

Chemical Engineering Thermodynamics
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Lecture 38 - Partial Molar Properties of Ideal Gas Mixtures

Welcome back. In the last class last few lectures actually we have been talking about calculating partial molar properties through analytical and graphical means. In today's lecture I will start with the ideal gas mixtures and basically to find out the changes in the properties of ideal gas and using the definitions of the partial molar properties which you have learned.

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I G Mixtures

$$PV = N_T RT = \sum N_i RT$$

$$\bar{V}_i^{IG} = \left. \frac{\partial V}{\partial N_i} \right|_{T, P, \{N_{j \neq i}\}} = \frac{\partial}{\partial N_i} \left(\frac{\sum N_j RT}{P} \right)$$

$$= \frac{RT}{P}$$

At a given T, P, molar prop of pure comp i (IG)

$$\underline{V_i} = v_i = \frac{RT}{P} = \bar{V}_i^{IG}$$

Let us go with so let us start with the basic definition of ideal gas. So it is a PV, NRT right? That is the equation of state where we say that well, the ideal gas mixture does not have any interactions. The only thing which has in its internal energy is the kinetic energy. So this is NT total number of moles which I can also write like this: $\sum N_i RT$. So let us extend our learning of partial molar properties to ideal gas mixtures. Here if I were to obtain the partial molar volume of ideal gas component here then I am going to take the partial derivative of V with respect to N_i at T, P, right ok and then if I use this equation of state here replace this equation of state V from here the equation of state.

Then I should be able to write this as, right and this is again summation $\sum N_i$, so RT and V is not dependent on N_i and here from here that partial derivative of this term with respect to N_i is nothing but 1. So what you obtain is RT by P here, this is P, okay. So this is for the ideal gas, the partial molar volume is I of ideal gas is nothing but RT and now let us look at for the case

of the pure component ideal gas, so at a given temperature and pressure molar property of pure component I in the ideal gas would be written as something like this: It is V_i this is one nomenclature. I can write since it is pure I can write a small v_i and this is nothing but RT by P as far as the ideal gas is concerned.

And that is same as \bar{V}_i^{IG} , right so for the pure case of the component I molar volume is nothing but RT by P and that is same as the partial molar volume of that component in ideal gas. Now let us take it take this definition and extend this to obtain the ΔV_{mix} for the case of ideal gas mixture.

$$PV = N_T RT = \sum N_i RT$$

$$\bar{V}_i^{IG} = \left. \frac{\partial V}{\partial N_i} \right|_{T,P,\{N_{j \neq i}\}} = \frac{\partial}{\partial N_i} \left(\frac{N_T RT}{P} \right) = \frac{RT}{P}$$

$$\text{at a given } T, P \quad V_i = v_i = \frac{RT}{P} = \bar{V}_i^{IG}$$

$$\Delta V_{mix}^{IG} = \sum N_i (\bar{V}_i - v_i) = 0$$

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The image shows a whiteboard with handwritten mathematical derivations. At the top, there are some small symbols and a color bar. The main derivation is as follows:

$$\Delta V_{mix}^{IG} = \sum N_i (\bar{V}_i - v_i) = 0$$

Below this, the text "Internal Energy" is written and underlined. Then the equation for internal energy is given:

$$U^{IG}(T, N) = \sum N_i u_i(T)$$

Below a horizontal line, the derivation continues:

$$\Rightarrow \bar{U}_i^{IG} = u_i(T)$$

Underneath this, there is a downward arrow and the partial derivative:

$$\frac{\partial U}{\partial N_i}$$

So this would be the change in the volume of the mixture in ideal gas okay and this by definition is nothing but summation and $N_i \bar{V}_i$ minus small v_i okay, now this of course small v_i and this \bar{V}_i is equal to zero. And small v_i bar is nothing but equal to \bar{V}_i and hence this is nothing but zero and thus this is zero, okay.

So that is one of the property of ideal gas mixture that the volume does not change upon mixing, that is what it clearly says that, that is why ΔV makes ideal gas is equal to zero, okay. Well, it is understandable also because we also consider ideal gas does not have any volume particles, as such it does not have any volume as such, not that ideal gas does not have volume. Ideal gas of course has volume but ideal gas particles do not occupy any specific size itself and hence they can pass through each other when they mix, so they do not collide as such, they the particles does have kinetic energy but they do not collide with each other. They collide with the walls, so considering that the molecular nature of the ideal gas this is kind of intuitive that the volume essentially should not change upon mixing because the particle does not have any specific sizes or does not occupy any specific volume as such particles.

So that is the subtlety in this kind of definition. So let me now extend this exercise to internal energy. Now internal energy of an ideal gas depends on the temperature and number of course particles. We can also write this as summation N_i and molar internal energy which only depends on temperature because the internal energy contribution of an ideal gas is due to the only the kinetic energy which of course has a direct relation with the temperature. Now if you look at this then straightforward to obtain the partial molar internal energy which will be nothing but $U_i T$ because this is nothing but $\frac{\partial U}{\partial N_i}$, so this is clearly U_i IG is equal to $U_i T$.

$$U^{IG}(T, N) = \sum N_i U_i(T)$$

$$\bar{U}_i^{IG} = U_i(T)$$

$$\Delta U_{mix}^{IG} = \sum N_i (\bar{U}_i^{IG} - u_i) = 0$$

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$$\Delta U_{mix}^{IG} = \sum N_i (\bar{U}_i^{IG} - u_i) = 0$$

Similarly $\Delta h_{mix}^{IG} = 0$

$$h_i^{IG} = \bar{U}_i^{IG} + P V_i^{IG}$$

$$= \bar{U}_i^{IG} + RT = h_i^{IG}$$

\bar{U}_i^{IG} → molar inter energy, comp.
 RT → molar enthalpy of comp.

Now if you have been asked to find out Delta U that means change in the internal energy upon mixing, then the answer would be this is zero hence this has to be zero. So that is also the case for the delta U. So we have the volume change zero for the ideal gas mixture, internal energy change zero for the case of ideal mixture ideal gas mixture. So we can also extend this thing for enthalpy. Similarly, we can show that the delta h IG mixture is zero, okay and how to do that? We start with our definition that H i is nothing but U i plus P V i or we can say here directly partial derivative of H here is, okay.

Directly we are extending it as we have done this, we have shown this particular expression that the thermodynamic relations as we write it for the pure component can be extended for this and we can extend it for the partial molar properties as well. So I am just writing that, now given this I can write this as a PV IG is nothing but RT and U i IG which is nothing but H i bar IG because this is U i small, ok molar volume or smaller one, okay.

So this is in other word this is a molar internal energy. So with this you have molar internal energy plus RT of a component I okay and thus this will give you H i IG that is your molar enthalpy of component I, okay. So this we have calculated, right this we have derived it earlier

as we have shown there that U^{IG} is nothing but U^I , right. So, I can actually write this also in order to have a clear thing, this is nothing but saying it this, so this is equivalent. So this I write it, usually for the pure component I write it like that but for the case of mixtures is better that we write it in this way.

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Handwritten derivation on a whiteboard:

$$\bar{H}_i^{IG} = \frac{H_i^{IG}}{N_i} = \frac{U_i^{IG}}{N_i} + P V_i^{IG}$$

$$= \frac{U_i^{IG}}{N_i} + RT = \bar{H}_i^{IG}$$

Annotations: U_i^{IG} is circled and labeled "molar inter energy, comp.". \bar{H}_i^{IG} is labeled "molar Enthalpy of comp.". Below the equations, it says "molar inter energy, comp." and "molar Enthalpy of comp.".

$$\Delta H_{mix}^{IG} = \sum N_i (\bar{H}_i - \bar{H}_i^L)$$

$$\text{or } \sum N_i (\bar{H}_i - h_i)$$

$$= 0$$

Handwritten notes on a whiteboard:

any Gas mixture

Define partial pressure $P_i = y_i P$

$$= \frac{N_i}{N_T} P$$

$$IG \quad P_i = \frac{N_i}{\sum N_i} \left(\frac{\sum N_i RT}{V} \right) = \frac{N_i RT}{V}$$

$$P_i(N_1, \dots, N_n, T, V) = P(N_i, T, V)$$

for IG

So with this definition of course that H_i bar is nothing but the molar one, then I have now that ΔH_{mix}^{IG} is nothing but summation $N_i H_i$ bar minus okay H_i this or I can write this as summation $N_i H_i$ bar minus H_i okay, for the basically this is for the pure component. So this is what we are trying to write and since this is same as this as we have seen here, a molar component of this has to be equal to zero.

$$\Delta H_{mix}^{IG} = 0$$

$$\overline{H}_i^{IG} = \overline{U}_i^{IG} + P\overline{V}_i^{IG} = \overline{U}_i^{IG} + RT = \underline{H}_i^{IG} = \text{molar enthalpy of component } i$$

$$\Delta H_{mix}^{IG} = \sum N_i (\overline{H}_i - \underline{H}_i) = 0$$

So it is a straightforward exercise of systematic analysis here, okay I would like now to extend this to the entropy but before we proceed further we must understand a bit of the pressure component in the gas mixtures of ideal gas. So for the case of the gas mixture or any mixture basically, we can define something like partial pressure which is usually defined by a symbol P_i and this is nothing but the total pressure multiplied by the mole fraction in the gas phase.

I can write this as an N_i number of moles of the component i divided by the total number of moles in the system N_i by N_T . If it is an ideal gas P_i is N_i by summation N_i and here P can be written as summation $N_i RT$ by V . So, this gets cancelled so this is nothing but $N_i RT$ by V which is nothing but the pressure of the system with N_i moles of component i at the temperature T and V . And this P_i is nothing but P_i with all the components and this composition at temperature and volume, right so this P_i becomes P here for only ideal gas.

$$\text{Partial Pressure } P_i = y_i P = \frac{N_i}{N_T} P$$

$$\text{Ideal Gas: } P_i = \frac{N_i}{N_T} \left(\frac{N_T RT}{V} \right) = \frac{N_i RT}{V}$$

$$P_i(N_1 \dots N_N, T, V) = P(N_i, T, V) \text{ for ideal gas}$$

So let us try to understand this a bit so when you mix it what happens to this pressure. So let me consider the case that as I said you know we are trying to reach towards understanding how to bring the entropy calculations or the change in the entropy upon mixing.

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$P_i(N_1, \dots, N_N, T, V) = P(N_i, T, V)$
 for IG

Effect of removing the partition & mixing the comp
 \Rightarrow greater vol. within which particles can move
 \Rightarrow Entropy increases

$\sum N_i (H_i - h_i) = 0$

any Gas mixture
 Define partial pressure $P_i = y_i P = \frac{N_i}{N_T} P$

IG $P_i = \frac{N_i}{\sum N_i} \left(\frac{\sum N_i R T}{V} \right) = \frac{N_i R T}{V}$
 $P_i(N_1, \dots, N_N, T, V) = P(N_i, T, V)$

So what I am going to consider is a system where you do have a couple of components which are separated something like this and they are separated by this partition. So you have of course molecules here, here and here, okay. Upon removal of the partition you expect you know mixing of these particles here. So the what the effect of this removal of phase is basically effect of removing the partition and mixing the component if you think about that a particle which is here was able to only access the volume available in these regions.

Once you take out the partition the same particle now have more volume to access. So there is a greater volume within which the particles can move, so that is one effect of removing the partition, okay.

Now when you have greater possibilities because you can the particles can move various different locations and all the particles can access more possible locations leading to more such

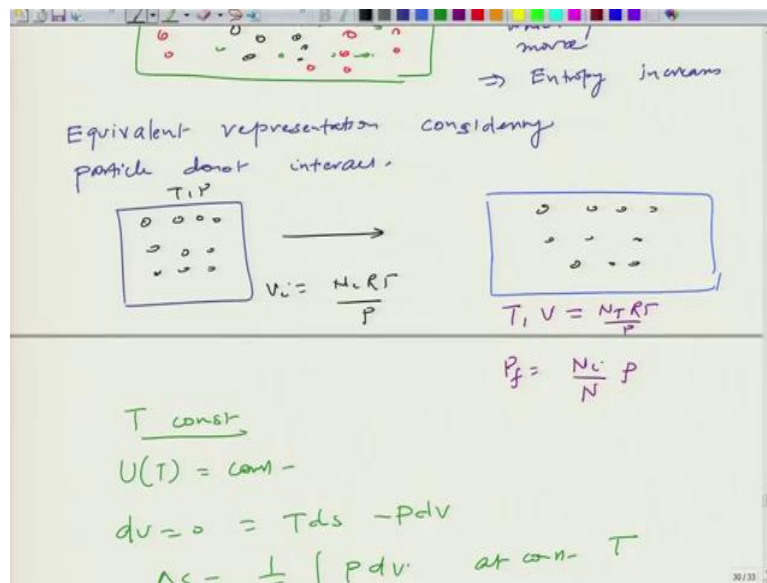
you know arrangements, only the word if you think from the concepts of the you know the number of possible confirmations, number of possible access or leading to variety of different in the molecular level confirmations, this would also indicate that there is an increase in the disorder because of the fact that the particles are moving and they are able to access more. So essentially this indicates that they should be now increase in the entropy upon mixing the particles even if it is an ideal gas, okay.

Now that is something which is very interesting. So we notice that for ideal gas the change in the volume upon mixing is zero, change in the internal energy enthalpy should be zero but when it comes to entropy it appears that upon removing the partition the possibilities of access to the different volumes increases for each particles leading to more randomness in some sense. So that is something which we would like to know explore.

So let us see what happens now. Why did we describe the pressure? Because of the fact here initially each of them had like the pressure corresponds to their number of molecules, number of moles present in that and then once that is mixed, each of them each species in some sense, so here for example in this case I have mixed it with all same color but we can consider that this is let us say different colors indicates a different kind of species and when you mix it you have all kind of you know arrangements here.

Now the question is very clear is that of course you have the pressures which is due to this pure one and when they are mixed each of them is contributing to the total pressures, so each species has something called partial pressure. That is what we talked about here, this is the partial pressure corresponding to each species. So let me try to the graphically explain what happens, how do we interpret this whole behavior because it is an ideal gas. So for example, these black particles are not interacting with the green particle and same for this red and green and red and black. The only thing which they are able to do is they are able to access more volume compared to the case where the earlier okay, because they are ideal gas.

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So the equivalent representation considering particles do not interact would be the following: where I can consider that well for a single species let us say it is black particles here which were at temperature T and P , the volume initially was let us say V_i in $N_i R T$ by P because of the ideal gas, now upon removing the partition you have now much bigger space, alright. The same set of particle now can access more volume here but this is now temperature T and V that is the total volume now.

And essentially this volume now can be written as total (temp) number of moles $R T$ by P , okay and the final pressure which is going to be N_i and P , P is the total pressure of the system but the contribution due to this particular black particle would be N_i by $N P$. So in the world what you are trying to say is that well, the particle this particular blue component is expanded, our box is expanded such that the volume changes from V_i to total volume V and the pressure changes from its the pressure which was given P to corresponding P_f or in this case P_i for example for the specific component because each of them are independent.

The only thing which is differing is the number of moles and the initial the volume here but finally the final volume is fixed. So considering that how do you now calculate the ΔS from this exercise or from this particular understanding? So, let us again look at it. Since T is constant here and I know that upon mixing or even if expanding here if T is constant essentially what means that the $U(T)$ is constant and now U of T is constant, U is equal to zero but dU is nothing but $T dS$ minus $P dV$, right.

So I can write Delta S as $\frac{1}{T} \int P dV$ at constant T. Now the relation I have, I have to find out the Delta S of this particular expansion of the volume of this particular component and we can just look at only the pure component here at this point because each of them will contribute to the Delta S or the change in the entropy and since the entropy is extensive property we can simply add it up.

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Handwritten derivation on a whiteboard:

$$\Delta S = \frac{1}{T} \int P dV$$

entropy change for pure comp i

$$V_i \rightarrow V \text{ at } T$$

$$\Delta S_i = \frac{1}{T} \int_{V_i}^V P dV \quad P = \frac{N_i RT}{V}$$

$$\Delta S_i = \frac{R T N_i}{T} \int_{V_i}^V \frac{dV}{V}$$

Molar Entropy

$$\frac{\Delta S_i}{N_i} = R \int_{V_i}^V \frac{dV}{V} = R \ln \frac{V}{V_i}$$

$$= R \ln \frac{N}{N_i}$$

Handwritten derivation on a whiteboard:

$$\Delta S_i = \frac{1}{T} \int_{V_i}^V P dV$$

$$\Delta S_i = \frac{R T N_i}{T} \int_{V_i}^V \frac{dV}{V}$$

Molar Entropy

$$\frac{\Delta S_i}{N_i} = R \int_{V_i}^V \frac{dV}{V} = R \ln \frac{V}{V_i}$$

$$= R \ln \left(\frac{N}{N_i} \right) y_i$$

$$\frac{\Delta S_i}{N_i} = -R \ln y_i$$

$\therefore V = \frac{N_i RT}{P}$
 $V_i = \frac{N_i RT}{P}$

$$V_i = \frac{N_i RT}{P} \quad T, V = \frac{N_T RT}{P} \quad P_f = \frac{N_i}{N} P$$

T const

$$U(T) = \text{const} ; dU = 0 = TdS - PdV$$

$$\Delta S = \frac{1}{T} \int PdV \quad \text{at constant } T$$

Entropy change for pure comp. i

$$V_i \rightarrow V \text{ at } T$$

$$\Delta S_i = \frac{1}{T} \int_{V_i}^V PdV \quad P = \frac{NRT}{V}$$

$$\Delta S_i = N_i \int_{V_i}^V \frac{dV}{V}$$

$$\underline{\Delta S_i} = R \int_{V_i}^V \frac{dV}{V} = R \ln \frac{V}{V_i} = R \ln \frac{N}{N_i} ; \frac{N}{N_i} = \frac{1}{y}$$

$$\underline{\Delta S_i} = -R \ln y_i$$

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Handwritten derivation on a whiteboard:

$$\Delta S_i = -R \ln y_i$$

$$\Delta S_{mix}^{IG} = \sum N_i \Delta S_i$$

$$= -R \sum N_i \ln y_i$$

$$\Delta S_{mix}^{IG} = -R N \sum \frac{N_i}{N} \ln y_i$$

$$= -NR \sum y_i \ln y_i$$

$$\therefore \Delta S_{mix}^{IG} = -NR \sum y_i \ln y_i$$

$$\Delta S_{mix}^{IG} = \sum N_i \Delta S_i = -R \sum N_i \ln y_i$$

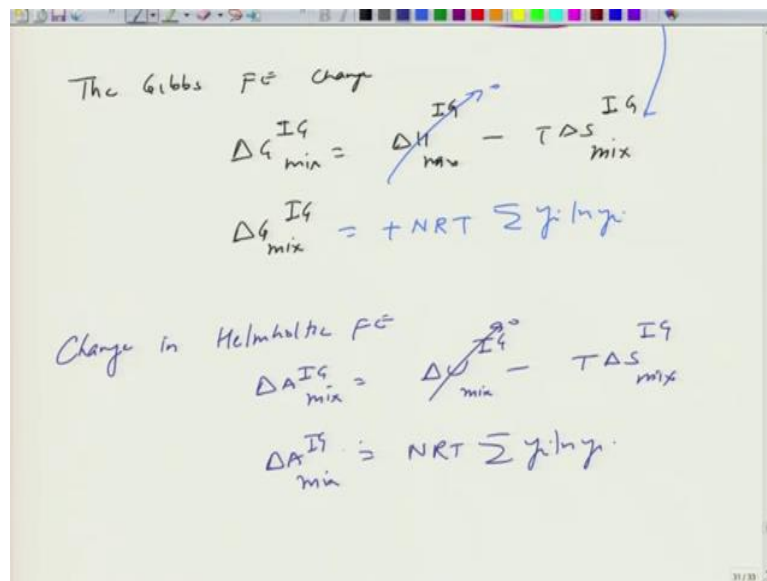
$$\Delta S_{mix}^{IG} = -NR \sum y_i \ln y_i$$

So I have now an expression the Delta S i is minus R Ln S i bar here y i. So, this is my change in the entropy of a component i upon in the mixture from the pure state to the mixtures. Now given this I have to now add it up for the other cases. So if you add it up others, so others will be straightforward because Delta S ideal gas mixture would be nothing but your summation N i okay and Delta S i okay. Because it is extensive so we are simply adding the contributions for each particular component, that is the relation I am just simply adding here.

So Delta S i ideal gas mixture nothing but simply the summation of others. So, here I can expand it now, S N I am replacing it this here and now at this point if at this point if I divide this by let us say if I consider N i by total N here, R Ln y i here then I can multiply N here and that is the total number of particles and then I have a relation now Delta S ideal gas mixture as minus NR summation y i. This is the double R here which should not be the case.

So this would be now Ln y i. So therefore delta S IG mixture is minus NR summation y i ln y i. So this is how we have now come up to that expression which relates the change in the entropy of the ideal gas in the mixtures to the compositions of different components. You can extend now these to obtain the Delta G also because you do have now all the information. So let me just try to do that and that will be end of the lecture.

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$$\Delta G_{mix}^{IG} = NRT \sum y_i \ln y_i$$

$$\Delta A_{mix}^{IG} = NRT \sum y_i \ln y_i$$

So the Gibbs free energy change would be Delta G ideal gas mixture would be Delta H minus T Delta S and since this mixture and I am going to put here Ideal gas, I am going to put here ideal gas and we know from that this is going to be zero. So with this Delta G ideal gas mixture is nothing but plus NRT summation $y_i \ln y_i$. So you put it here, you get this expression that is your Delta G ideal gas mixture. Similarly you can also obtain the Helmholtz free energy change, so basically the change in Helmholtz free energy.

So that is Delta A IG mixture, this is going to be Delta U minus T Delta S, again this is ideal gas hence I am putting it here and this is for the mixture. So that is the beauty of thermodynamics you know the relations remain the same, only you are concerned now with the change of the individual properties here. So here of course this is going to be zero and this is still minus here, so you plug in the same expression you get again NRT summation $y_i \ln y_i$. So change in the Helmholtz free energy and the Gibbs free energy for the ideal gas mixtures is the same. So that summarizes the expressions which we wanted to calculate or which we wanted to develop rather for the ideal gas mixture. So let me summarize essentially all the some you know what we have developed for the ideal gas mixture just for the sake of having it here.

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Change in Helmholtz FE

$$\Delta A_{mix}^{IG} = \Delta U_{mix}^{IG} - T \Delta S_{mix}^{IG}$$

$$\Delta A_{mix}^{IG} = NRT \sum y_i \ln y_i$$

IG mix

$$\Delta U_{mix}^{IG} = 0$$

$$\Delta V_{mix}^{IG} = 0$$

$$\Delta H_{mix}^{IG} = 0$$

$$\Delta S_{mix}^{IG} = -NR \sum y_i \ln y_i$$

$$\Delta G_{mix}^{IG} = NRT \sum y_i \ln y_i$$

$$\Delta A_{mix}^{IG} = NRT \sum y_i \ln y_i$$

So ideal gas mixture we observed that the change in the internal energy is going to be zero, the change in the volume is also going to be zero, change in the Delta H mixture is also zero whereas Delta S i mixture is minus NR summation y i ln y i for the case of delta G IG mix. We have NRT summation y i ln y i and Helmholtz free energy change is same as that of the Gibbs free energy and hence we write the same expressions, okay.

So the only difference in between this Delta S to other free energy is the presence of temperature and the sign is positive. I think for now we will stop here because we wanted to just look at first the ideal gas mixtures and subsequently in the next class we are going to extend this understanding and particularly for Non-ideal gas mixtures and the reason why you wanted to take this ideal gas because this would always be used as a reference for our non-ideal gas systems or non-idle systems, okay. So with this we stop here and I will see you in the next.