Chemical and Biological Thermodynamics: Principles to Applications

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Lecture - 20
Thermodynamics of mixing, Excess functions

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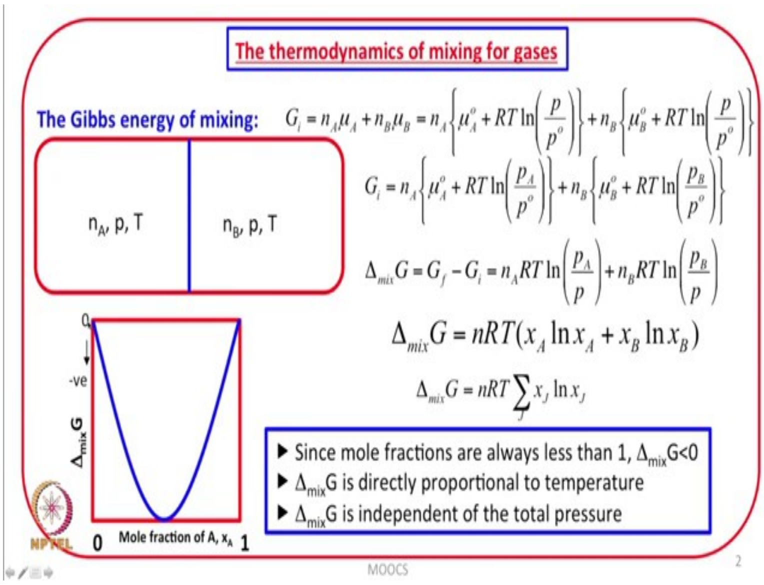

The thermodynamics of mixing for gases

The Gibbs energy of mixing: $G_i = n_A\mu_A + n_B\mu_B = n_A\left\{\mu_A^o + RT\ln\left(\frac{p}{p^o}\right)\right\} + n_B\left\{\mu_B^o + RT\ln\left(\frac{p}{p^o}\right)\right\}$

$$G_i = n_A\left\{\mu_A^o + RT\ln\left(\frac{p_A}{p^o}\right)\right\} + n_B\left\{\mu_B^o + RT\ln\left(\frac{p_B}{p^o}\right)\right\}$$

$$\Delta_{mix}G = G_f - G_i = n_A RT\ln\left(\frac{p_A}{p}\right) + n_B RT\ln\left(\frac{p_B}{p}\right)$$

$$\Delta_{mix}G = nRT(x_A\ln x_A + x_B\ln x_B)$$

$$\Delta_{mix}G = nRT\sum_J x_J\ln x_J$$

- Since mole fractions are always less than 1, $\Delta_{mix}G<0$
- $\Delta_{mix}G$ is directly proportional to temperature
- $\Delta_{mix}G$ is independent of the total pressure

In this lecture, we will discuss on thermodynamics of mixing both for ideal solutions or ideal mixing and non-ideal mixing. First of all, let us discuss the case of gases perfect gases. And after that we will move towards the liquid form the solutions form. Let us consider this figure. Let us consider these two chambers. On the left hand chamber, let us consider a gas in which n A number of moles of gas at pressure p and T are enclosed; and on the right hand side of the chamber, you have n B number of moles of gas B at pressure p and T. We want to develop equations for the thermodynamic changes in thermodynamic properties when this partition is removed or when these two gases are allowed to mix. To begin with we will develop equations for perfect gases. If you look at the figure here, the partition is there which separates gas A from gas B. However, the total Gibbs function of the system - combined system can be expressed in terms of chemical potential that we have discussed in the previous lecture.

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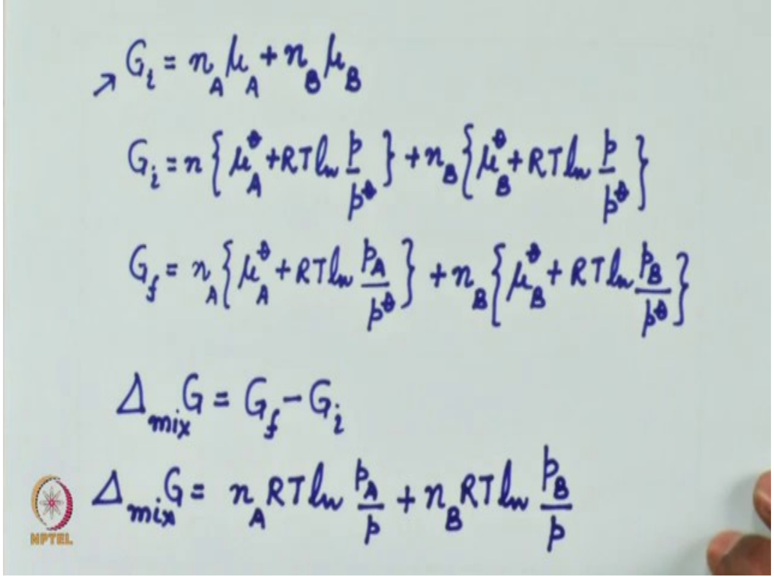

$$\nearrow G_i = n_A \mu_A + n_B \mu_B$$

$$G_i = n \left\{ \mu_A^{\ominus} + RT \ln \frac{p}{p^{\ominus}} \right\} + n_B \left\{ \mu_B^{\ominus} + RT \ln \frac{p}{p^{\ominus}} \right\}$$

$$G_f = n_A \left\{ \mu_A^{\ominus} + RT \ln \frac{p_A}{p^{\ominus}} \right\} + n_B \left\{ \mu_B^{\ominus} + RT \ln \frac{p_B}{p^{\ominus}} \right\}$$

$$\Delta_{mix} G = G_f - G_i$$

$$\Delta_{mix} G = n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p}$$

That initial Gibbs function will be equal to since there are n A number of moles of A chemical potential of A is mu A then you have n B number of moles of B and chemical potential is B. Before these gases are allowed to mix, both the gases are in their pure form, they are not mixed, they are in separately, but both are perfect gases. so therefore, I can for mu A, I can write mu A is equal to mu A naught plus R T log p by p naught, because pressure is p naught it is given plus n B and inside I can write mu B naught plus R T log p by p naught pressure is p.

Now, let us allow these gas system mix. Let us take a look at the figure. What we have done is that when these gases were not mixed then the total initial Gibbs function is n A times mu plus n B times mu B. And since pressure is same on both sides for mu A, B written mu a naught plus R T log p by p naught plus n B into mu B naught plus R T log p by p. Now, let us remove this partition once you remove this partition, these gases will mix with each other. However, since the pressure on both sides is same, there is going to be no change in pressure, there is going to be no change in temperature, but how will the Gibbs functions change.

Let us now again work on it. The final Gibbs function, I will again act on this equation n A and expand mu A, it is going to be mu A naught plus R T log. Now, since both the gases are mix, I will talk in terms of partial pressures partial pressure of A in the mixture plus n B into mu B naught plus R T log partial pressure of B in the mixture by p naught.

Note the changes. When the partition was not removed, the pressure on both sides was p; when the partition is removed although the total pressure remains p, but each gas will exert its own partial pressure in the mixture. So, instead of p here in final after mixing, it will be partial pressure. And free energy of mixing will be equal to G final minus G initial. So we need to subtract this from this. And when you subtract the two the resulting equation is going to be many quantities will get cancelled what we will be left over with is n A R T log p A by p plus n B R T log p B by p.

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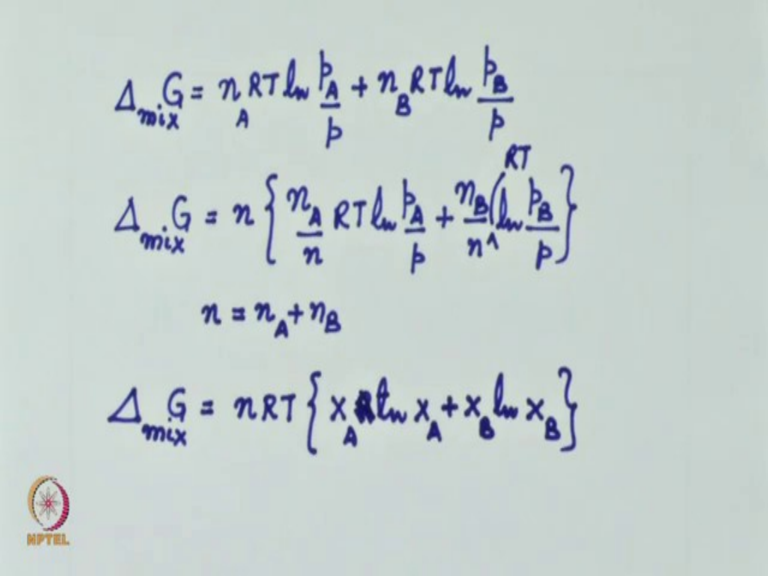

$$\Delta_{mix} G = n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p}$$

$$\Delta_{mix} G = n \left\{ \frac{n_A}{n} RT \ln \frac{p_A}{p} + \frac{n_B}{n} \overset{RT}{\wedge} \left(\ln \frac{p_B}{p} \right) \right\}$$

$$n = n_A + n_B$$

$$\Delta_{mix} G = nRT \left\{ x_A \ln x_A + x_B \ln x_B \right\}$$

So, what we have up to this point is that delta mixing g is equal to n A R T log p A by p plus n B R T log p B by p. Let me further simplify it n n A by n R T log p A by p plus n B by n log p B by p. What I have done is n total number of moles, which is n A plus n B. I have divided and multiplied by the same number. Now, this will allow me to write the equation in this form delta G mixing is n. If I take RT, there is an R T over here common n R T inside what I have n A by n which is mole fraction of A into R T or R T is taken out. What I have is now x A into log p A by p, p A by p Daltons law of partial pressure p A by p is mole fraction of A plus x B log p B by p Daltons law of partial pressure, it is x B. What i have delta g mixing is n R T x A log x A plus x B log x B.

Let us take a look at now the figure that we have derived this equation delta G mixing by taking the subtraction or difference of G final minus G initial and we have derived this equation delta mixing g is equal to n R T x A log x A plus x B log x B. Since this is for a two component system if there are more components, I can generalize this equation into n RT summation J x J log x J where J is the species J. The point to be noted let us say if we look at this expression, mole fraction is always less than one if mole fraction is less than one then logarithmic term will become negative. log x A will be negative log x B will be negative and overall free energy of mixing is going to be negative, and that is consistent with that the system tend towards lower energy.

So, delta G mixing in all proportions because mole fraction is always going to be less than one in all proportions the gases will be miscible and free energy of mixing is negative. And what we have is these comments. Since mole fractions are always less than 1, delta G mixing will always be negative. Another point to be noted here is that free energy of mixing is directly proportional to temperature. And we do not see any pressure term, therefore delta G mixing is independent of the total pressure. These comments are to be kept in mind. And the behavior of delta G mixing starting from zero to negative, you see as the mole fraction of A increases in the solution delta G mixing first decreases and then starts increasing and throughout the mixing delta g you see in the entire range is negative therefore, the gases are miscible in all proportions.

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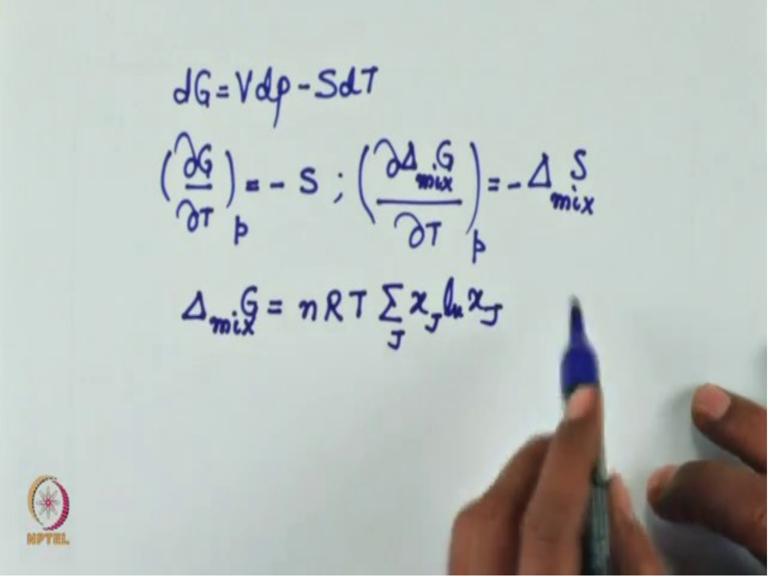

$$dG = Vdp - SdT$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \; ; \; \left(\frac{\partial \Delta_{mix} G}{\partial T}\right)_p = -\Delta_{mix} S$$

$$\Delta_{mix} G = nRT \sum_J x_J \ln x_J$$

After having discussed the free energy of mixing as we always talk about delta G in terms of delta H and delta S. Now, here also let us see what are the enthalpy and entropy contributions to free energy of mixing, and how to get those expressions. We remember that d G is equal to V dp minus S dT. And from here we talked about dou G by dou T at constant pressure is equal to minus S. And this I can write in this form dou mixing of g divide by dou T at constant pressure is equal to minus delta mixing S. So, temperature derivative of free energy of mixing at constant pressure is going to give me an expression for the entropy of mixing. We have just discussed that the free energy of mixing is equal to n R T summation J x J log x J.

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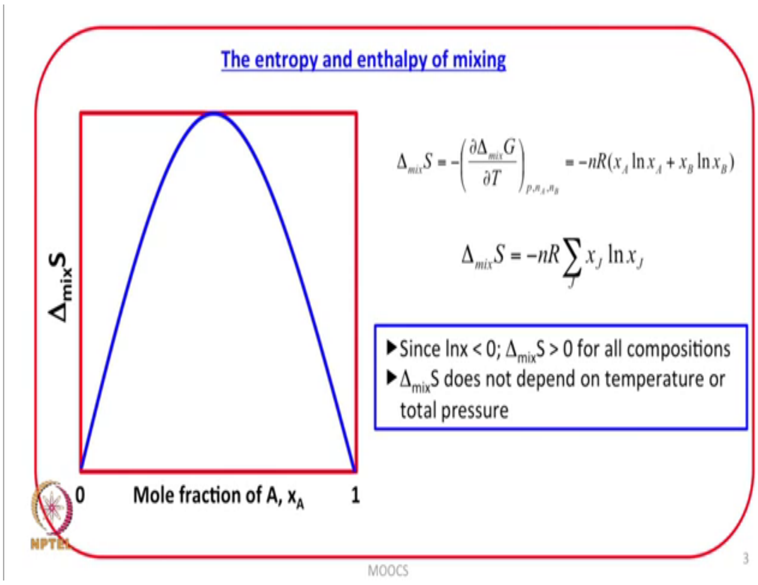

The entropy and enthalpy of mixing

$$\Delta_{mix}S = -\left(\frac{\partial \Delta_{mix}G}{\partial T}\right)_{p,n_A,n_B} = -nR(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta_{mix}S = -nR\sum_J x_J \ln x_J$$

- Since lnx < 0; $\Delta_{mix}S > 0$ for all compositions
- $\Delta_{mix}S$ does not depend on temperature or total pressure

And if I take the temperature derivative of this, the T term from delta G mixing will disappear and delta S mixing will turn out to be minus n R x A log x A plus x B log x B and which for the mixture of A and B delta S mixing will always be positive. Because if you look at this expression logarithmic term x A is less than 1, therefore this is going to be negative quantity, this is going to be negative quantity overall delta S mixing is going to be positive and throughout the composition range you see delta S mixing is positive. So, therefore, this is one of the main this is the main driving force for mixing. In general delta S mixing will be minus n R summation x J log x J. I have just extended this derivation into a general form.

Now, also let us take a look at the comments because log x is a negative quantity delta S mixing for all compositions will be positive. And here again if you see there is no temperature term there is no pressure term, therefore the entropy of mixing does not depend on temperature, does not depend on the total pressure. Since, it is a change therefore, it is not depending upon the initial temperature. When you increase the temperature, decrease the temperature, the amount of increase or decrease in disorder is going to be same. And it is also not depending upon the total pressure.

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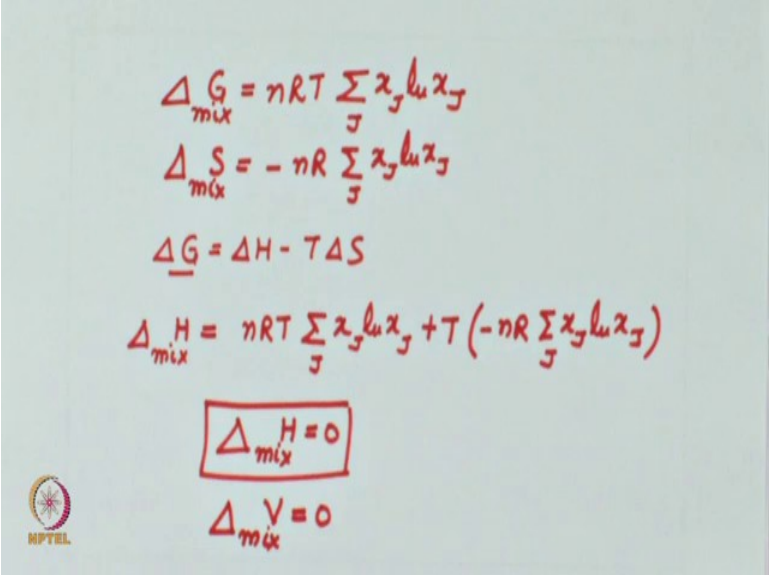

$$\Delta_{mix} G = nRT \sum_J x_J \ln x_J$$

$$\Delta_{mix} S = -nR \sum_J x_J \ln x_J$$

$$\Delta \underline{G} = \Delta H - T\Delta S$$

$$\Delta_{mix} H = nRT \sum_J x_J \ln x_J + T\left(-nR \sum_J x_J \ln x_J\right)$$

$$\boxed{\Delta_{mix} H = 0}$$

$$\Delta_{mix} V = 0$$

How about now delta S is mixing. We discussed that delta G mixing is equal to n R T summation J x J log x J and delta S mixing is minus n R summation J x J log x j. Now, i can use this delta G is equal to delta H minus T delta S. And from this I can derive an equation for enthalpy of mixing which is equal to free energy of mixing which is n R T summation J x J log x J this is for delta G plus T delta S T times delta S is minus n R summation J x J log x J. And you can yourself see that both the terms will cancel and enthalpy of mixing is equal to 0. Obviously, if there are no intermolecular interactions, then the enthalpy of mixing is supposed to be 0. And since there are no intermolecular interactions, we can also write that the volume change is also going to be 0, because any change in volume can arise from intermolecular interactions a discussion which is still pending. We will discuss it a bit later. So, what we discussed is that the entropy of mixing will always be positive whereas, enthalpy of mixing for perfect gas is going to be 0.

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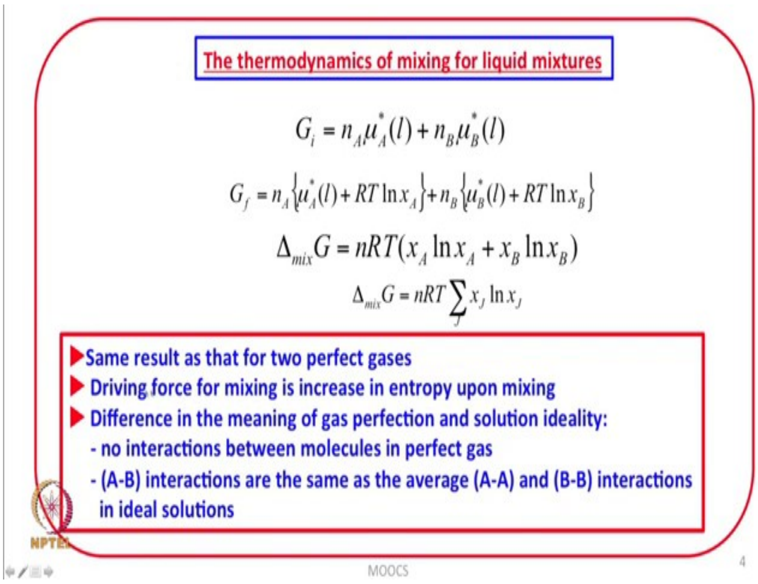

The thermodynamics of mixing for liquid mixtures

$$G_i = n_A \mu_A^*(l) + n_B \mu_B^*(l)$$

$$G_f = n_A \left\{ \mu_A^*(l) + RT \ln x_A \right\} + n_B \left\{ \mu_B^*(l) + RT \ln x_B \right\}$$

$$\Delta_{mix} G = nRT(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta_{mix} G = nRT \sum_J x_J \ln x_J$$

- Same result as that for two perfect gases
- Driving force for mixing is increase in entropy upon mixing
- Difference in the meaning of gas perfection and solution ideality:
  - no interactions between molecules in perfect gas
  - (A-B) interactions are the same as the average (A-A) and (B-B) interactions in ideal solutions

Now, let us talk about the liquid mixtures. For liquid mixtures, the situation is little different, because the gas perfection or ideal gas and the concept of ideal solution are a bit different, because in an ideal gas in a perfect gas there are no intermolecular interactions. However, in an ideal solution, when a solution is to be formed, there has to be interactions between the solute and solvent molecules; otherwise, it will not form a solution.

Let us discuss about that. This is how we have introduced the chemical potential and connection with the Gibbs energy in the beginning. Before mixing initial Gibbs function will be n A times mu A star l plus n B times mu B star l is the same argument as we gave it for while discussing for gases. And it is since I am saying that it is before mixing; that means, both the liquids are pure and I am using star for that all right.

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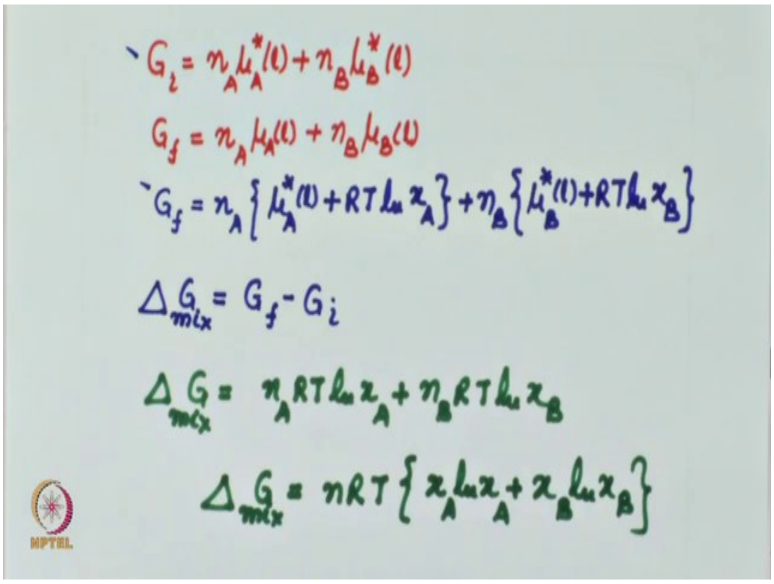

$$G_i = n_A \mu_A^*(l) + n_B \mu_B^*(l)$$

$$G_f = n_A \mu_A(l) + n_B \mu_B(l)$$

$$G_f = n_A \left\{ \mu_A^*(l) + RT \ln x_A \right\} + n_B \left\{ \mu_B^*(l) + RT \ln x_B \right\}$$

$$\Delta_{mix} G = G_f - G_i$$

$$\Delta_{mix} G = n_A RT \ln x_A + n_B RT \ln x_B$$

$$\Delta_{mix} G = nRT \left\{ x_A \ln x_A + x_B \ln x_B \right\}$$

What we discussed is initial Gibbs function is equal to n A times mu A star l plus n B times mu B star l then it is pure. Now, mix them, once you mix them, G final is going to be n A times mu A l removing the star plus n B times mu B times l. Now, what I will do is I will expand this further for G final is equal to n A instead of mu A, I will write the definition of chemical potential for a liquid plus R T log x A we have earlier discussed plus n B then I have mu B star liquid plus R T log x B. And delta mixing G is equal to G final minus G initial. So, this and this need to be subtracted. Once you subtract the two, the resulting equation is going to be n A R T log x A plus n B r T log x B. And by the same arguments as we have discussed for the ideal gases, I can transform this into this form n r T into x A log x A plus x B log x B.

Let us take a look at the slide that is what I was discussing that this is the initial Gibbs function. This is the final Gibbs function. When you take the difference of the two, we get the equation n R T x A log x A plus x B log x B this is what we also earlier derived for the gases. Let us look at the comments. This is the same result as that for two perfect gases. And here also the entropy of mixing will have the same form as for the gases. And enthalpy of mixing will also turn out to be 0 that means, the driving force for mixing is increasing entropy upon mixing.

And as I was earlier commenting on that the difference there is a difference in the meaning of gas perfection and solution ideality. When a gas a for a perfect gas there are no intermolecular interactions; however, for two components to be miscible to form a solution there has to be interaction. So, in a solution formed by mixing a liquid A with liquid B, if average A-A interactions and a B-B interactions that is if A-A interactions and B-B interactions are equal to average A-B interactions then the solution is ideal. And if A-A interactions and B-B interactions are different from A-B interactions then it is a non ideal solution that is what is commented over here. There are no interactions between molecules in perfect gas A-B interactions are same as average A-A and B-B interactions with ideal solutions. That means, if the nature of intermolecular interactions within the solute molecules within the solvent molecules or between solute and solvent molecules are same, then it will form an ideal solution. If these are different then it will form a real solution, a non-ideal solution.

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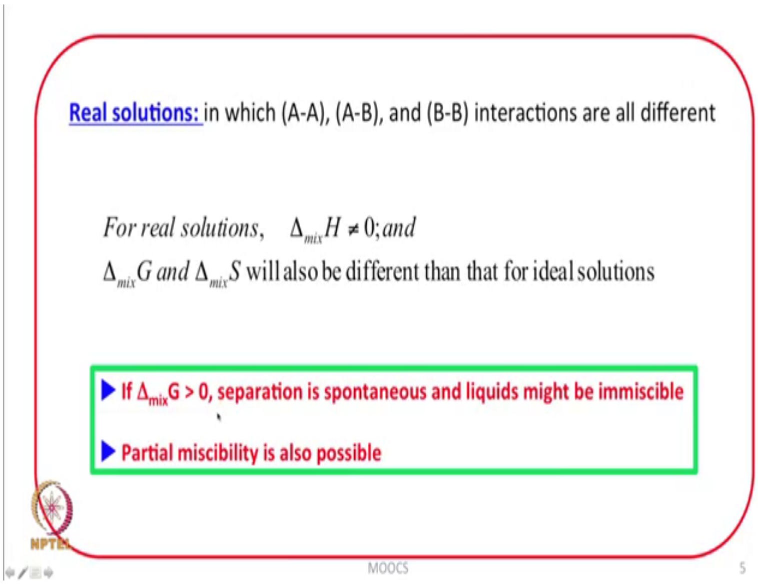

Real solutions: in which (A-A), (A-B), and (B-B) interactions are all different

For real solutions, $\Delta_{mix}H \neq 0$; *and*
$\Delta_{mix}G$ *and* $\Delta_{mix}S$ will also be different than that for ideal solutions

- If $\Delta_{mix}G > 0$, separation is spontaneous and liquids might be immiscible
- Partial miscibility is also possible

So, what is a real solution? A real solution is the one in which A-A, A-B and B-B interactions are all different there is a deviation from ideality. Now, and when we saw the positive deviations or negative deviations from Raoult’s law or Henrys law that is because of the deviations from ideality. For a real solution, the enthalpy of mixing will not be 0, because the interactions are different. If the interactions are different if A is going to interact with B in a different manner than between A-A and B-B then there is going to be net enthalpy of interaction or enthalpy of mixing.

So, delta H mixing will not be 0 and delta G mixing and delta S mixing will also be different than that for the ideal solutions. And if enthalpy of mixing turns out to be positive, positive enthalpy of mixing free energy of mixing, we know that if delta G at constant temperature and pressure is greater than 0 then the reaction is not going to be spontaneous in that direction. And that is what is commented over here that if the free energy Gibbs free energy of mixing is positive, then instead of mixing the component separation is spontaneous and the liquids will be immiscible. And if delta G mixing is positive for a large range, and negative for a small range, then we can call that the solution is partially miscible, partial miscibility is possible.

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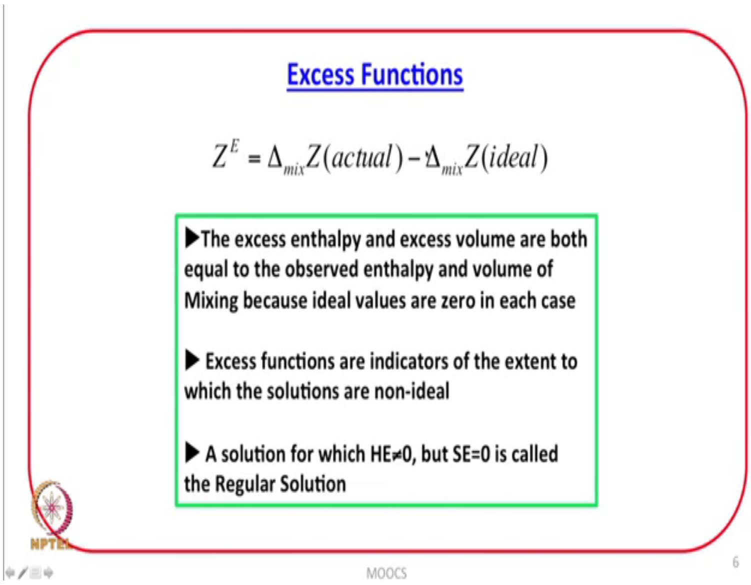

Excess Functions

$$Z^E = \Delta_{mix}Z(actual) - \Delta_{mix}Z(ideal)$$

- The excess enthalpy and excess volume are both equal to the observed enthalpy and volume of Mixing because ideal values are zero in each case
- Excess functions are indicators of the extent to which the solutions are non-ideal
- A solution for which HE≠0, but SE=0 is called the Regular Solution

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This deviation from ideality leads to another terminology, which is called excess functions. And as the name suggests excess function means excess over something excess over what excess over ideality. So, the consistent with the terminology, the definition of an excess function is if I say Z is any property, excess Z is equal to delta Z mixing actual, actual means experimental minus delta Z mixing ideal. Delta Z mixing actual will be experimentally determined and delta Z mixing ideal will be as predicted by the various equations that we developed today.

Now, let us look at the comments. Since, in an ideal case delta H mixing is 0, delta V mixing is 0, therefore excess enthalpy and excess volume are both equal to the observed enthalpy and volume of mixing. Whatever we experimentally determine in case of delta

H mixing that will be excess enthalpy, because the enthalpy of mixing for ideal case will be 0. And the same applies to volume that means the excess functions are indicators of the extent to which the solutions are non-ideal, because the deviations from ideality will be more if the non-ideality is more and non ideality arises because of the difference in the intermolecular interactions.

Finally, a solution for which excess enthalpy is not 0, but excess entropy is equal to 0 this is called a regular solution. This is another definition. A regular solution is the one in which the excess enthalpy is 0, excess entropy sorry in which the excess enthalpy is not 0, but excess entropy is 0. That means, the random orientation of the molecules in the mixture is similar to as if it is in the pure liquids; however, the way it interacts with the solute with the way the solute interacts with the solvent is different than the way solute-solute and solvent-solvent interact with each other.

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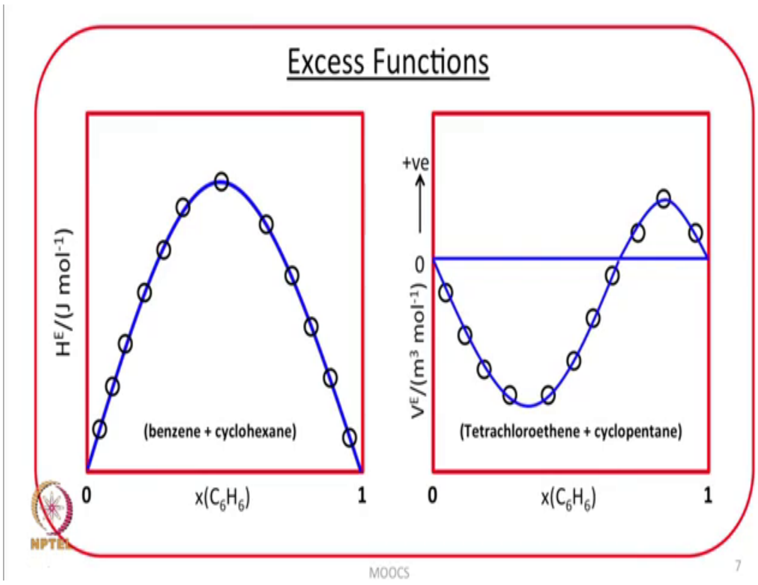

Excess Functions

These are some figures which describe the excess enthalpy variation against mole fraction of benzene, when benzene and cyclohexane are mixed. And for ideal solution, ideal mixing, it should have been 0, but since it does not form an ideal solution, you see there is a deviation from ideality. And this deviation from ideality or this excess function arises because of the difference in the intermolecular interaction between benzene and cyclohexane compared to benzene-benzene and cyclohexane-cyclohexane interactions.

And same way we can see that the excess volume in such cases show either positive deviation or negative deviation depending upon the composition range.

So, what we have discussed in this lecture is the deviation from ideality, and how to deal with the deviation from idealities. We derived the expressions for the Gibbs energy of mixing entropy of mixing and enthalpy of mixing for ideal solutions. Then we discussed the deviations that when the solution is real, how the excess functions can tell us about the deviations from ideality and the intermolecular interactions. And later on we will see that the excess functions give us lot of information including the nature and extent of intermolecular interactions.

Thank you very much.