Phase Equilibria in Materials (Nature and Properties of Materials – II)
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Lecture - 10
Thermodynamics of Real Solution

Ok, so now, we begin with the new lecture in Phase Equilibrium module that is lecture number 10. So, I will just briefly recap, what we did in the last lecture.

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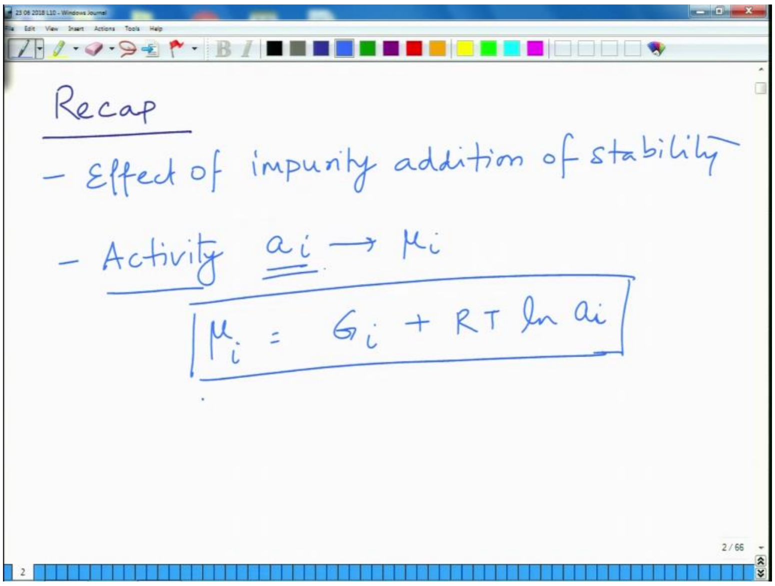

Recap

- Effect of impurity addition of stability

- Activity $a_i \rightarrow \mu_i$

$$\boxed{\mu_i = G_i + RT \ln a_i}$$

So, in the last lecture, we basically discussed about effect of impurity addition on stability of solutions. So, basically, when you add a small amount of impurity to a, to a pure phases, it is thermodynamically stable and mainly driven by, even though ΔH_{mix} can be may be positive, the impure phase is, slightly impure phase is more stable because of increase in the configurational entropy which drives the free energy of mixing to become negative in the impure phase

And then secondly, we introduced the concept of activity, a_i. So, you have activity is basically related to μ_i. So, you have element

$$\mu_i = G_i + RT \ln(a_i)$$

So, this is the relation of chemical potential with respect to activity. So, higher the activity of a system, higher the chemical potential is. So, and it basically depicts the tendency of an element to leave or remain within the system.

So, if activity of a component is high which means it does not like to stay in the solution, it wants to get out of the solution and what that depicts is basically the ΔH_{mix} is higher, positive and when, activity is lower what it means is that the chemical potential is also lower and the element likes to remain within the solution with the other elements, lowering the free energy of that state and which is manufactured in lower enthalpy of mixing as well.

So, this is what we discussed in the last lecture. Now, will move on to we call as a real solutions.

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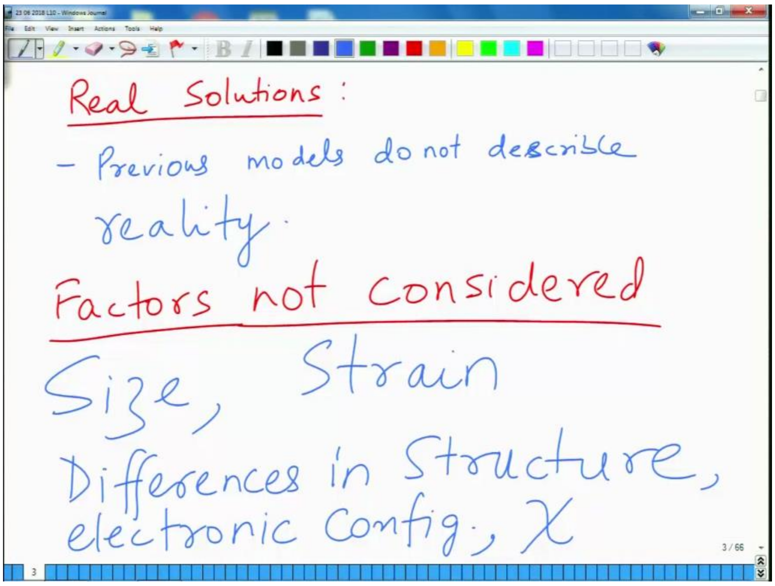

Real Solutions :

- Previous models do not describe reality.

Factors not considered

Size, Strain

Differences in Structure, electronic Config., χ

Now, Real Solutions basically are different from ideal and regular solutions because whatever we have discussed previously, they do not really describe the reality. So, previous models do not describe reality and this is because we have not considered, we we assume that A and B do not have size differences, but if you have two elements, they are going to have size differences. So, the factors, which we did not consider first was the size, we did not consider any strain fields.

When you have size differences, you will have strain and this strain leads to enthalpy of mixing So, these size differences and corresponding strain fields lead to changes in the enthalpy of mixing, we did not consider differences in structures, differences in crystal structure of elements. We assume that both of them are similar structure, but they may not necessarily be the same, the structures may be different.

Similarly, you can have differences in structure not only in structure, but also electronic configurations, electronegativity and so on and so forth. So, all these differences lead, so when we when we, so as we saw in the structure of materials module, the formation of solid solution is governed by certain rules called as Hume Rothery rules which say that you know solid solution will form when there is a certain, the size difference is smaller than a certain number, when the valences of those two elements ideally similar or the electronegativities are similar and the structures are similar.

So, these factors, which were not considered in the first two models of ideal and regular solutions make the situation far more complicated and as a result, you do not necessary form a substitution solution. Your solid solution could be interstitial solid solution and this interstitial solid solution will have completely different free energy considerations, enthalpy of mixing for instance as compared to regular or ideal substitutional solid solution.

So, these factors were not taken into account. As a result, the solid solution and thermodynamics associated, also is different. And then, we also did not consider whether two elements, we considered that they, both the elements will extend the solution, solid solution all throughout whereas in reality there could be formation of other phases.

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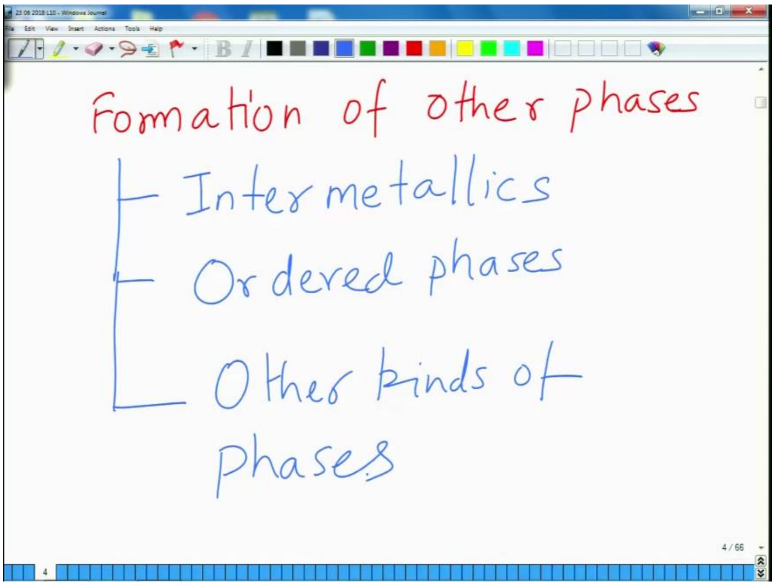

Formation of other phases

- Intermetallics
- Ordered phases
- Other kinds of phases

So, at certain compositions these two may react with each other and they may lead to formation of phases whose structure and properties and bonding etcetera are very different from the solid solution itself. So, for instance, they may form, so these phases could be for instance Inter metallics which are compounds. Basically, Inter metallics are line compounds, they may form ordered phases, they may form various other kinds of phases.

So, these kind of differences may lead to a completely different situation as far as free energy considerations are concerned. So, so the assumptions that you know, random arrangement of atoms will always provide a more stable structure is not necessarily true because of these differences.

And actual arrangement of the atoms in such situations will be the one which yields minimum free energy with sufficient amount of entropy. So, as we know that entropy cannot be 0, so entropy makes a very, entropy so, it is a balance between delta H mixing and entropy changes, considering the differences that I just narrated, that will determine the minimization of free energy. So, the possible, you may have various possible solid solutions.

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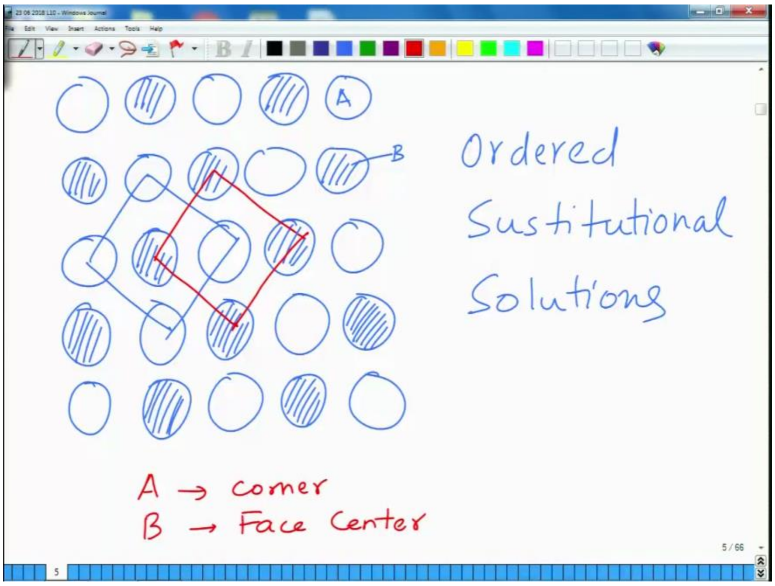

For instance, the ordered solid solution as we know is something like this; my apologies for the differences in sizes, but assume that sizes are same. So, let just change the first row and make it slightly bigger, ok.

Now, here let us say the first arrangement could be like this. So, these are basically ordered substitutional solutions.

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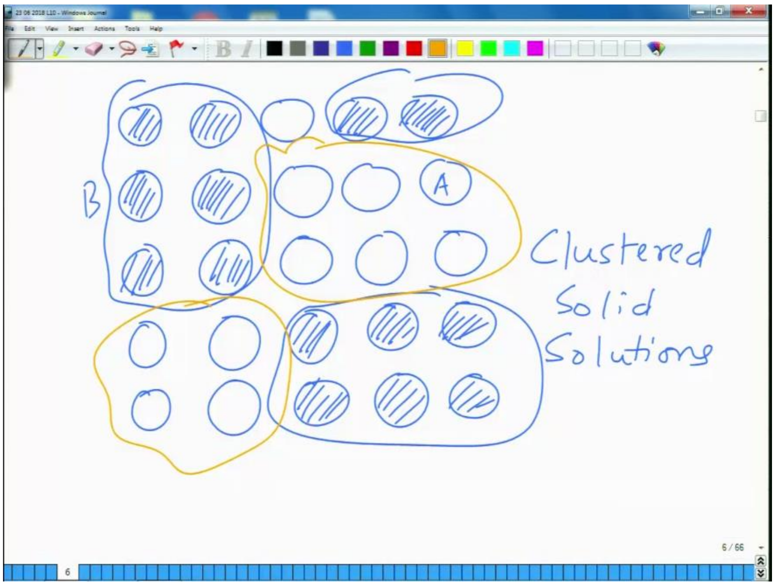

You can have another scenario in which, you have situations like these. And you can have some sort of clustering; let us say few atoms here, clustered in this fashion. So, they do not have as such, absolute randomness, they have some sort of clustering. So, this is you can have a clustered solid solution. So, it is not exactly periodic because there is no ordering as such here but atoms tend to cluster at various places.

So, you can see that B atoms have clustered. So, this is if this is B, this is A, you can see that B have clustered in different pockets whereas, A is present as well in certain different pockets. So, this is for example pocket of A, this is pocket of B. So, this is pocket of B ok, this is again a pocket of B, this is again a pocket of A, on the other hand this is the pocket of A, this is the pocket of A. So, they have clustered each other in different regimes and this may happen in cases where A and B do not like each other which means A, B bonds is not preferable.

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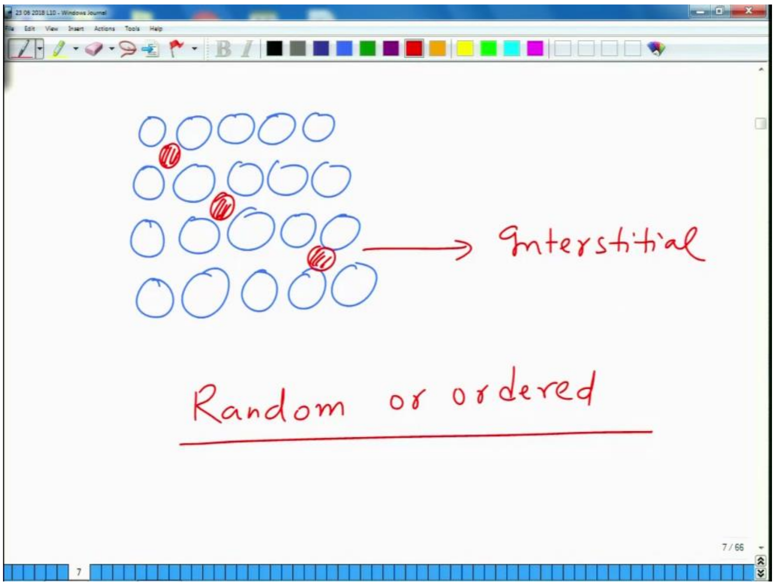

If you have excessive size differences, you may have completed different scenario; for instance, you may have these atoms present somewhere here and this will lead to either a contraction.

So, this will, this is basically interstitial and this will lead to contraction or dilation of the lattice, depending upon the size difference and the size of the void and these are basically again interstitial solid solution, could again be random or ordered depending upon the enthalpy of mixing.

And also, this is further complicated by differences in electronegativities as well as differences in the bonding of between different items. So, there are various factors which are which, which go behind defining the phase formation what kind of solid solution will form eventually. So, let us first define the kind of phases that can form, if they do not form completely random solid solution.

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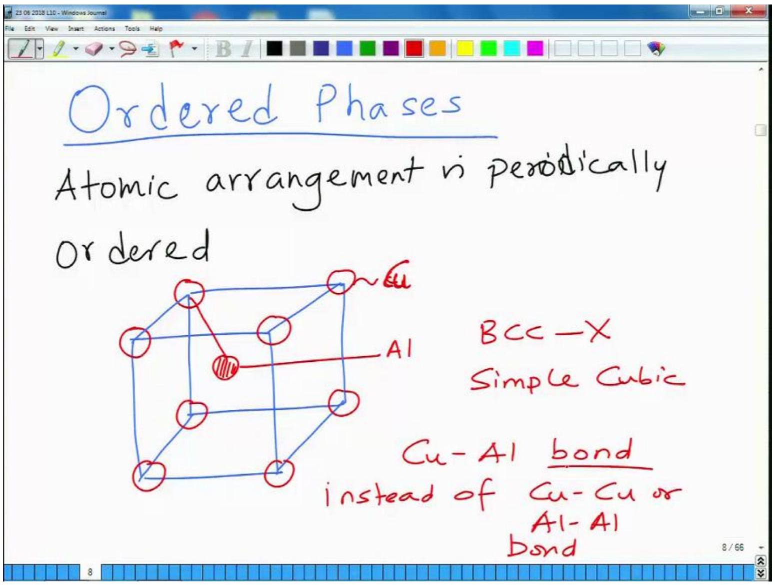
Ordered Phases

Atomic arrangement is periodically ordered

BCC — X
Simple Cubic

Cu - Al bond
instead of Cu - Cu or
Al - Al
bond

So, in this series, the first type of solid solution; first type of mixture that we consider, so, it is not solid solution as such it is Ordered Phases. Now, in this class of ordered phases, there are two categories. The ordered phases are those phases in which atomic arrangement is periodically ordered.

So, that we saw in crystal structures module 1, that you can have arrangement like, for instance, you can have a phase like this. So, basically the manifestation of ordered solid solution is this. You have ordered solid solutions. So, you have this is A atom, this is B atom. You can see that A and B are arranged in such a fashion, so that you can define a lattice either like this or like this and in this you can see that if you if you choose this as a blue one as a unit cell, then A is at the corner and B is at the face center and this is always the case. So, we can have either B at the corner or A at the corner or B, at the A at the centre or B at the centre depending upon which one is at the, but the pattern remains same all throughout.

So, this is basically ordered solid solution in three dimensional; for example, materials like, so this is Cu Au. So, this atom is Cu and this is Al ok, Cu Al. So, this makes a structure which is periodic, but it is not a BCC lattice. It is a simple cubic and this is what repeat itself. So, you can see that A, all throughout the structure, the bond that is preferred is Cu Al bond instead of Cu - Cu or Al - Al bond and this is because of stability of these bonds. This is because of stability of thermodynamic stability of Cu Al bond because the ΔH_{mix} in such case is low. As a result, copper likes to be in close to, in close proximity with the aluminium.

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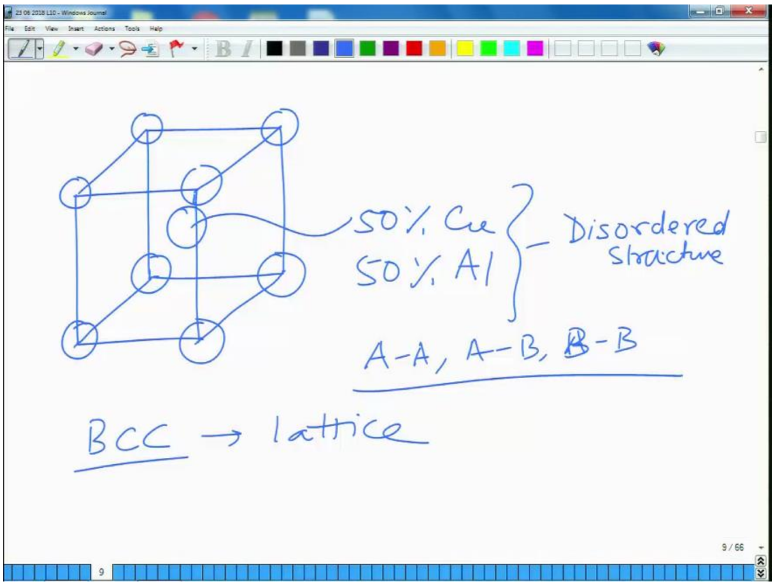

However, you can have disordered form. Disordered form would be in which, in the same lattice, so, each atom is now 50% Cu and 50% Al. So, in such a scenario each site is occupied, the probability, the occupation, the probability of occupation of the site is 50 % copper, 50% aluminium. As a result, this makes a disordered structure which means A- A; A-B And B-B bonds are equally probable. In such a scenario, this makes a BCC structured lattice but in a disordered form. So, each atom is mathematically considered as 50% copper and 50% aluminium.

So, in this case, the perfectly ordered phase, there is no Cu Cu bond, there is no aluminium-aluminium bond, nearest neighbor as far as considered. All the bonds that are considered are Cu Al bond. In this case, there is a possibility that you can have Cu Cu Cu bond, there is a possibility you can have Al-Al bond, there is a possibility you can have Cu Al bond.

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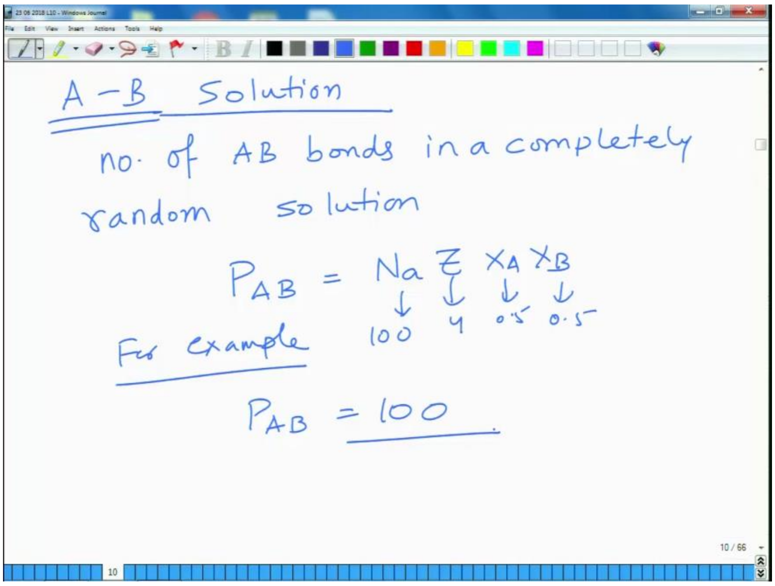

A – B Solution

no. of AB bonds in a completely random solution

$$P_{AB} = \underset{\substack{\downarrow\\100}}{N_a}\ \underset{\substack{\downarrow\\4}}{Z}\ \underset{\substack{\downarrow\\0.5}}{X_A}\ \underset{\substack{\downarrow\\0.5}}{X_B}$$

For example

$$P_{AB} = 100$$

So, this is, so depending upon, so now, you go to generalized A - B solid solution. Go back to generalized A-B solution. And let us say in a number of, number of A B bonds in a completely random solution that would be

$$P_{AB} = N_a Z X_A X_B$$

So, N a is the Avogadro number, Ƶ is the number of bonds per atom, X_A and X_B are atomic fraction.

So, for instance if you have ; for example, if you have this as 100, this as 4, this as 0.5, this as 0.5, then $P_{AB} = 100$but if the propensity of, if there is a propensity to, if let us say propensity of A B bond formation then $\Delta H_{mix} < 0$, so, this says that A B bonds form more than what they would in a random solution.

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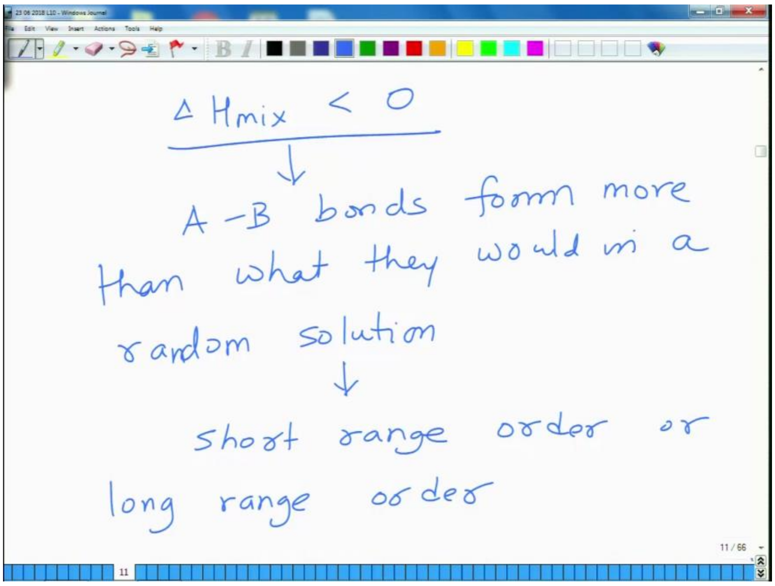

$\Delta H_{mix} < 0$

↓

A – B bonds form more than what they would in a random solution

↓

short range order or long range order

So, basically, more A B bonds will be formed, than what you will form in a random solution. In such a case, the alloy may form either short range order or long range order.

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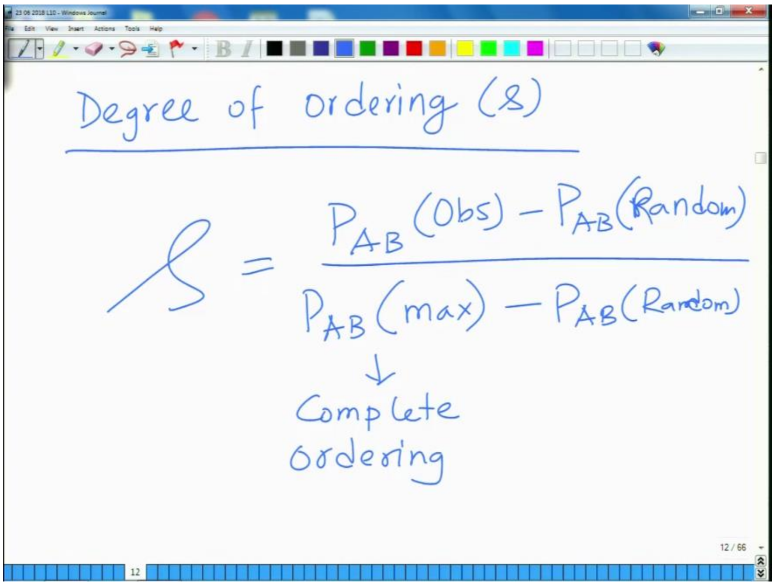

Degree of ordering (s)

$$s = \frac{P_{AB}(Obs) - P_{AB}(Random)}{P_{AB}(max) - P_{AB}(Random)}$$

↓

Complete ordering

And this is depicted by a parameter called as degree of ordering.

And this is determined as

$$s = \frac{P_{AB}(Obs) - P_{AB}(Random)}{P_{AB}(\max) - P_{AB}(Random)}$$

ok. So, basically, this would be state of complete ordering. This would be random solid solution and this is the observed.

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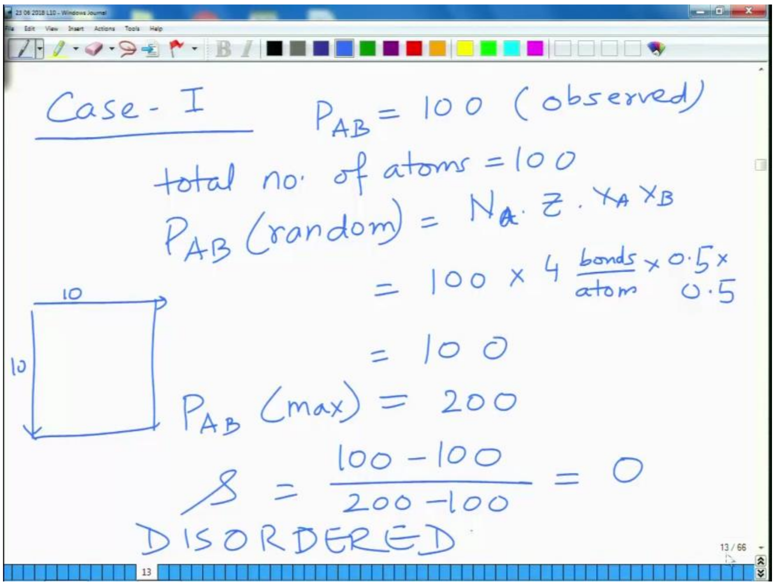

Case - I

$P_{AB} = 100$ (observed)

total no. of atoms = 100

P_{AB} (random) $= N_A \cdot Z \cdot X_A X_B$

$= 100 \times 4 \frac{bonds}{atom} \times 0.5 \times 0.5$

$= 100$

P_{AB} (max) $= 200$

$s = \frac{100 - 100}{200 - 100} = 0$

DISORDERED

So, now let us say, we have a situation case 1, in which let us say we have P_{AB} as 100 which is the observed. Total number of atoms, let us say is equal to 100, so in that case

$$P_{AB}(random) = N_a Z X_A X_B$$

$$= 100 \times 4 \frac{bonds}{atom} \times 0.5 \times 0.5$$

=100

And P_{AB} (max), so, you have you know let us say 100 atoms. So, 100 atoms means 10 row, so 10 this way 10, this way. So, you will have 100 in place. So, total number of 100, 200 bonds that you will have. So, total number of 10 horizontal bonds, 10 vertical bonds sorry, 100 horizontal, 100 vertical bonds; as a result $P_{AB}(max) = 200$. So, this small s in this case will be

$$s = \frac{100 - 100}{200 - 100} = 0$$

So, which means it is completely random solid solution, disordered solid solution. So, this means Disordered.

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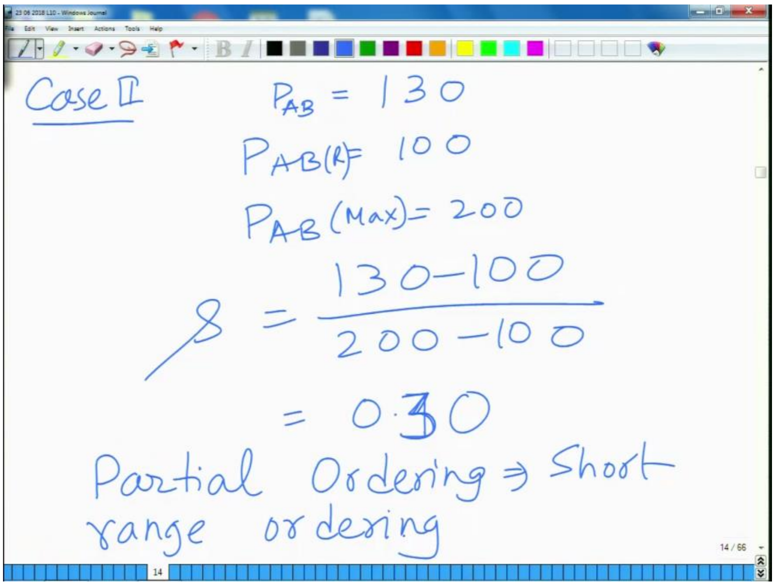

Case II

$P_{AB} = 130$

$P_{AB(R)} = 100$

$P_{AB}(Max) = 200$

$$s = \frac{130-100}{200-100}$$

$$= 0.30$$

Partial Ordering ⇒ Short range ordering

However, if you have s to be equal to, let us say P_{AB} observed which is equal to ; however, so, let us, case 2 let us say, so P_{AB} observed is let us say 130, P_{AB}(random) that we have worked out is 100 and P_{AB} max. So, this is random, this is max, is 200, in such a case

$$s = \frac{130-100}{200-100} = 0.30$$

So, this will have certain degree of ordering, it is complete. So, it is partial ordering which is called as Short range ordering.

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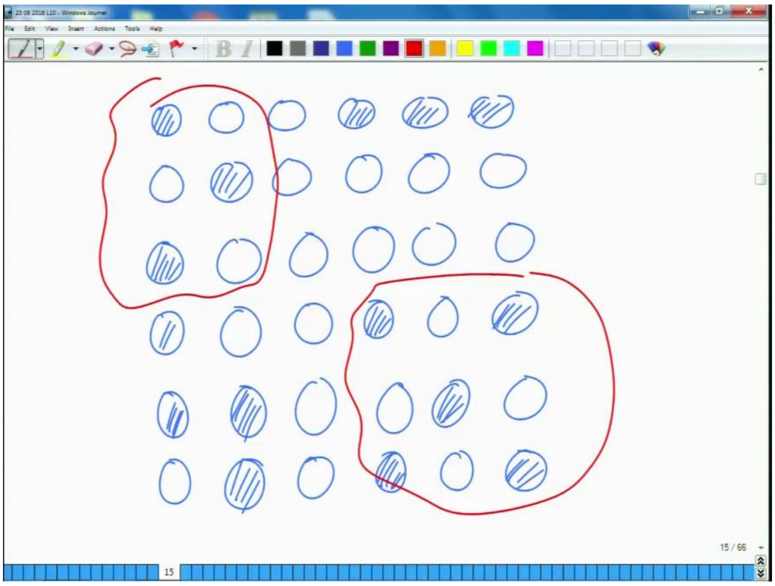

And this would look something like you know if you have, so in certain regions, you will have ordering. Here also, let us say you have ordering but in other regions you have disordering. So, they do cluster tend to form. So, you can see that, you can see that certain regions are ordered, certain other reasons are disordered or you can say sorry certain regions are perfectly ordered. So, there is short range order but other regions are random. So, clustered and so, this is sort of example of partial or short range ordering.

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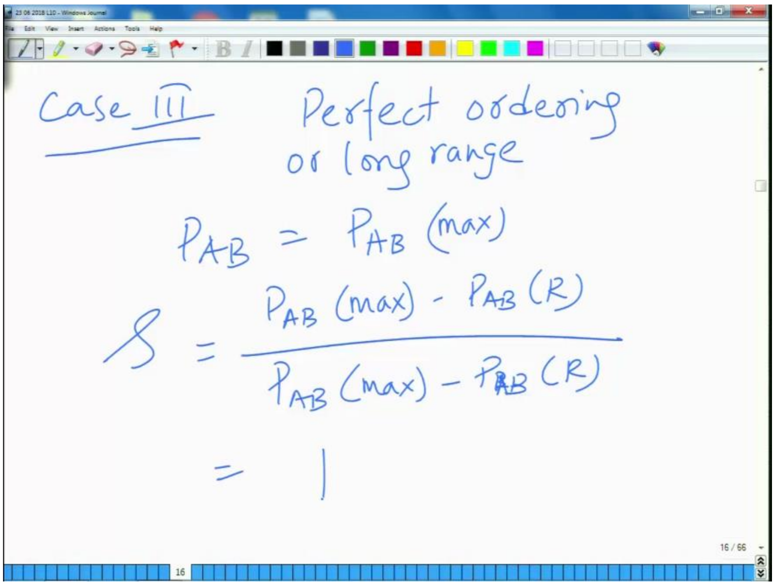

Case III

Perfect ordering or long range

$$P_{AB} = P_{AB}\,(max)$$

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

$$= 1$$

And of course, perfect ordering will have case 3, perfect ordering or long range, you can say long range. In that case, $P_{AB} = P_{AB}(max)$. So,

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

this will be equal to 1. So, for a for a long range ordered solid solution, s will be equal to 1; for a completely random solid solution, s_{AB} equal to 0 and for short range ordering, it would be intermediate values. So, these are the mathematical tools to define the ordering disordering. However, in the context of, in the context of thermodynamics basically, what it means is that, ordered structure defines low entropy of mixing and disordered structure has high entropy of mixing.

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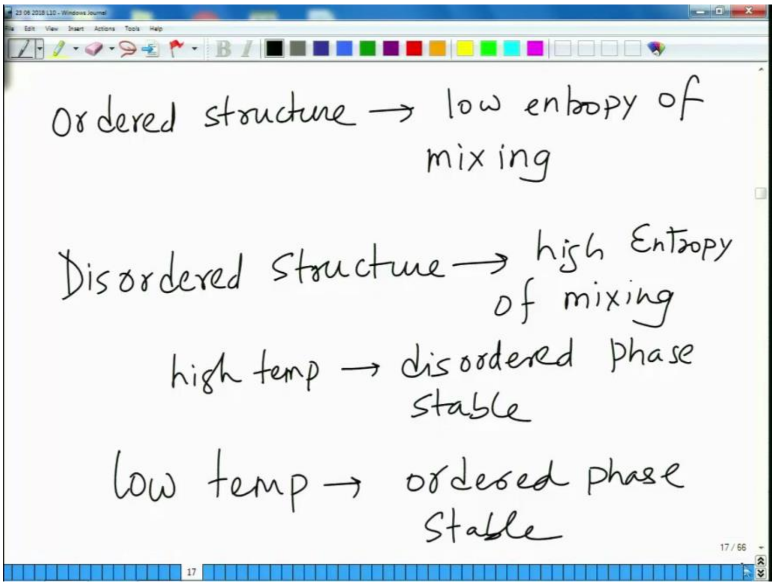

Ordered structure → low entropy of mixing

Disordered Structure → high Entropy of mixing

high temp → disordered phase stable

low temp → ordered phase Stable

So, if you just consider the entropy because high disordered phase will have higher configurational entropy; as a result, higher configurational entropy of mixing. So, what is that? Now, but in reality what is observed is that generally at high temperature, your disordered phase is stable; whereas, low temperature, ordered phase is stable.

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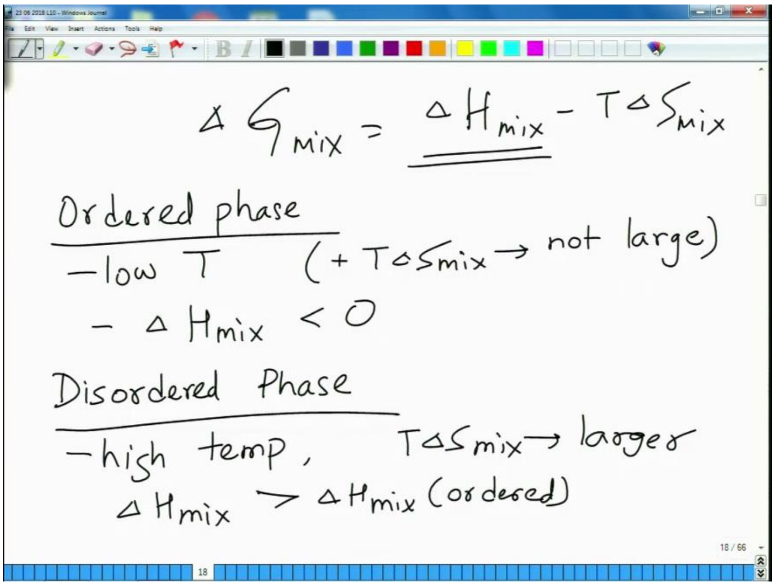

$$\Delta G_{mix} = \underline{\underline{\Delta H_{mix}}} - T\Delta S_{mix}$$

Ordered phase

- low T ($+ T\Delta S_{mix} \rightarrow$ not large)
- $\Delta H_{mix} < 0$

Disordered Phase

- high temp, $T\Delta S_{mix} \rightarrow$ larger

$\Delta H_{mix} > \Delta H_{mix}$ (ordered)

And we know that $\Delta G_{Mix} = \Delta H_{Mix} - T\Delta S_{Mix}$. So, as far as the comparison of two phases is concerned, $T\Delta S_{mix}$ term is surely higher for the disordered phase; however, this enthalpy term is also is an important factor. So, it is a relative competition between ΔH_{mix} and $T\Delta S_{mix}$ which governs at which temperature, which phase is stable

So, as far as ordered phase is concerned, for them they are stable, generally at low temperature and for them, $-T\Delta S_{mix}$ is not, so, I can say that $+\Delta T$ not large, but $\Delta H_{Mix} < 0$. So, it typically happens at lower temperatures when ΔH_{mix} is lower, $T\Delta S_{mix}$ is not large. And in comparison to disordered phase, ΔH_{mix} term of this phase dominates.

As a result, they are more stable whereas disordered phase, high temperature, $T\Delta S_{mix}$ larger; as a result, entropy term is bigger but ΔH_{mix} is relatively, it is higher than ΔH_{mix} of ordered. So, it generally happens at high temperature. So, it is the competition between ΔH_{mix} and $T\Delta S_{mix}$ terms of two phases which dictate which term will be stable.

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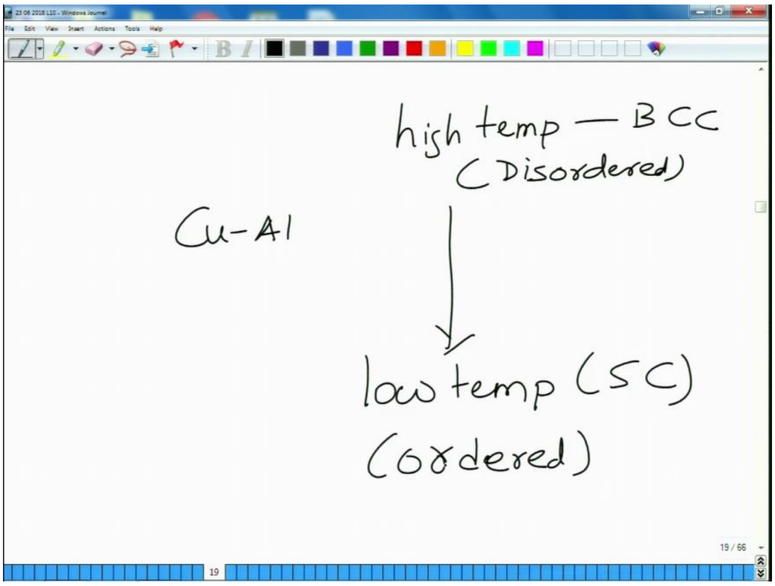
Cu-Al

high temp — BCC
(Disordered)

low temp (SC)
(ordered)

So, in general for example, Cu Au, Cu Al at high temperature, it is the BCC phase which is stable disordered. And at low temperature, it is the simple cubic phase which is stable which is ordered. And there are various other systems in which these phases exist; for example, copper gold system and various other systems in which ordering disordering happens and which is determined by competition of enthalpy of mixing and entropy of mixing.

So, we will finish here this lecture, in which we have discovered, we have talked about the real solutions in which enthalpy and entropy term can be very different from the order substitution, from the ideal and regular solutions which considered- which did not which did not consider the factor such as size difference, valence difference, electronegative difference, strain difference and so on and so forth. So, we will take up in the next class some other issues related to the real solutions.

Thank you.