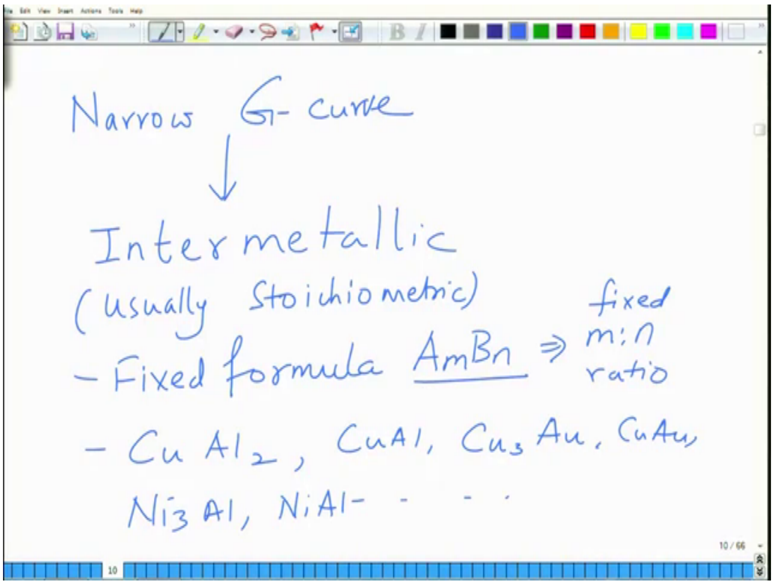

Narrow G- curve

↓

Intermetallic

(usually Stoichiometric)

- Fixed formula $\underline{A_mB_n}$ ⇒ fixed m:n ratio

- $CuAl_2$, $CuAl$, Cu_3Au, $CuAu$,
  Ni_3Al, $NiAl$ - . . .

So, basically a narrow G curve signifies a phase called as Inter metallic. Inter metallics are compounds typically with partially covalent or partially ionic bonding as we have seen in structural materials module. They are usually Stoichiometric and they have generally a fixed formula.

So, you can have A m B n with fixed m is to n ratio and there are example such as you know inter metallic's you can have Cu Al Cu Al 2, Cu AL Cu 3 Au Cu Au Ni 3 Al NiAl various types of inter metallic's are there. These are very these are compounds made from these atoms with fixed formula and they have a narrow G curve and there are other compounds as well.

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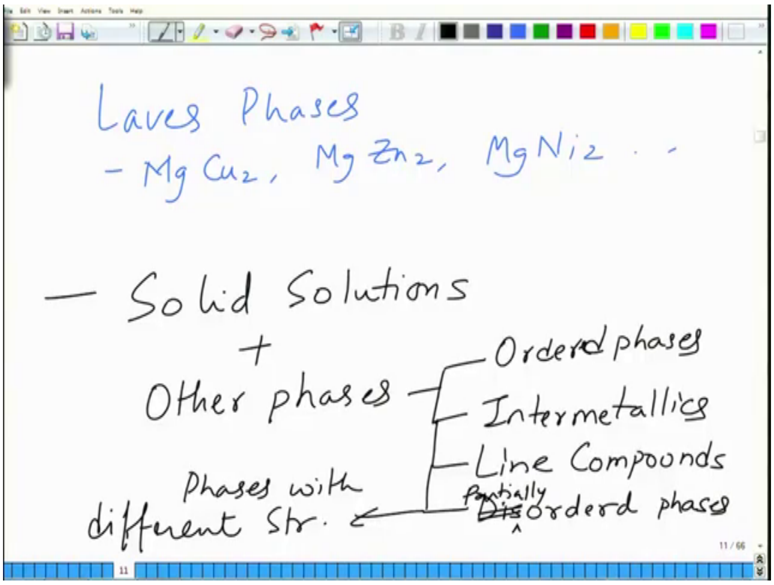

Laves Phases

- $MgCu_2$, $MgZn_2$, $MgNi_2$ . .

— Solid Solutions

+

Other phases
- Ordered phases
- Intermetallics
- Line Compounds
- Partially ~~Dis~~orderd phases

Phases with different Str.

For example we saw in structure laves phases there examples could be Mg Cu 2 Mg Zn 2 Mg Ni 2 and so on and so forth. So, if you want to look at these things when I go to the module one which is structure of materials and you can find more details there.

So, now these are the phases which can form in systems which you can have Phase.

So, in addition to solid solutions in addition to solid solutions you can have other phases which could be ordered phases could be Inter metallic's there is something called as Line compounds with very very fixed formula could be disordered phases disordered mean partially ordered let us say and other structures phases with other structures. So, there are various possibilities and these are not only possibilities there are other possibilities as well.

So, now we know that in real solutions things are little bit more complicated as compared to ideal systems they do not make extended solid solution all throughout. So, it was ideal solution what will what you will obtain is basically.

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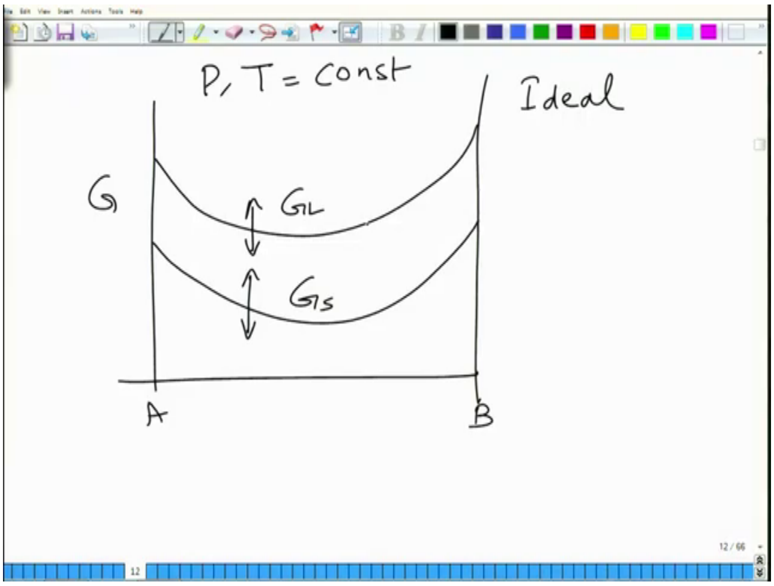

You will have if you plot free energy versus composition at a constant temperature and pressure generally pressure is kept at one atmosphere. So, we will whenever I do not mention pressure it means 1 pressure is constant. So, you will have.

So, this would be for example, liquid phase GL. Similarly you can have GS which is the solid phase. If it is a ideal system; if it is a non ideal system in that case and it is the relative in this figure it is the relative now as you change the temperature we know that the free energy decreases the temperature and free the shape of free energy curve changes and relative positions change. So, it is the relative change of these curves and there in the composition free energy landscape as a function of temperature which will determine which phase is stable.

For example in this case I have shown GS to be lower than GL all across the composition range which means solid is the most stable phase at this temperature. It might happen that GL is lower than GS in certain case the liquid phase is more stable as compared to solid phase, but there will be instances where this these two will overlap with at intermediate temperatures at those temperatures the phase two phase coexistence will come into picture.

So, now let us look at phase coexistence in homogeneous systems.

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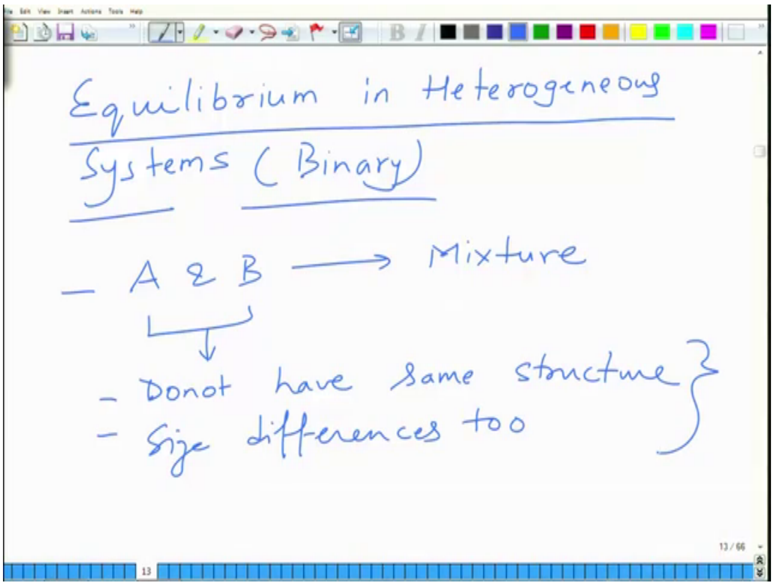

Equilibrium in Heterogeneous Systems (Binary)

- A & B → Mixture
- Donot have same structure
- Size differences too

So, we will look at basically equilibrium sorry equilibrium in heterogeneous systems not homogeneous. So, basically you have generally let us begin with binary system. So, we will just consider binary for the sake of simplicity we will introduce ternary later on. So, consider that you have two elements A and B which are mixed and how these A and B mix with each other and how they react with each other what kind of solid solutions they form what is the free energy profile that will determine what will exist under given set of conditions.

So, let us say A and B do not have same structure and there are size differences as well.

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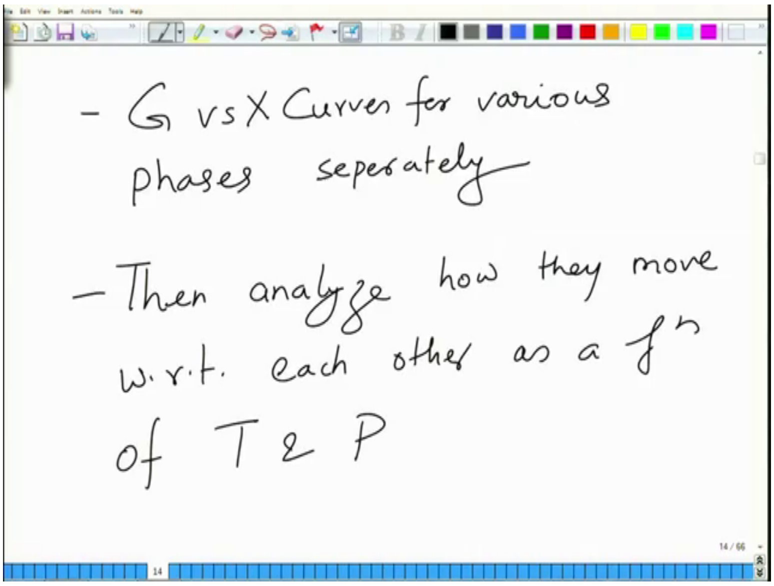

- G vs X Curves for various phases seperately
- Then analyze how they move w.r.t. each other as a f^n of T & P

now these two if these are the things we need be we able to draw one needs to draw the free energy versus G versus X curves for various phases separately, and then analyze how they move with respect to each other as a function of temperature and pressure and then analyze the (Refer Time: 21:27).

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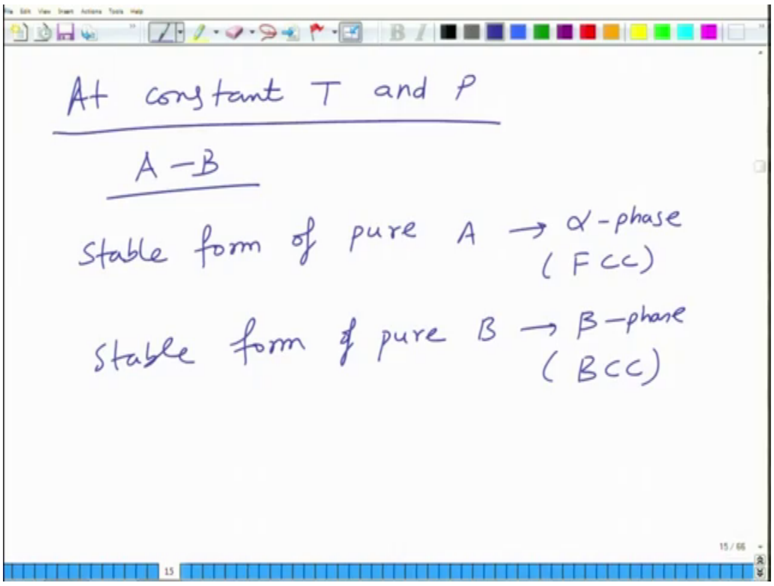

At constant T and P

A – B

Stable form of pure A → α-phase (FCC)

Stable form of pure B → β-phase (BCC)

So, let us say we have at constant. So, at constant temperature and pressure let us say we have two phases we have two components A B and stable form of pure A is basically it is the stable form of pure A to alpha phase they assume structure which is at FCC whereas, the stable form of pure B as well as the terminal solid solution beta which is B rich phase we will assume a crystal structure which is BCC in nature and then we will look at how the free energy versus composition plots of these two phases these two these two components and phases look like and what happens to free energies of A and B and when they are at pure A and pure B and when they are when they when the composition has changed on respective side a A to B or B to A.

So, now if I plot the free energy of a particular phase.

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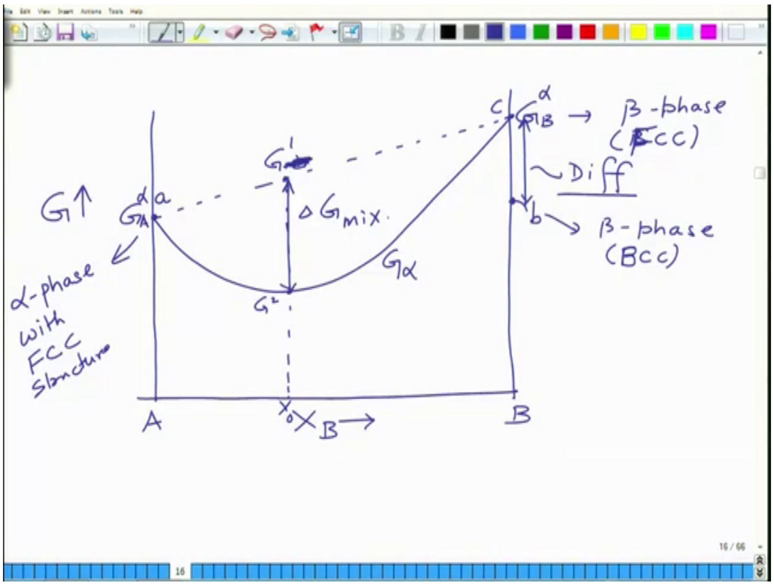

If I let us say draw free energy curve for a particular phase let us edge this is some phase and the rule of mixtures gives me free G. So, this is G A in that phase and this is G B in that phase for a composition X naught this is the G of mixing 1 and this is the mixture to 2. So, this is let us say instead of writing G mix let us just write it at G 1 this is G 2 and the difference is delta G mix.

So, this point here let us say this is point A and this is let us say is point C. Now this point signifies the basically we have said that beta phase has the BCC structure this point this point signifies alpha phase with FCC structure and so, let us say this is for BCC FCC structure. If you had FCC structured beta then this would be, let us say is the point B and this will be the. So, this will correspond to beta phase if it was FCC. And this is the difference between the two phases. So, beta and.

So, we need to draw in this case the free G curves for both the phases. So, for both. So, this is sorry I am sorry this is alpha phase. So, this is let us say G alpha. So, this is G A alpha this is G B alpha and.

So, this alpha phase we know is FCC structured. So, this is pure A in FCC structure this is pure B if it was in FCC structure this is and since we know that B is a pure beta which is pure B as BCC structured the free energy of this phase is lower so in fact, if it was FCC its phase its free energies raised by this much amount.

So, now what I need to do is draw is that I need to draw the free energy curve. So, both the phases.

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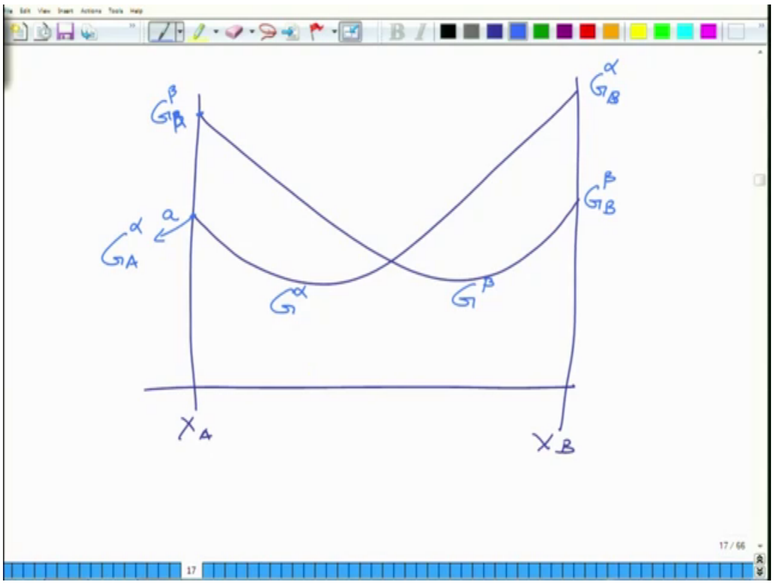

So, when I draw the free energy curves on both the phases X A and XB. So, this is let us say for alpha and this is let us say for beta. So, this is G alpha this is G beta sorry subscripts I can G alpha and G beta. So, this point represents a which is G A alpha this will determine G B alpha this will determine G B beta and this will determine G A beta.

So, now you can see clearly because the equilibrium structure of pure A is FCC. An alpha being FCC phase the free energy of a is lower than that of free energy of a in alpha is lower than that of free energy in B in beta phase which is B C phase has come at the pure a similarly at pure B the free energy of BCC structured B which is beta phase is lower than that of FCC phase of B if it was slicing in that. So, you can see that for both pure A and pure B for pure A FCC is stable and for B for pure B it is the BCC that is the stable.

Now, what happens Intermediate compositions, that is what remains to be seen in case of equilibrium between the two things. So, just a modification you want to make here that here it was in this slot in this figure it was G B alpha. So, if this was G alpha it would be G alpha and G B alpha and, but since beta phase with BCC structure is more stable the free energy of that phase will be lower and that is what we saw in the next slide.

So, we will stop here. So, what we have done in this lecture is we have just defined various phases like or disordered Inter metallic phases what they are? How they are? So, how does the free energy composition plot the shallowness of the plot changes of the function of whether it is a fixed compound or whether its it has a composition tolerance and then we looked at the free energy composition variation with for different phases which we will extend further in the next lecture. So, we will stop here.

Thank you.