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

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Lecture - 09
Activity and Thermodynamics of Regular Solution

So welcome to this new lecture, lecture number 9 in Phase Equilibria course. So, we will just recap what we did in the last class.

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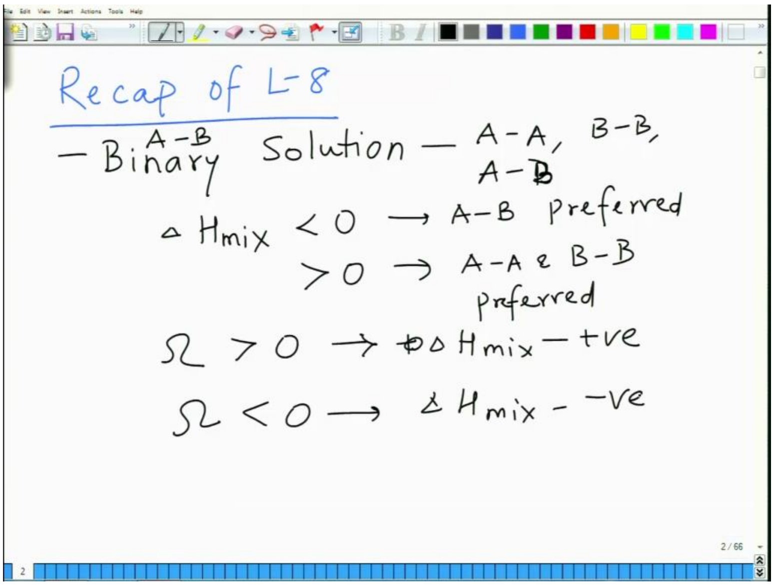

Recap of L-8

— $\overset{A-B}{\text{Binary}}$ Solution — A-A, B-B, A-B

$\Delta H_{mix} < 0 \rightarrow$ A-B preferred

$> 0 \rightarrow$ A-A & B-B preferred

$\Omega > 0 \rightarrow \Delta H_{mix}$ — +ve

$\Omega < 0 \rightarrow \Delta H_{mix}$ - −ve

So, in the last lecture we were talking about binary solutions which are non-ideal. So, non-ideal will mean that you have 3 kinds of bonds. If you have A B binary solution, let us say A B. Then you have 3 kind of bonds A-B B-B and A-B. And depending upon whether or not they, A and B have affinity for each other that is determined by ΔH_{mix}.

So, depending upon whether this is positive or negative. So, if it is negative then you will have preference for A B bonds. And if you have positive then AA and BB bonds are preferred. And this is manifested by another parameter interaction parameter which is Ω. So, if it is greater than 0 then you have positive ΔH_{mix}, and if we this is less than 0 then ΔH_{mix} is negative.

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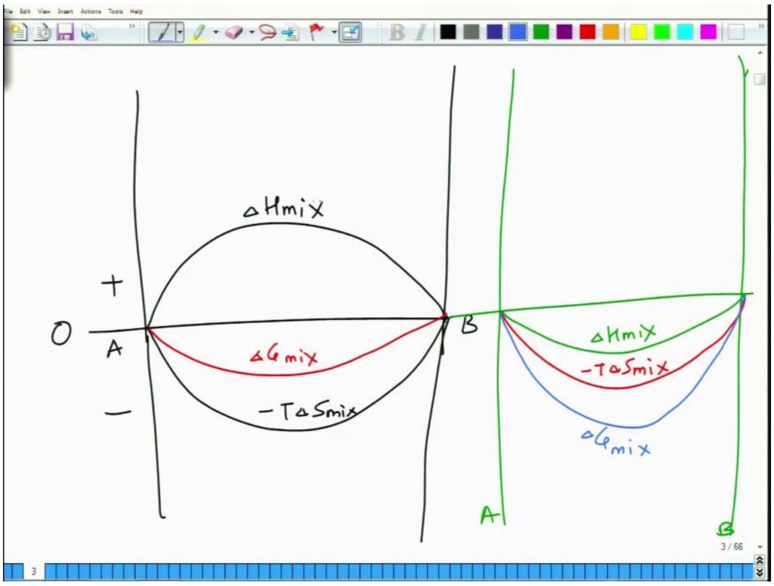

And depending upon these parameters you have; so, if you if you draw the free energy versus composition. So, if you plot let us say this is X B sorry.

So, if ΔH_{mix} is positive, then this is what ΔH_{mix} going to look like ok. So, this is ΔH_{mix}, and this is 0. So, this is positive this is negative; however, $-T\Delta S_{mix}$ will look something like that. This is $-T\Delta S_{mix}$. And eventually the free energy of mixing may look something like what you have in between. So, it might look, so, this might be ΔG_{mix}.

So, depending upon the, now you can have another situation in which you know delta H mix is negative. So, if I draw another plot here for instance. So, you have another plot in which A and B are there. And delta if ΔH_{mix} is negative. So, this is ΔH_{mix}, and if you have, this is delta $-T\Delta S_{mix}$.

And eventually the free energy will be even further lower, because both of the terms are negative so, this is ΔG_{mix}. So, you can see the driving force, that is ΔG_{mix}, changes depending upon the relative magnitudes of ΔH_{mix} and $-T\Delta S_{mix}$, with respect to each other. So, if ΔH_{mix} is negative which means the driving force for making a solid solution is higher, but if ΔH_{mix} is positive the driving force for making the solid solution is lower; however, even at higher ΔH_{mix}, it turns out that in certain cases, where you have situations like this.

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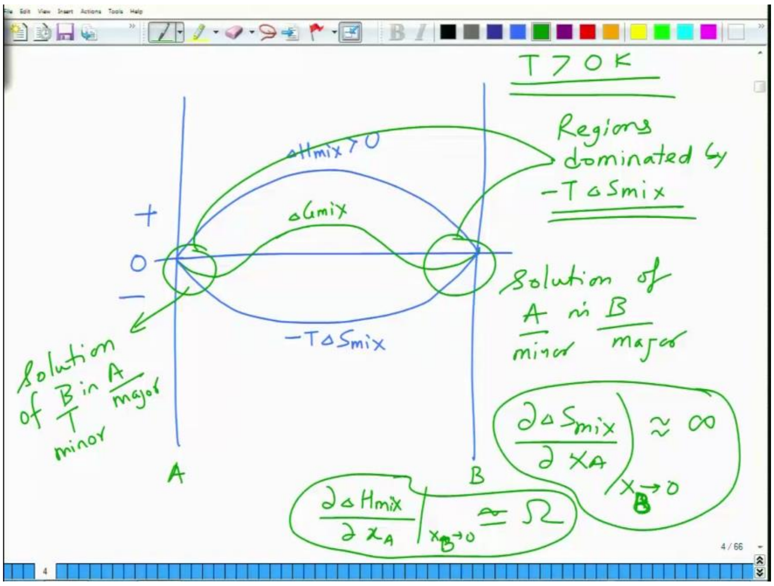

So, positive negative; so, here ΔH_{mix} is greater than 0 and it is positive.

And $-T\Delta S_{mix}$ is also, it is negative, but it is not usually negative because the temperature maybe lower. As a result, the ΔG_{mix} plot will have a behavior something like this. So, it will not make a solid solution for throughout the composition range, but it will make a solid solution of A and B, and B and A. So, what this tells you is that even though ΔH_{mix} is higher and $-T\Delta S_{mix}$ is not so negative. The ΔG_{mix}, when the system, when the solutions are dilute, that is, so, this is A, this is B. So, this is solution of, on this side, you will have solution of B in A. So, you have A as major element, and B as minor element.

On this side, you will have solution of A in B. So, B is minor and A is minor and B is major. So, even though they, preference for A B bounds is very low, adding a little bit B in A or adding a little bit A in B, lowers the free energy, and this can be proved by, if you take the derivative for instance of,

$$\left.\frac{\partial \Delta S_{mix}}{\partial X_A}\right)_{X_B \to 0} \approx \infty$$

And

$$\left.\frac{\partial \Delta H_{mix}}{\partial X_A}\right)_{X_B \to 0} = \Omega$$

So, since the change in entropy becomes infinity at pure compositions.

So, when you add very little. So, this is sorry, this is X_B tends to 0, and this is again X_B tends to 0. So, very little amount of X_B. So, at these compositions the; since the free energy changes; entropy change is negative, infinity, the free energy change tends to be, because of entropy because enthalpy changes finite. And the entropy changes infinite as a result of free energy tends to be negative at so, basically these are the regions which are dominated by, you can say, regions dominated by $-T\Delta S_{mix}$contribution.

So, configurational entropy changes a lot when you add little bit of impurity in something. So, you add little bit of B into A or little bit of B into A, the configurational entropy changes substantially. As a result, even at lower temperatures, impure material is preferred over pure state because of negative free energy of mixing in the impurity state dominated by the changes in the entropy.

And so, as long as T > 0 K as long as T > 0 K, the ΔG_{mix}will always decrease for a pure component, if you add little bit of impurity to it. That is why in nature pure things do not exist. Always everything will always consist of minute amounts of impurities which will lower the free energy of that particular phase resulting in negative ΔG_{mix}. And which is mainly dominated by the entropy term or the enthalpy term, and this is because of changes in configurational entropy.

You can work this out using the ΔS_{mix} expression and ΔH_{mix} expression which I have showed before. So, these 2 expressions, the balance between these 2 these 2 entities, ΔS_{mix} and ΔH_{mix}will determine negative free energy of mixing at impure, in the impure states.

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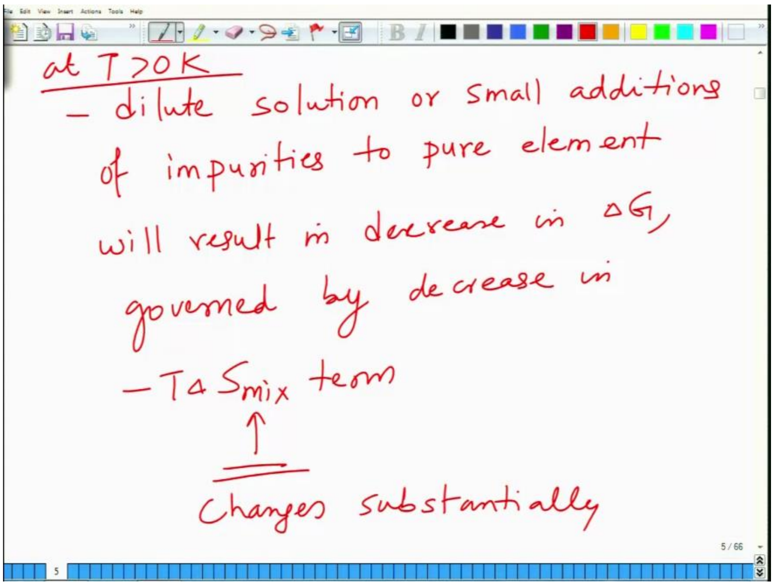

at $T > 0\,K$

– dilute solution or small additions of impurities to pure element will result in decrease in ΔG, governed by decrease in

$-T\Delta S_{mix}$ term

$\uparrow$

Changes substantially

So, basically what you say that is; so now, you know it is a recap is over. So, what we have here is basically that, what we are concluding here is that dilute solutions, or small additions of to pure element will result in and decrease in ΔG dominated by governed by decrease in $-T\Delta S_{mix}$. And mainly it is the configuration entropy that changes. So, as long as T > 0 Kelvin.

When you add impurity to a pure phase, pure metal or material pure element, impurity addition leads to changes in, leads to negative free energy of mixing which means impure phase becomes more stable as compared to pure phase, and this is mainly dominated by increase in the configurational entropy as a result $-T\Delta S_{mix}$ become more negative. And, however, this is only true about the dilute solutions. Not about the highly impure solutions. So, in very very small, the impurity has to be present in a small quantities, of course, the relative change will be governed by the value of ΔH_{mix} as well, but even though ΔH_{mix} is very positive, and every system can tolerate small amount of impurities in it driven by thermodynamic changes.

So now let us move to another concept. So, what we have done is we have learnt about chemical, we have, basically we have started from ideal solutions. And following that we have discussed; discussed the; so, we have we have discuss the change in entropy, change in free energy of mixing in ideal solutions. And then we invoke the concept of chemical potential, which is basically the changes in the free energy when minute additions are made to an alloy of A or B let us say.

And then we looked at, what happens when the solution is not ideal, it is a regular solution which has, whose delta, whose enthalpy of mixing is not 0. So, ΔH_{mix} is not 0 rather it is positive and negative. So, depending upon the magnitude of ΔH_{mix}, and corresponding changes in $-T\Delta S_{mix}$, you will have a system's stability predicted.

But in many cases wherever ΔH_{mix} is negative, and you will always have stable solid solution. And even though ΔH_{mix} is positive, depending upon the temperature and configurational entropy changes. you will you will have either complete range of solid solution which is thermodynamically stable, or at least at the ends of A and B, you will have thermodynamic stability of impure phases. So, this is what we have discussed so far, in this lecture, now we take forward; we take this forward by introducing another concept called as activity.

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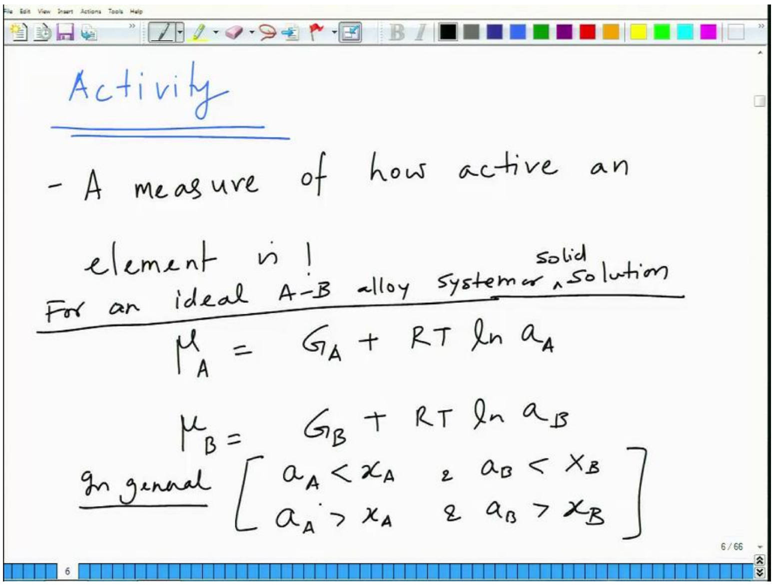

Activity

- A measure of how active an element is!

For an ideal A-B alloy system or solid solution

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

$$\mu_B = G_B + RT \ln a_B$$

In general $\left[\begin{array}{l} a_A < x_A \ \& \ a_B < x_B \\ a_A > x_A \ \& \ a_B > x_B \end{array} \right]$

So, activity is basically very similar to chemical potential, it is a measure of how active an element is. So, basically it is going to, it determines whether or not that particular element would like to stay in the solution phase, or it would like to come out of solution phase. So, depending about the magnitude of this activity, the solutions are made stable or unstable.

So, basically one can define activity in such a manner so that chemical potential is related to activity as

$$\mu_A = G_A + RT\ln(a_A) \text{ and } \mu_B = G_B + RT\ln(a_B)$$

This is for an ideal A-B alloy, alloy system or basically or solution, solid solution, alright.

So, $\mu_A = G_A + RT\ln(a_A)$ and $\mu_B = G_B + RT\ln(a_B)$

we have replaced X_A and X_B by a term called as activity which is a_A and a_B. Now, in general

$$\begin{bmatrix} a_A < x_A \,\&\, a_B < x_B \\ a_A > x_A \,\&\, a_B > x_B \end{bmatrix}$$

So, depending upon how active the element is, your activity can be higher or lower than the atomic fraction of that particular element in the alloy.

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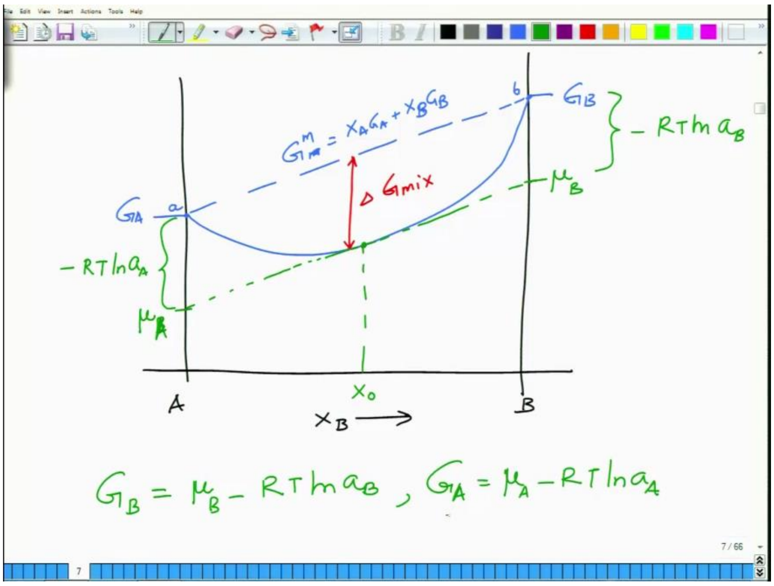

$G_B = \mu_B - RT\ln a_B$, $G_A = \mu_A - RT\ln a_A$

So, in general they are not equal to X_A and X_B, A-A is not equal to X_A. And graphically how do you represent it? It is like this, you make a plot of free energy versus composition. A B in this direction you have X_B varying. So, when you plot let us say free energy of an alloy, alright this is let us say point a, this is point b. And this line gives the rule of mixture free energy of alloy.

So, basically this is you can say $G_m^M = X_A G_A + X_B G_B$ before mixing, alright. This point is G_A, this point is G_B. And in reality you from a mixture which is table, as a result this is what is ΔG_{mix}. And this is what we have done earlier. Activity is determined by, so, you take a, so, you draw a common tangent. You draw a tangent, and this tangent intercepts on; so, correspondingly you will have a chemical potential for a given composition, let us say this is X naught. So, correspondingly you have chemical potential of A and chemical potential of B.

So, for this alloy of composition X naught, the chemical potential of A is μ_A and chemical potential of B is μ_B in the in the alloy, for this particular composition. and correspondingly this term is $-RT\ln(a_A)$ and this term is $-RT\ln(a_B)$. So, you can see that in the previous relation, the

$$G_B = \mu_B - RT\ln(a_B) \text{ and } G_A = \mu_A - RT\ln(a_A)$$

So, depending upon the activities, now we will see, how the, how these 2, these things add up. So, this is how we define activity for a, now.

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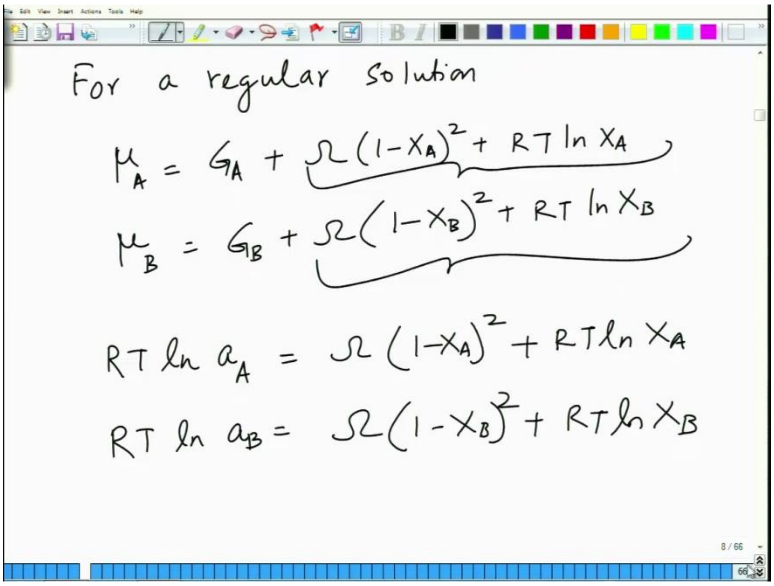

For a regular solution

$$\mu_A = G_A + \underbrace{\Omega(1-X_A)^2 + RT\ln X_A}$$

$$\mu_B = G_B + \underbrace{\Omega(1-X_B)^2 + RT\ln X_B}$$

$$RT\ln a_A = \Omega(1-X_A)^2 + RT\ln X_A$$

$$RT\ln a_B = \Omega(1-X_B)^2 + RT\ln X_B$$

For a regular solution we know, we know that

$$\mu_A = G_A + \Omega(1 - X_A)^2 + RT\ln(X_A) \text{ and } \mu_B = G_B + \Omega(1 - X_B)^2 + RT\ln(X_B)$$

Of this term and this term, they are what become equal to RT l n. So,

$RT\ln(a_A) = \Omega(1 - X_A)^2 + RT\ln(X_A)$ and $RT\ln(a_B) = \Omega(1 - X_B)^2 + RT\ln(X_B)$

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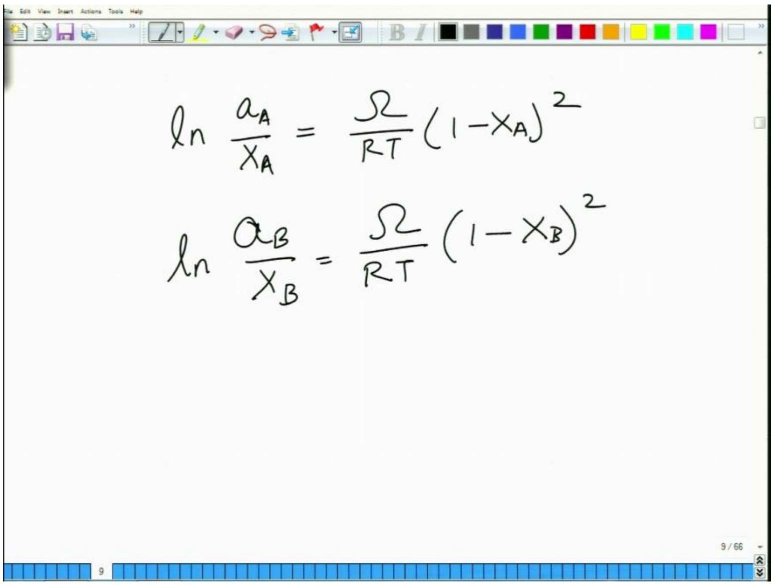

$$\ln\frac{a_A}{X_A} = \frac{\Omega}{RT}(1-X_A)^2$$

$$\ln\frac{a_B}{X_B} = \frac{\Omega}{RT}(1-X_B)^2$$

So, if I, if you now simplify this, what you get is,

$\ln\left(\frac{a_A}{X_A}\right) = \frac{\Omega}{RT}(1 - X_A)^2$ and $\ln\left(\frac{a_B}{X_B}\right) = \frac{\Omega}{RT}(1 - X_B)^2$

And this is assuming that A and B have similar structure.

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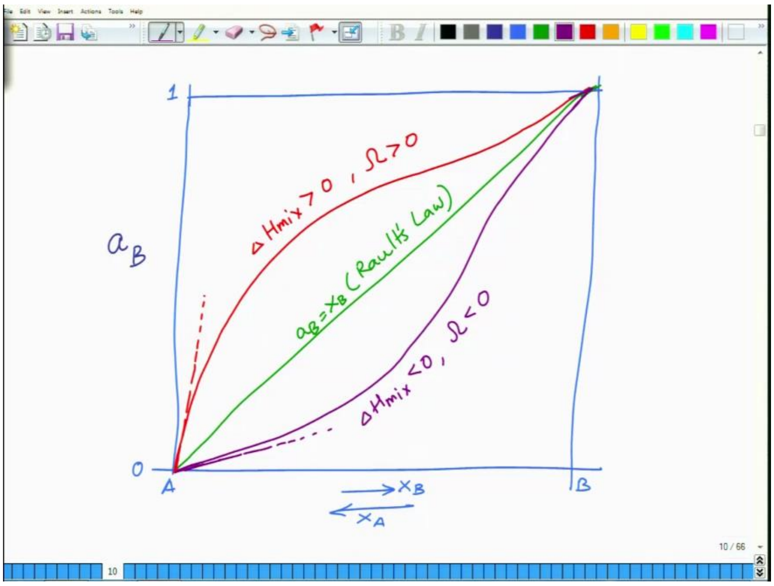

So now, if you plot these activities as a function of composition; so, this is as a function of composition. So, let us say this is 1, this is 0, this is pure A, this is pure B. So, this is X_B and this is X_A. So, first thing I plot is A B, the activity of B in A, ok. For ideal solution, the activity of a A, a B is equal to X_B. And this is basically given by what we call as Raoult's law. And depending upon, now ΔH_{mix}, whether it is positive or negative, the activity deviates. So, if you have a non-ideal solution, then so, this is for delta H mix greater than 0. Which means, the B is more active, A and B do not mix. So, when $\Delta H_{mix} > 0$, which means elements are more active. They do not like to, they do not like to stay in the bound form, they rather prefer independent forms as a result, their activity is higher, ok.

And we will come back to the slope later on. So, basically this is $\Delta H_{mix} > 0$, and second state, that you might have is the other way round, when you have, when you have $\Delta H_{mix} < 0$. So, in such a situation, when A and B bonds are preferred when A and B are not very active, as a result the activity of B for instance, is lower than it's mole fraction; which is determined by the ideal solution Raoult's law. In this case, the activity is lower because of $\Delta H_{mix} < 0$. And again you can draw a slope at this point. So, this is 100 percent B, this is dilute solution when B is very small, ok.

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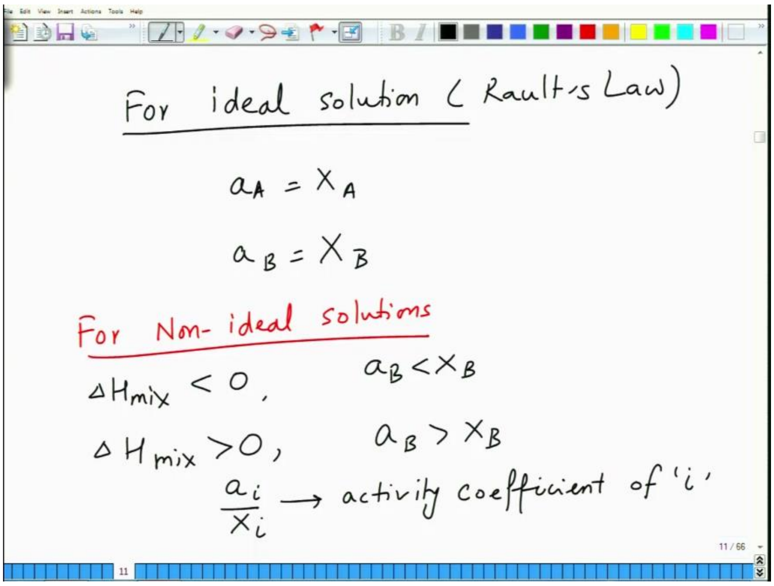

For ideal solution (Rault-s Law)

$$a_A = X_A$$

$$a_B = X_B$$

For Non- ideal solutions

$\Delta H_{mix} < 0$, $a_B < X_B$

$\Delta H_{mix} > 0$, $a_B > X_B$

$\frac{a_i}{X_i} \longrightarrow$ activity coefficient of 'i'

So, we can say that for ideal solution, you can have, which is basically Raults law, $a_A = X_A$ and $a_B = X_B$. And for non-ideal solutions to say if

$$\Delta H_{mix} < 0, \quad a_B < X_B$$

$$\Delta H_{mix} > 0, \quad a_B > X_B$$

$$\text{so } \frac{a_i}{X_i} \rightarrow \text{Activity coefficient of 'i'}$$

So, you can see that when element is in ideal solution. So, this activity will be γ_i.

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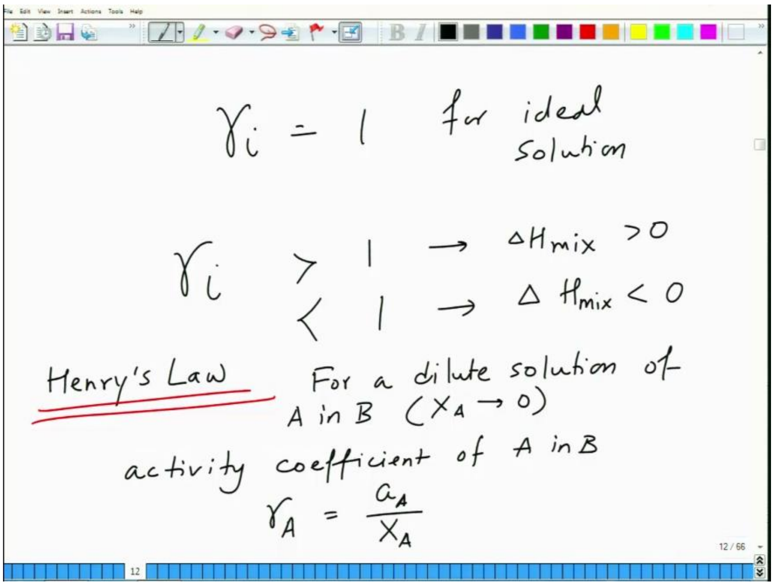

$\gamma_i = 1$ for ideal solution

γ_i $> 1 \rightarrow \Delta H_{mix} > 0$

$< 1 \rightarrow \Delta H_{mix} < 0$

Henry's Law For a dilute solution of A in B $(X_A \to 0)$

activity coefficient of A in B

$\gamma_A = \frac{a_A}{X_A}$

So, $\gamma_i = 1$ for ideal solution. And γ_i will be greater than or less than 1 depending upon, So, it will be later, when $\Delta H_{mix} > 0$. And it will be less than 1, when $\Delta H_{mix} < 0$.

And this is what is called as Henrys law. So, Henrys law says that, for a dilute solution of, let us say A in B; that is, $X_A \to 0$, the activity coefficient of A in B that is

$$\gamma_A = \frac{a_A}{X_A}$$

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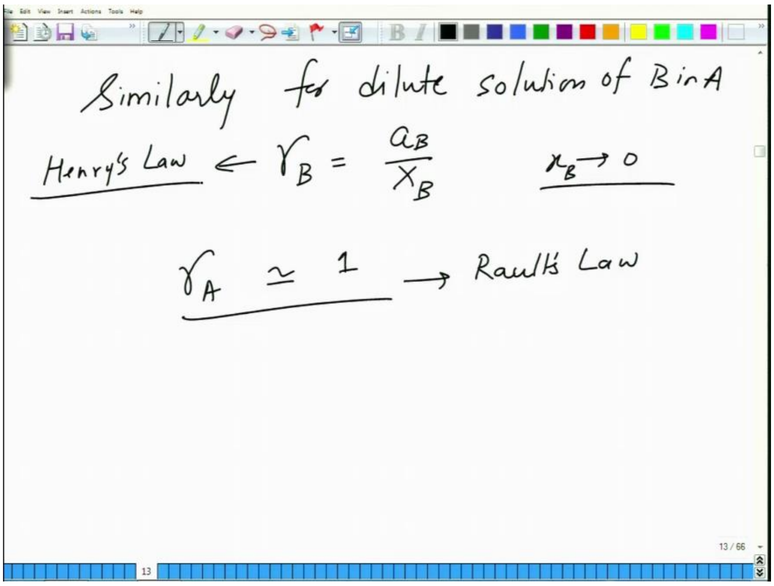

Similarly for dilute solution of B in A

Henry's Law $\leftarrow \gamma_B = \frac{a_B}{X_B}$ $x_B \to 0$

$\gamma_A \simeq 1 \rightarrow$ Rault's Law

Similarly, for a dilute solution of B in A when $X_B \rightarrow 0$, activity coefficient of B in A would be

$$\gamma_B = \frac{a_B}{X_B}$$

gamma B, that is equal to a B by X B. So, similarly for dilute solution of B in A

$$\gamma_B = \frac{a_B}{X_B}$$

So, for this solution your when $X_B \rightarrow 0$ so, this is basically $X_B \rightarrow 0$. And $\gamma_a = 1$.

So, A, the majority element will act as if it is, like a ideal think, and where as the minority element which is a dilute element will act as a, as per the Henrys law. So, this is this will act as per Raoult's law, and this will act as per Henry's law.

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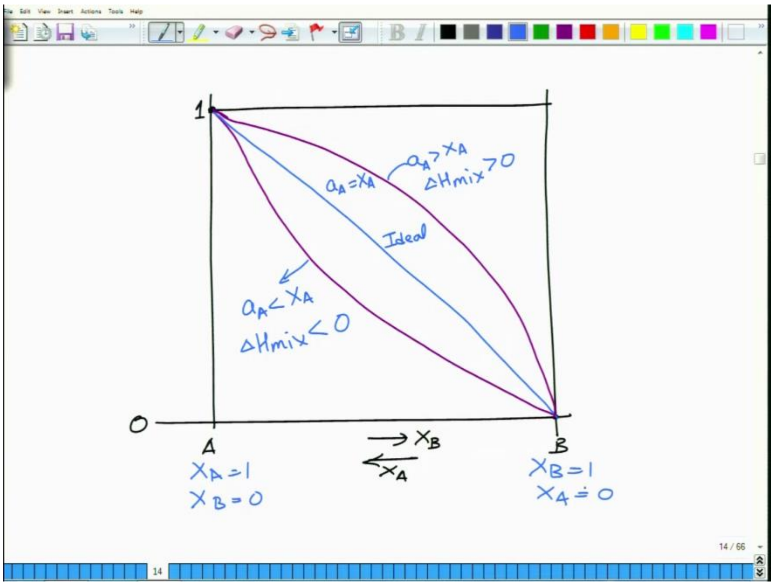

You can also plot similarly, the a_A with respect to X. So, this is 1, this is 0, this is pure A. So, this is X_B, this is X_A. So, for a pure element a_A will be here, for pure B, a_A will be equal to 0. So, ideal case would be, I am sorry so, this would be a straight line when it is ideal. So, this is a_A is equal to X_A. For, now you can have 2 more cases, the first case could be like this, the second case could be like this.

So, in this case, this is $a_A > X_A$ when $H_{mix} > 0$. And this is $a_A < X$ A, when $H_{mix} > 0$. So, this is at this point your X_A is 1, and X_B is 0, at this point X_B is 1 and X_A is 0. So, this is how it will vary.

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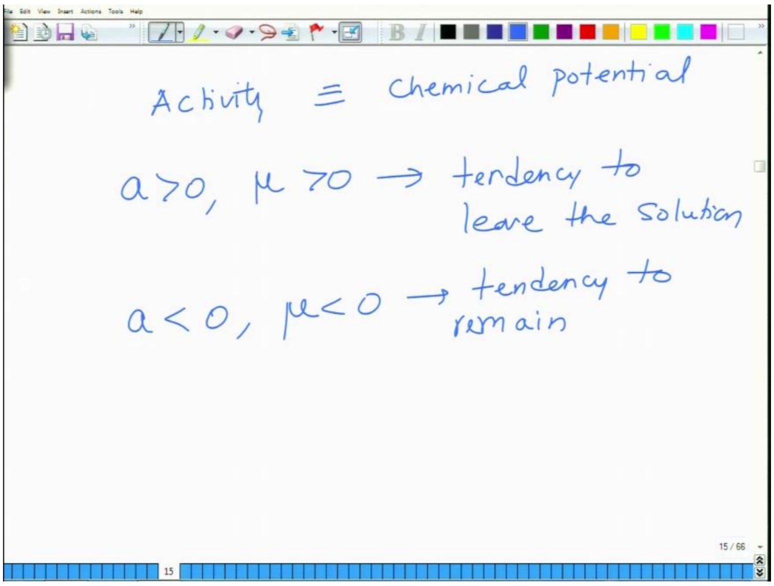

Activity $\equiv$ Chemical potential

$a > 0$, $\mu > 0$ → tendency to leave the Solution

$a < 0$, $\mu < 0$ → tendency to remain

So, in this; so, basically the activity of an element is equivalent to chemical potential. So, it tells you that basically both of them tell about a state of that component in the system. Both basically measure the tendency of the element to leave or remain in the system, ok.

So, if your $a > 0$, it means $\mu > 0$, which means tendency to leave the solution. And if $a < 0$, $\mu < 0$, it is tendency to remain. And basically what it means is that when a is very, when a is large and μ is large, the partial pressure of that element is high, and when a is small μ is small, the partial pressure of that element is low. So, this tells you about the propensity of the element to remain or leave the system, both these activity and chemical potential. So, we will stop here in this lecture. We will start the next lecture with further moving onto the real solutions. So, we have looked ideal and regular solutions. Now we will be looking in the real solutions.

Thank you.