Phase Equilibria in Materials (Nature and Properties of Materials -II)
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Lecture-07
Chemical Potential

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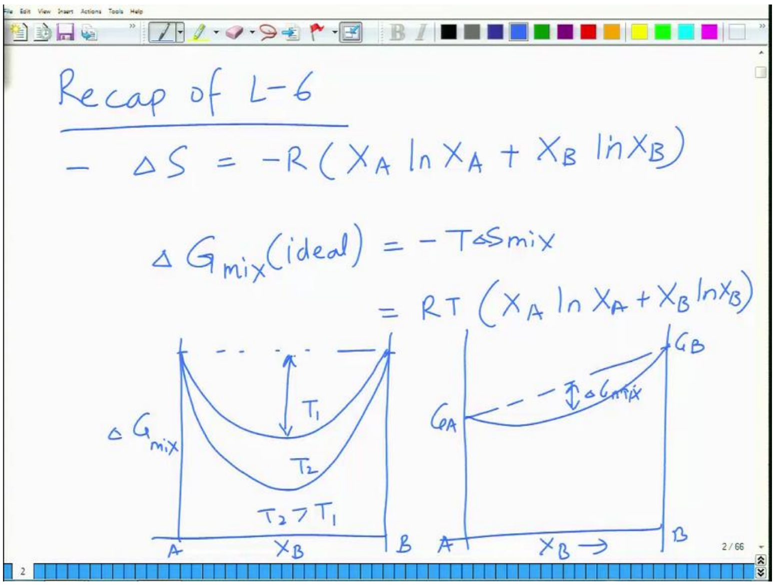

Recap of L-6

- $\Delta S = -R(X_A \ln X_A + X_B \ln X_B)$

$\Delta G_{mix}(ideal) = -T\Delta S_{mix}$

$= RT(X_A \ln X_A + X_B \ln X_B)$

So, we again start a new lecture. So that is lecture number 7 in Phase Equilibria. So, just do a recap of last lecture. Now, the recap of last lecture; in that lecture, we worked out what is the change in the entropy, which was basically configurational entropy change. And that worked out to be; your ΔS worked out to be $-R[X_A \ln X_A + X_B \ln X_B]$. And from this we determine, what is ΔG; this was for ideal solution for which ΔH_{mix} was 0. As a result, we just made it delta; $T\Delta S_{mix}$, and this was $RT[X_A \ln X_A + X_B \ln X_B]$

So, when we plotted this; so, when we plot this ΔG_{mix} as a function of mole fraction of B; so ΔG_{mix} goes; so it was like that ok, so it is this is what is ΔG_{mix}. And of course, as you increase the temperature, it goes further down. So, this is at T_1; this is at T_2; where T_2 is greater than T_1; this is ΔG_{mix} here. If you plot the free energy; so the free energy went like this. So, this was G_A; this was G_B; and this was the mixing term ΔG_{mix}, and that is when you went from A as a function of X_B.

Of course; so this ΔG_{mix} being negative, you can see that it will be negative, because X_A <1, and X_B <1, so $\ln X_A$ and $\ln X_B$ will be minus. As a result ΔG_{mix} will be negative; this tells you; this is basically the driving force for making a stable solid solution, when two elements are mixed into each other.

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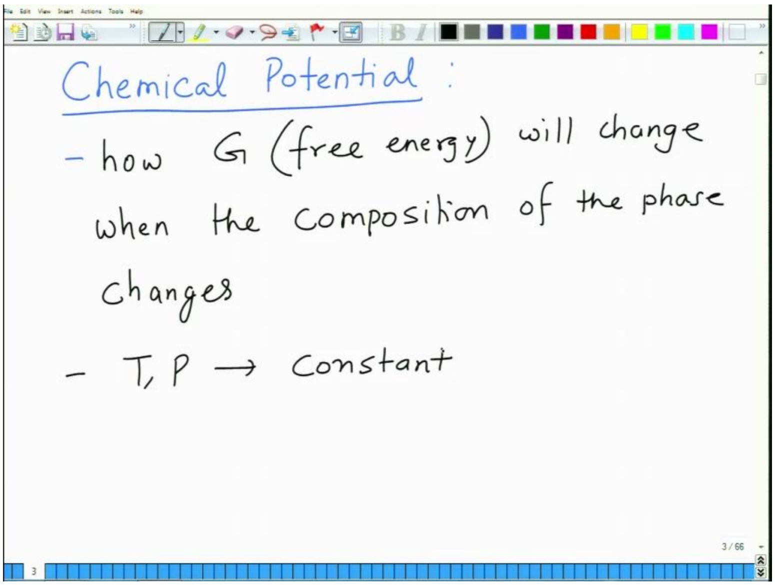

Chemical Potential :

- how G (free energy) will change when the composition of the phase changes
- T, P → constant

So, now what we do is that we look at the, we look at some other aspects of phase formation, and moving away from ideality is important. So, first, in this aspect, we will; because you know ideal solid solution, which say that ΔH_{mix} is no longer valid in case of; in most cases because of atomic interactions, and different bonds and so on and so forth.

So, we will have to move into regular solutions. Before we do that we first discuss another important aspect of thermodynamics that is chemical potential. Now, basically chemical potential is a measure of how free energy G will change, when the composition of the system is changed, then if we talk in terms of a phase, when the composition of the phase changes, all right. Now, this requires us to assume to begin with that other thermodynamic parameters such as temperature, pressure are constant. So, basically we are looking at the changes in the; incremental changes in the free energy, when you make very small changes to the composition of a given phase at constant temperature and pressure.

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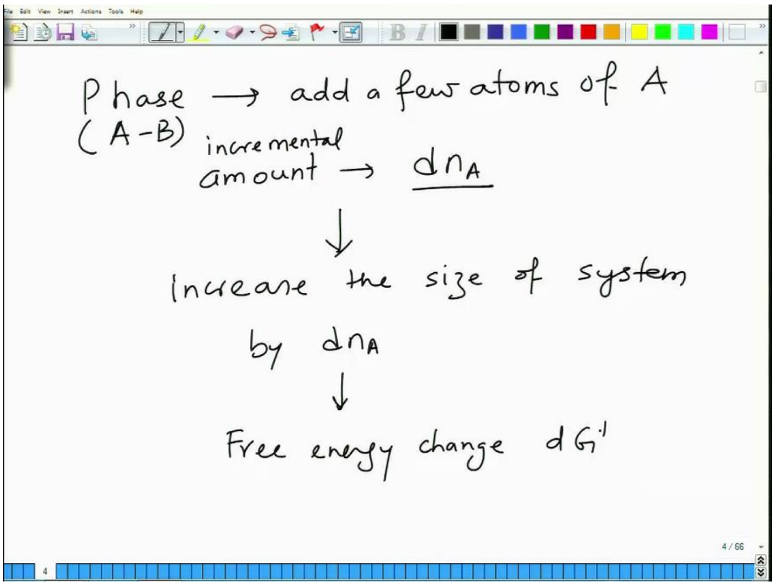

Phase → add a few atoms of A
(A-B) incremental amount → $\underline{dn_A}$

↓

Increase the size of system by dn_A

↓

Free energy change dG'

So, essentially what we do is that let us say, you have a phase and you add a few atoms of if it consists of A-B ok, a few atoms of A whose amount is; so basically the amount is very small, let us say dn_A this is the incremental change to; so, number of A atoms present originally in A phase are much larger than the amount; so this is the incremental amount; let us say incremental amount. So, number of atoms, which are originally present in phase A are much larger than this incremental amount that is dn_A. So, as a result, we increase the size of the system by same amount that is dn_A, and this also leads to changes in the free energy. So, free energy change correspondingly; let us say as another quantity called as dG'

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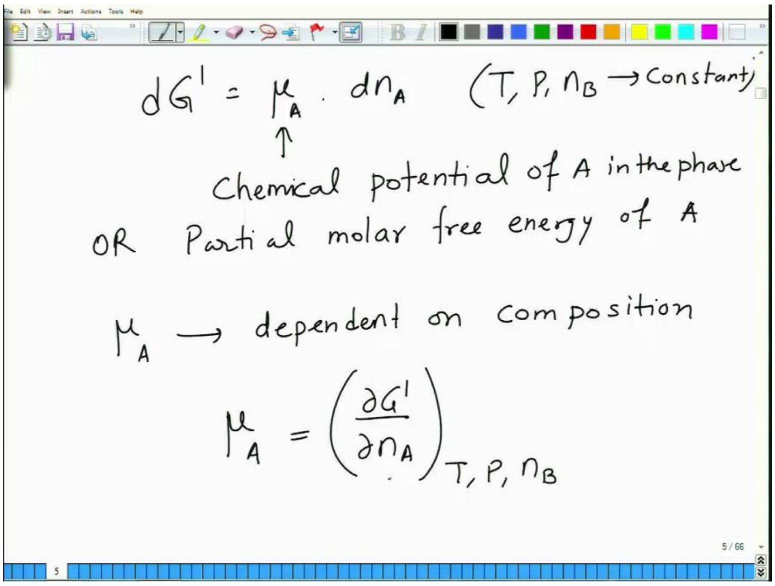

$dG' = \mu_A \cdot dn_A$ ($T, P, n_B \rightarrow$ Constant)

$\uparrow$

Chemical potential of A in the phase

OR Partial molar free energy of A

$\mu_A \rightarrow$ dependent on composition

$$\mu_A = \left(\frac{\partial G'}{\partial n_A}\right)_{T, P, n_B}$$

So, if dG; if dn_A is very small, then dG' can be expressed as $dG' = \mu_A dn_A$ and at this point temperature, pressure, and n_B, which is the number of B atoms, they remain constant. So, now here this proportionality factor μ_A is called as chemical potential. So, basically this is chemical potential of A in the phase, which consists of both A and B. Or alternatively, it is also called as partial molar free energy of A in the phase.

So, this μ_A is generally; μ_A is, as we can see is dependent upon composition. So, we can represent this

$$\mu_A = \left(\frac{\partial G'}{\partial n_A}\right)_{T,P,n_B}$$

So, basically we are making this dn_A so small, so that there is no appreciable change in the overall composition of the phase. It is a very minute change, this minute change gives raise to changes in the free energy. So, incremental changes in the free energy, upon incremental changes in the composition are represented by a quantity called as chemical potential. So, this is chemical potential of element A in the phase. So, now you can have; you can extend this approach to other elements also.

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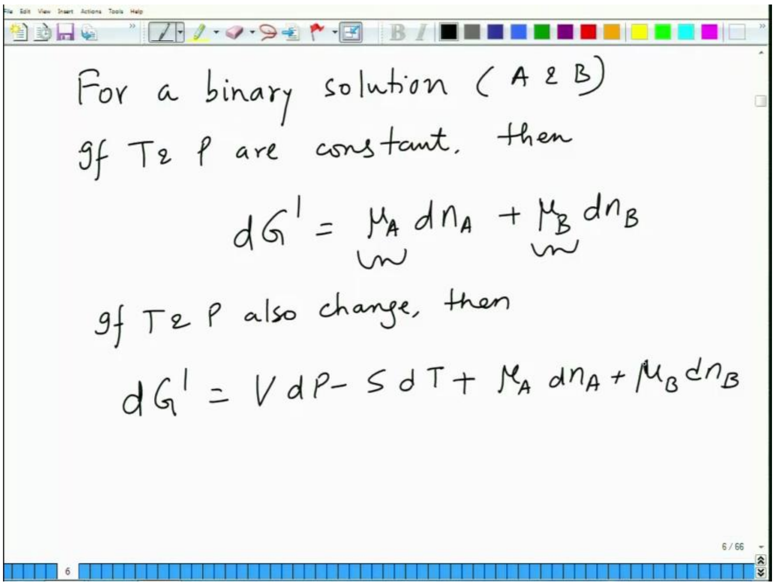

For a binary solution (A & B)

If T & P are constant, then

$$dG' = \underbrace{\mu_A} dn_A + \underbrace{\mu_B} dn_B$$

If T & P also change, then

$$dG' = VdP - SdT + \mu_A dn_A + \mu_B dn_B$$

For a binary solution, let us say it is A-B binary solution. So, at; again if temperature and pressure are constant, then we can say

$$dG' = \mu_A dn_A + \mu_B dn_B$$

dn_B. So, this is the quantity, which is corresponding to changes made in A, and this is the correspond(ing); chemical potential of B, corresponding to the changes that are made in B. So, if you change the pressure and temperature also, then free energy will be;

$$dG' = VdP - SdT + \mu_A dn_A + \mu_B dn_B$$

So, this is about like a generalized equation of energy change in a in a system. So, you can extend this approach to a multi component system.

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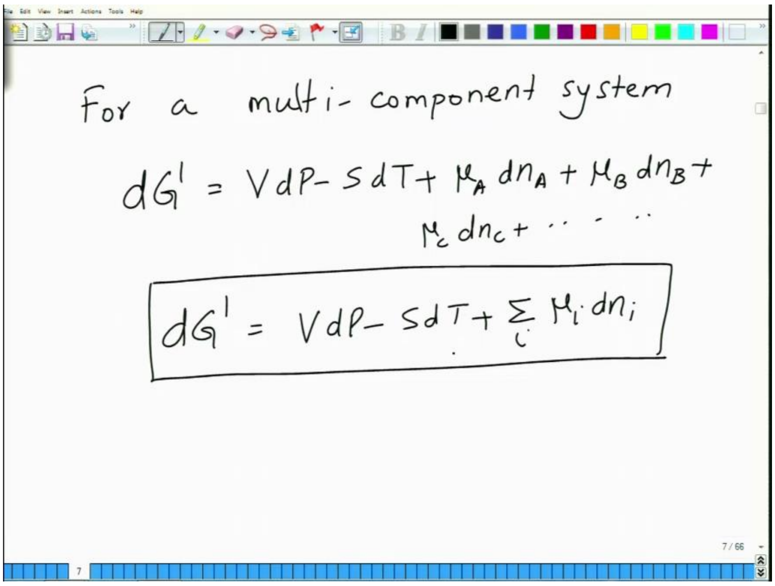

For a multi- component system

$$dG' = VdP - SdT + \mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \dots$$

$$\boxed{dG' = VdP - SdT + \sum_i \mu_i dn_i}$$

So, for a multi component system, this

$$dG' = VdP - SdT + \mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \dots \dots \dots \dots$$

or in a general form, you can write this as

$$dG' = VdP - SdT + \sum_i \mu_i dn_i$$

So, this would be the general form of changes in the free energy. When you; when changes in the various variables are made, so not all of them are made simultaneously. If so when you; for example, change compositions, these are generally kept as constant, so as a result you only worry about the changes in the composition. So, this is a generalized free energy equation for incremental changes in the composition correlating the chemical potential with the changes in the composition.

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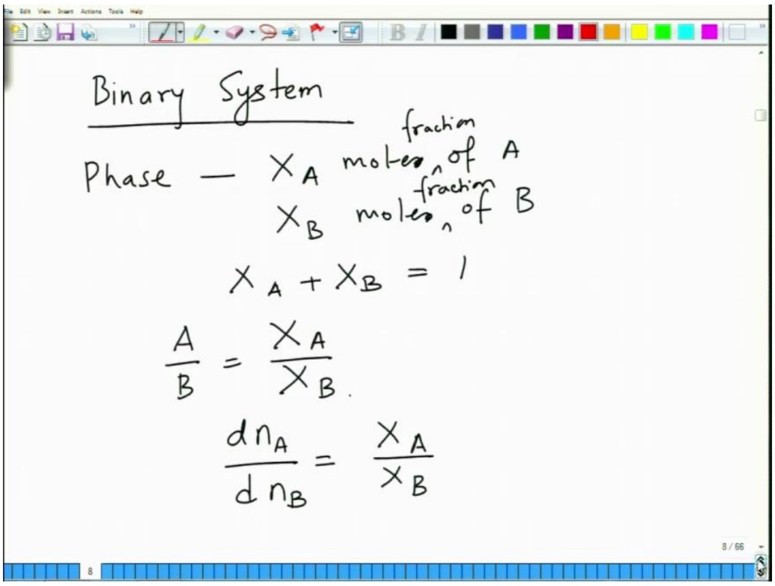

Binary System

Phase — X_A moles fraction of A

X_B moles fraction of B

$$X_A + X_B = 1$$

$$\frac{A}{B} = \frac{X_A}{X_B}.$$

$$\frac{dn_A}{dn_B} = \frac{X_A}{X_B}$$

So, now; let us now come back to binary phase, so we have a binary system ok. In this system you have a phase, which consists of X_A moles of A and X_B moles of B, as we started earlier. So, X_A; basically X_A is nothing but mole fraction. I would say it is not mole; it is rather mole fraction, such that $X_A + X_B = 1$.

So, since we know the ratio of A and B. So, what is, A is to B ratio; it is nothing but X_A divided by X_B ok. So, since,

$$\frac{A}{B} = \frac{X_A}{X_B}$$

you can increase the size of the system appropriately, so that the ratio of X_A is to X_B does not change. So, what you can do is that; so this I wrote as 1 mole; let us say, you take 2 moles, so this will become $2X_A$ and $2X_B$ and so on, and so you can you can write this as $1.1X_A$ and $1.1X_B$ this will become 1.1. So, you correspondingly increase the size of system without changing the corresponding; without changing the ratio of two elements, so as a result what we can write is that

$$\frac{dn_A}{dn_B} = \frac{X_A}{X_B}$$

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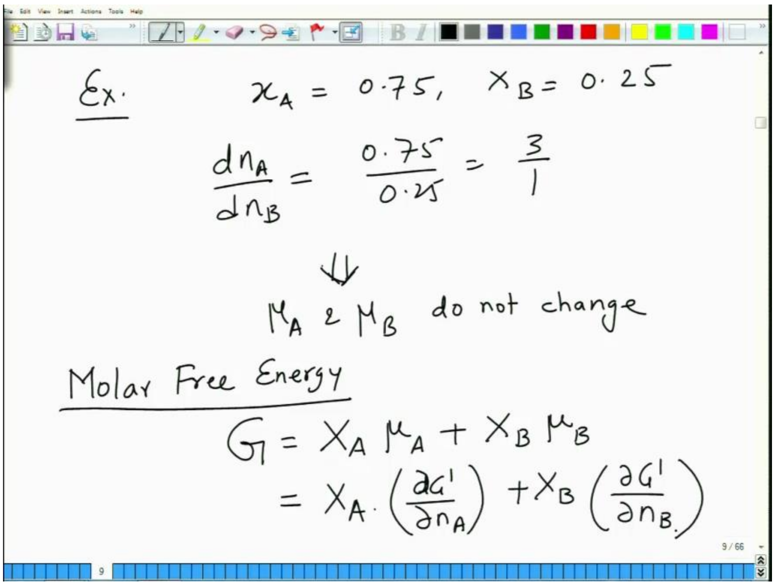

Ex. $x_A = 0.75$, $X_B = 0.25$

$$\frac{dn_A}{dn_B} = \frac{0.75}{0.25} = \frac{3}{1}$$

$$\Downarrow$$

μ_A & μ_B do not change

Molar Free Energy

$$G = X_A \mu_A + X_B \mu_B$$

$$= X_A \cdot \left(\frac{\partial G'}{\partial n_A}\right) + X_B \left(\frac{\partial G'}{\partial n_B}\right)$$

So, let us say for example, if $X_A = 0.75\ and\ X_B = 0.25$, then

$$\frac{dn_A}{dn_B} = \frac{0.75}{0.25} = \frac{3}{1}$$

So, when you make a change in dn_A and dn_B, if it is in this ratio of 3 is to 1, so you add 1 atom of n, 1 atom of B, and 3 of A or 2 of B, and 6 of A then this ratio is always maintained. As a result, the overall fraction of A and B in the system does not change. So, so overall composition is maintained without altering; so in; what you do in this situation is if you if you maintain this ratio, then μ_A and μ_B, which are; which are function of composition do not change all right.

So, now let us calculate what is the molar free energy. The molar free energy can be written in this case as

$$G = X_A \mu_A + X_B \mu_B$$

$$= X_A \left(\frac{\partial G'}{\partial n_A}\right) + X_B \left(\frac{\partial G'}{\partial n_B}\right)$$

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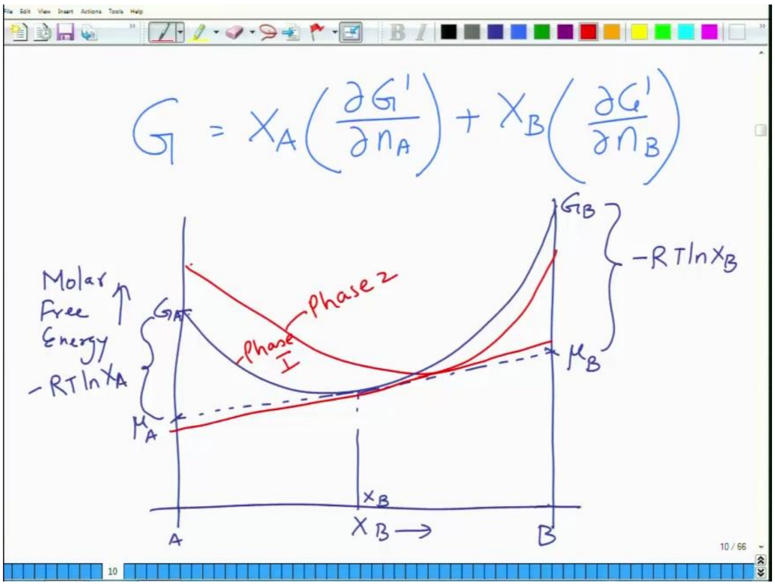

$$G = X_A\left(\frac{\partial G'}{\partial n_A}\right) + X_B\left(\frac{\partial G'}{\partial n_B}\right)$$

So, this is the; so, we can write in this slide,

$$G = X_A\left(\frac{\partial G'}{\partial n_A}\right) + X_B\left(\frac{\partial G'}{\partial n_B}\right)$$

So, when you now plot this, this is A, this is B, so you go as X, so increase the mole fraction of B in the right direction. And on this Y axis, we plot molar free energy ok, and what we have here is basically a situation like this. So, the tangent we can see that; since it is a tangent to this; lets say this is a composition X_B that we are interested in X_B. So, the tangent will determine the chemical potential on two sides, this is mu, this is the free energy G_A, G_B. And what is this; that is what we will determine. So, let us see what are these.

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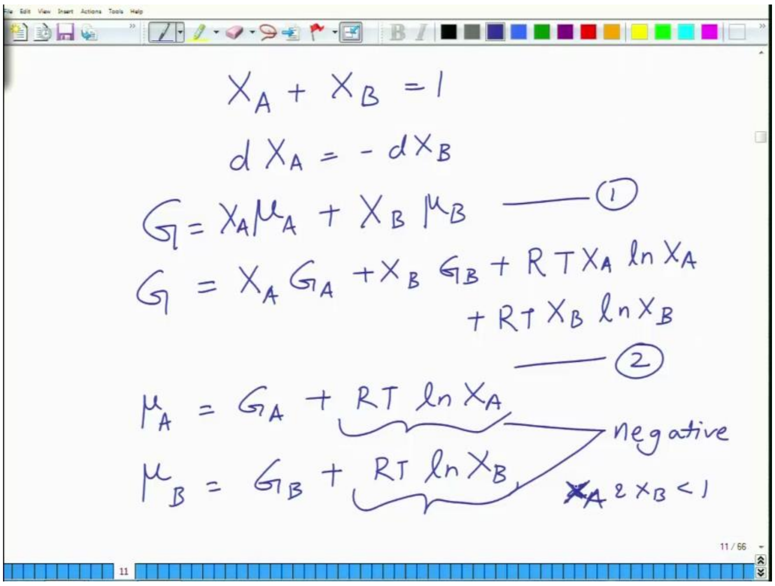

$$X_A + X_B = 1$$

$$dX_A = -dX_B$$

$$G = X_A\mu_A + X_B\mu_B \text{ —— } ①$$

$$G = X_A G_A + X_B G_B + RTX_A \ln X_A + RTX_B \ln X_B \text{ —— } ②$$

$$\mu_A = G_A + \underbrace{RT \ln X_A}$$

$$\mu_B = G_B + \underbrace{RT \ln X_B}$$

negative

$\cancel{X}_A$ & $X_B < 1$

So, we know that $X_A + X_B = 1$. So, we can write and $dX_A = -dX_B$. And we are writing

$$G = X_A\mu_A + X_B\mu_B$$

and we can write this as

$$G = X_A G_A + X_B G_B + RTX_A \ln X_A + RTX_B \ln X_B$$

So, this is what we did earlier when we calculate the mixing part. So, let us say; so, this is first expression.

So, this is; this is what is the relation with respect to chemical potential; this is what is the relation as we obtained from mixing when we calculate the ΔG_{mix}. So, basically its $X_A G_A + X_B G_B + RTX_A \ln X_A + RTX_B \ln X_B$. Now, you equate these two equations, if we equate these two equations, what you get is

$$\mu_A = G_A + RT \ln X_A$$

And
$$\mu_B = G_B + RT \ln X_B$$

And you can see that these; both of these terms, this and that, both of these will be negative, because X_B and X_A as X_A and $X_B < 1$.

So, if you go to previous plot, what is the difference going to be, this is going to be minus of $RT \ln X_A$. And what is this going to be, this going to be minus of $RT \ln X_B$. So, basically these are two expressions, you can represent. So, you can see the in this plot that when you make; when you have a free energy curve, of course you have free energy of mixing for a given composition, the slope and its intercept; so, you draw a tangent for a given composition, and the intercept of this tangent with respect to X and Y axis will give you the chemical potential, so this is chemical potential. And chemical potential is related to the free energy of that particular element; chemical potential is always chemical potential of a element in a phase.

So, chemical potential of A or chemical potential of B, and this is the phase; this is the free energy plot for a given phase with you have different phase, you will have to draw a different curve for different phase. So, if you have for example another phase, let us say that another phase has free energy curve something like that ok, then you will have to draw the tangent for that, so something like that; you will have to do that. So anyway this is for phase II; this is for phase I.

So, for a given phase, you can draw the tangent at the minimum, and the intercept of tangent with respect to X and Y axis that is A and B axis will give you the chemical potential. And this chemical potential is related to the free energy of a; that that molar free energy of element A, by magnitude called as; by magnitude minus $RT \ln X_A$ and in this case of element B, it would be minus $RT \ln X_B$. So, this is what is the chemical potential concept, as we have seen.

Chemical potential is nothing but; let us just redefine. So, chemical potential is, essentially it describes minute changes in the free energy, when you vary the composition of a particular, when you changes, when you change the amount of that particular element in a given phase. So, basically it is the partial molar free energy of A in the phase ok. Similarly, you can have the same thing for B. So, you are specifying the property of a particular element in a given phase.

So, from this we can determine, what is the overall change in the free energy, when you vary composition; all the phase; composition of all the elements. In the context of binary systems; in the context of binary system, the molar free energy can be, sum of the partial molar free energies, which is μ_A, the partial molar free energy of A multiplied by the fraction of A plus partial molar free energy of B multiplied by fraction of B.

And this can be equated with the overall free energy equation to give you the magnitude of μ_A and μ_B. So, chemical potential of A in a phase is related to molar free energy of A plus $RT \ln X_A$. And chemical potential of B is equal to molar free energy of B in that phase plus $RT \ln X_B$. So, this is what the concept of chemical potential is. And this is a very important concept as we will see later on, when we build up more about the phase diagrams, when we try to understand the phase diagrams and their formation for; specially for binary solutions.

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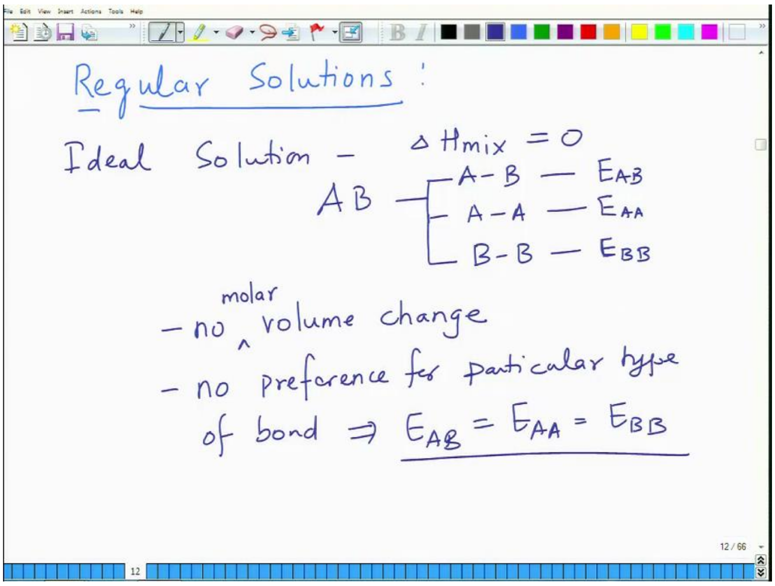

Regular Solutions :

Ideal Solution – $\Delta H_{mix} = 0$

AB
- A – B — E_{AB}
- A – A — E_{AA}
- B – B — E_{BB}

– no molar volume change

– no preference for particular type of bond $\Rightarrow \underline{E_{AB} = E_{AA} = E_{BB}}$

Now, from ideal solution, let us move onto what we call as regular solutions. Now, why do we want to study regular solutions is that, because we said that

for ideal solution $\Delta H_{mix} = 0$. Now, what this mean, what did this mean well this meant that in the in the solid solution of A, B; there was no preference for A B bonds or A A bonds or B B bonds, because the bond energies of all these three bonds were equal. So, if you have A A B solid solutions, A B solid solution will, if it is a random solid solution, you will have A-B bonds; you will have A-A bonds; and you will have B-B bonds. So, correspondingly you will have bond energy E_{AB}, you will have bond energy E_{AA}, and you will have bond energy E_{BB}.

So, delta H mixing is 0, because there is no change in the internal energy and that is, because there was there was; first of all there was no volume change, molar volume change. And there was no preference for particular type of bond, so which means probability of having A B bond is same as probability of having A A bond, which is same as probability of having B B bond. What it meant was basically $E_{AB} = E_{AA} = E_{BB}$. So all three bond energies are equal to each other, as a result there is complete randomization.

And also, there were no other electronic and structural changes, which may happen because a different; say for a different atomic sizes, different; there could be minute difference in electronegativities, there could be difference in electronic configurations etcetera. So, there were no, so it was ideal to; you put two atoms, this is randomly mix into each other, sizes are equal, structure is same electronegativities are same. So, there is no change in the internal energy of the system.

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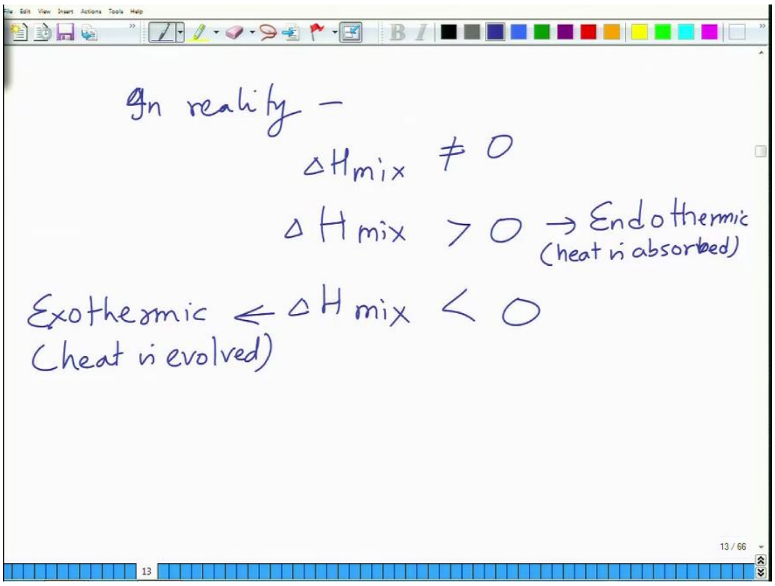

In reality –

$\Delta H_{mix} \neq 0$

$\Delta H_{mix} > 0 \rightarrow$ Endothermic (heat is absorbed)

Exothermic $\leftarrow \Delta H_{mix} < 0$ (heat is evolved)

But life is far from easier, so in reality this does not happens. In reality, what we have is, delta H mixing; in reality, for most cases, $\Delta H_{mix} \neq 0$, it is either greater than 0 or less than 0. So, ΔH_{mix}, so when you have $\Delta H_{mix} > 0$, the process of making the solid solution undergoes a reaction, which is endothermic, which means heat is absorbed. And if $\Delta H_{mix} < 0$, then we call it exothermic, which means heat is evolved, so that is the reality of things.

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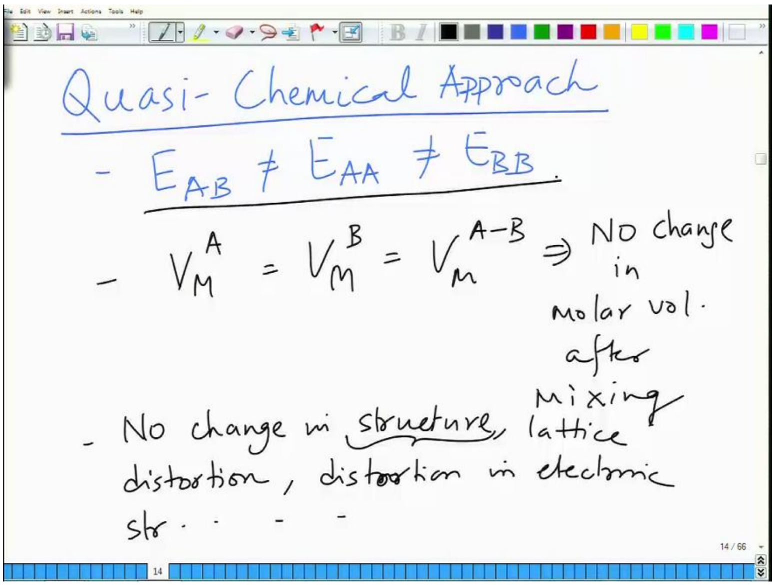

Quasi- Chemical Approach

- $E_{AB} \neq E_{AA} \neq E_{BB}$.
- $V_M^A = V_M^B = V_M^{A-B}$ $\Rightarrow$ No change in molar vol. after mixing
- No change in structure, lattice distortion, distortion in electronic str. . . - -

And in this context, when we take a formalism; when we build formalism about it, we take approach called as quasi-chemical approach. So, what do we do in this quasi approach, first thing is

$$E_{AB} \neq E_{AA} \neq E_{BB},$$

and that is because they are different atoms. So, when they are different atoms the bond energy of A, bond energy of B, and bond energy of A B, are not same as each other. However, for the sake of simplicity, we take

$$V_M^A = V_M^B = V_M^{A-B}$$

We do not take any change in the; no change in molar volume, after mixing ok.

And there are other things like; you know there is no change in structure. And you can say lattice distortion, no change in the structure by mean that you know, it has a; both of them were cubic, it remains cubic I mean, but there could be subtle variations within the cubic system itself. So, or you can have distortion in the electronic structure etcetera, etcetera. So, basically we are taking again slightly non-idealized situation that is, these three are different, the bond energies are different, other than that it is still fairly ideal.

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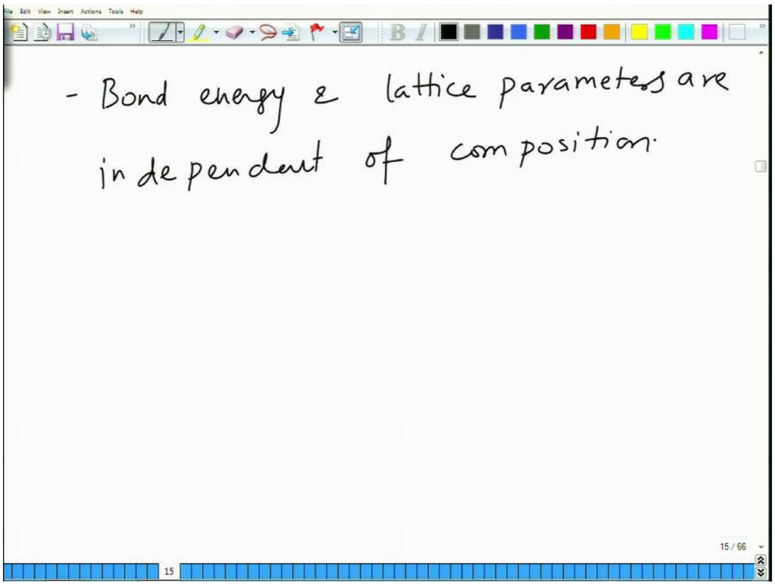

- Bond energy & lattice parameters are independent of composition.

And another thing is that the bond energy and lattice parameter are independent of composition. So, all we have made a difference with respect to a regu(lar); ideal solution is that, we have taken the bond energies to be different for A A, A B and B B bonds. Having assuming having assuming this, we will now move forward to determine the free energy of a regular solution, vis-a-vis the changes in the free energy of mixing. So, we will stop here in this lecture. We will develop this approach in the next lecture, and try to understand, what is its implication in terms of free energy?

So, thank you.