Chemical Engineering Thermodynamics

Prof. Sasidhar Gumma
Department of Chemical Engineering
Indian Institute of Technology, Guwahati
Solution Thermodynamics

Lecture - 20
Solution Thermodynamics

Hello and welcome back. In the previous lectures, we dealt with Calculation of the change in Thermodynamic properties which have a single component; one chemical species or in fact, those calculations we have done will also be applicable for systems, where the composition is constant even if it is a mixture. As long as the composition is constant all the equations we have dealt with are applicable.

So, what we will do in this lecture from now on is try to deal with the mixture of chemical species because that is most commonly encountered in a chemical process industry. When we have a mixture of chemical species, the behavior of such a mixture is going to be different from the pure component counterparts all right. When we mix there are going to be other types of interactions that take place in the mixture between the two distinct chemical species and somehow we need to account for these type of changes or at least know how to formulate a thermodynamic framework to handle a mixture of chemical species and we do that. One of the ways we do that is through what is known as a solution Thermodynamics approach.

We need to define additional thermodynamic properties, then what we have done so far to be able to lay the theoretical framework for dealing with mixtures that is what we will try to do in today's lecture. We start with a simple example, if you recall the one we discussed in one of the introductory lectures.

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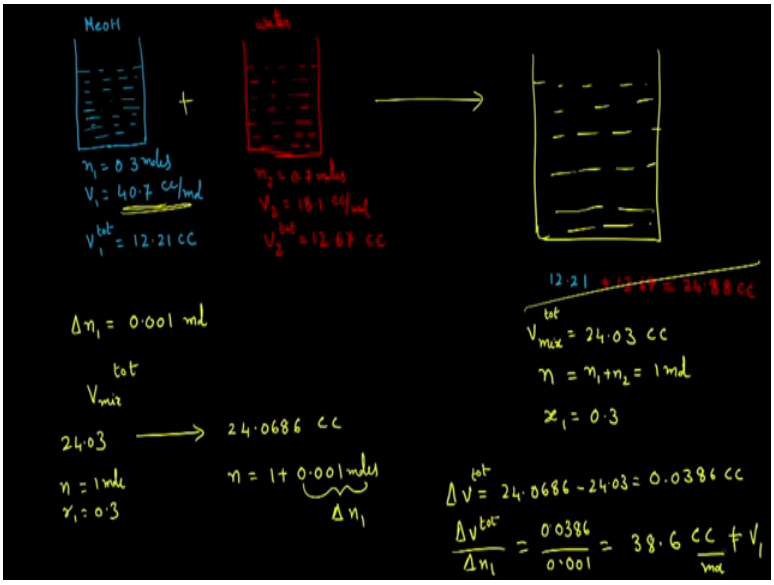

Let us say I have a mixture of methanol and water. This is methanol. Let us say I have 0.3 moles of methanol and the molar volume for methanol is about 40.7 cc per mole at temperature and atmospheric pressure. And then, I have another beaker which contains water and I have about 0.7 moles of water and the molar volume for water the same conditions is about the 18.1 cc per mole. Because I have 0.3 moles, this total volume for one; here is about 12.21 cc and the total volume for the water I am taking is about 12.67 cc. This is number of moles multiplied with the molar volume now one.

Once I have these two distinct chemical species and I try to mix them, the resultant would be a mixture of these two compounds right. And if I posed a question what would be the total volume for this mixture? Then, we would be tempted to say that it is going to be 12.21 plus 12.67 which is 24.88 cc.

However, it turns out when you do this exercise the volume you measure is not 24.88 cc rather it is 24.03 cc's lower than water you would expect by a simple additive rule mixing rule. You apply for this particular scenario that is because the interactions between methanol and water are going to play a role in determining the molar volume for this particular mixture.

So, then it turns out if I have a mixture, I cannot simply use the information on the pure components and try to tell what the molar volume for a mixture is. In fact, it is true not just for molar volume, but for any thermodynamic property bit enthalpy, bit entropy or

Gibbs free energy. The mixture is going to behave differently than the pure component counterparts or by simple edit addition of the pure component properties.

Now, let us also take this discussion a little forward so that we can define a new thermodynamic property. Let us say I have 1 mole of this mixture as we have seen here and this 1 mole is going to occupy 24.03 cc and this particular value let us call this as the volume of the mixture, this is the total volume of the mixture; the total number of moles, we will drop the subscript n 1 is for methanol and 2 is for water; n is simply n 1 plus n 2 which is 1 mole.

So, the molar volume of the total volume in this case because I have 1 mole is going to be 24.03 cc or cc per mole and then, the mole fraction in this scenario let us write the mole fraction for methanol with this subscript 1 in this scenario is 0.3. So, now, I have a case where I have a mixture with 0.3 mole fraction for methanol, whose total volume or the volume occupied by 1 mole of this particular mixture is 24.03 cc.

Now, if I take this mixture and I decide to add a little bit more methanol to this mixture, let us say I want to add some additional number of moles of methanol to this mixture; a small quantity 0.001 moles. Now, this additional number of moles is going to contribute to additional volume right and that will increase the total volume of the mixture right.

So, it turns out v total when I add this additional number of moles, this v total would go from 24.03; n equal the total mixture is n equal to 1 mole x 1 is 0.32 to 24.0686 cc's; n is 1 plus 0.001 moles of methanol. So, this particular quantity here is delta n 1. We have added pure methanol to this mixture and the mole fraction has changed from 24.03 to 24.0686, just as in case of adding methanol and water a pure additive volume is not going to work, even when I add the additional number of moles the difference is not going to be directly related to 0.001 or the volume of 0.001 moles of methanol.

So, if you look at it delta v is in this scenario delta v total is in this scenario 24.0686 minus 24.03 which is 0.0386 cc right and I have added 0.001 moles. So, if I divide this the change in the total volume with delta n 1 0.0386 over 0.001, if I divide the total number of moles I have added or the total volume change with the total number of moles, I have added for methanol this value turns out to be 38.6 cc or more and note that this value is not equal to v 1.

The molar volume of methanol molar volume for methanol is right here 40.7 cc; whereas, when I divide the volume change with the number of moles I have added what I get is 38.6 cc. So, this number is different from 40.7 cc as you would expect. Once we looked at the first scenario that when I add, they do not simply the volume simply do not add up. So, when I add additional number of moles of volume change is not going to be directly proportional to the molar volume of methanol.

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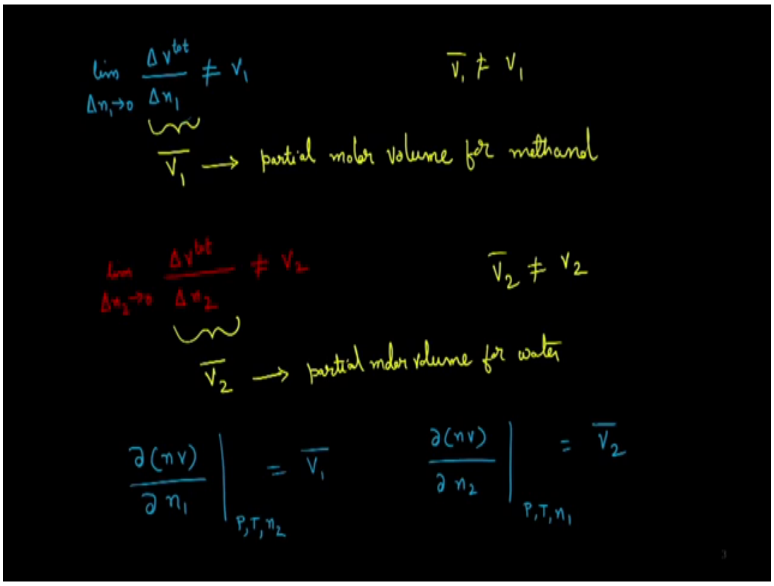

$$\lim_{\Delta n_1 \to 0} \underbrace{\frac{\Delta V^{tot}}{\Delta n_1}} \neq V_1 \qquad \bar{V}_1 \neq V_1$$

$\bar{V}_1 \longrightarrow$ partial molar volume for methanol

$$\lim_{\Delta n_2 \to 0} \underbrace{\frac{\Delta V^{tot}}{\Delta n_2}} \neq V_2 \qquad \bar{V}_2 \neq V_2$$

$\bar{V}_2 \longrightarrow$ partial molar volume for water

$$\left.\frac{\partial (nV)}{\partial n_1}\right|_{P,T,n_2} = \bar{V}_1 \qquad \left.\frac{\partial (nV)}{\partial n_2}\right|_{P,T,n_1} = \bar{V}_2$$

So, this is an important observation. This change limit of delta n 1 going to 0, delta v total over delta n 1 is not equal to v 1 in this scenario. So, we will give this particular limit; a name we will call it as v 1 over bar and we call it as partial molar volume. We will come back to why that name has been used for this particular case, when we derive more relations, but for now let us call it as partial molar volume. It is the change in total volume of the mixture divided by the change in additional number of moles I have added for methanol. In this case I have added methanol. So, this (Refer Time: 10:29) subscript for partial molar volume will be for methanol which is 1 right.

Similarly, if I take limit of delta n 2 going to 0, the change in the total volume of the mixture over delta n 2, this will not be equal to the molar volume of water. But rather it would be equal what we call as v 2 over bar this is still partial molar volume. But in this case it is partial molar volume for water; in the previous case, it was partial molar volume for methanol right. So, we have a scenario where the mixture behaves differently right than their pure cop pure component counterparts and v 1 bar is not equal to v 1, at least in this case. In certain cases they may be equal, but they do not have to be and v 2 bar is not equal to v 2. The partial molar volume for methanol is not same as the molar volume for methanol; the partial molar volume for water is not same as the molar volume for water.

So, we have defined a new property for a mixture partial molar volume right. In fact, we can mathematically write this limit as the derivative of the total volume of the mixture which is the number of moles multiplied with the molar volume of the mixture n times v over n 1, the derivative of this quantity.

Remember, we have taken that example at constant pressure and temperature, room temperature, atmospheric pressure we said and when we change the number of moles for methanol, we are holding the number of moles for water constant and to this quantity is called as the partial molar volume. This is this quantity is what the limit represents.

So, mathematically we are going to define v 1 bar as the partial derivative of the total volume with respect to the number of moles of methanol, when we hold the temperature pressure and number of moles for water constant. Similarly, if I need to define the partial molar volume for water it would be derivative of n v with respect to n 2 at P T and n 1. This is called as v 2 bar or partial molar volume for water.

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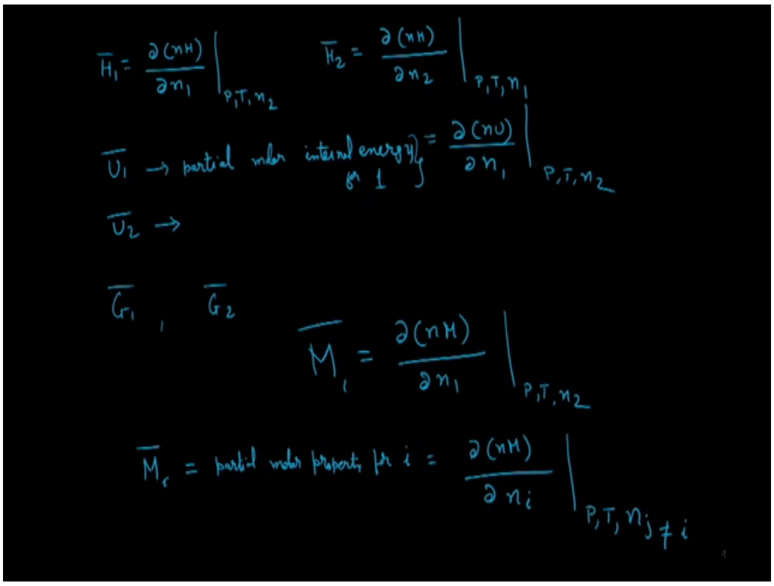

$\overline{H}_1 = \left.\frac{\partial(nH)}{\partial n_1}\right|_{P,T,n_2}$ $\quad\overline{H}_2 = \left.\frac{\partial(nH)}{\partial n_2}\right|_{P,T,n_1}$

$\overline{U}_1 \rightarrow$ partial molar internal energy for 1 $= \left.\frac{\partial(nU)}{\partial n_1}\right|_{P,T,n_2}$

$\overline{U}_2 \rightarrow$

$\overline{G}_1 , \quad \overline{G}_2$

$$\overline{M}_1 = \left.\frac{\partial(nM)}{\partial n_1}\right|_{P,T,n_2}$$

$$\overline{M}_i = \text{partial molar property for } i = \left.\frac{\partial(nM)}{\partial n_i}\right|_{P,T,n_{j\neq i}}$$

So in fact, not just these quantities I can define other thermodynamic quantities also. I can define H 1 bar; it would be derivative of the total enthalpy over n 1, when I hold the temperature pressure and n 2 constant. Similarly, H 2 bar is going to be derivative of the total enthalpy of the mixture over n 2, when I hold temperature pressure and n 1 constant etcetera. I can define U 1 bar which is the H 1 bar, remember is the partial molar enthalpy U 1 bar is partial molar internal energy right and again, this is equal to derivative of the total internal energy over n 1 at P T and n 2.

Similarly, I can define U 2 bar partial molar internal energy for let us call it as 1, I can define it for 2, I can define partial molar Gibbs free energy G 1 bar, G 2 bar etcetera. In fact, any partial molar property M can be defined in this fashion, it is the total property over n 1 P T and n 2. This will be M 1 bar in a binary mixture of course. I can extend this discussion to a multi component mixture, when there is more than two components and in that case it would we call this as M i bar, this is the partial molar property for i and this will be the derivative of the total property over n i.

Because I need M i bar, I would need to take the derivative with respect to n i and I need to hold the number of moles for all the other species j. It can be if I need it for 1, then I need to hold 2 and all the other species 3, 4 etcetera constants we represent it as n j not equal to i. So, it would be the derivative of the total property M with respect to n i when the temperature pressure and n j where that j is not equal to i; all those moles for all the other species j which are not i need to be held constant. When we do that we get what is known as M i bar, this is this expression for a multi component mixture.

So, we can extend this discussion from binary mixture to multi component mixture in a straightforward fashion. So, the partial molar volumes, partial molar enthalpies, partial molar Gibbs free energies etcetera can be defined in this way for a multi component mixture. Now, let us try to write some fundamental property relations for a mixture of chemical species.

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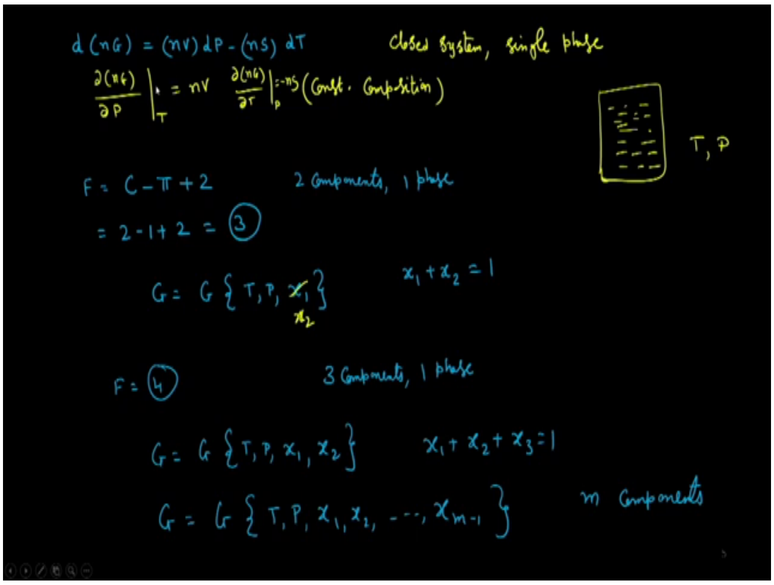

$d(nG) = (nV)\,dP - (nS)\,dT$ Closed System, single phase

$\left.\frac{\partial(nG)}{\partial P}\right|_T = nV \quad \left.\frac{\partial(nG)}{\partial T}\right|_P = -nS$ (Const. Composition)

T, P

$F = C - \pi + 2$ 2 Components, 1 phase

$= 2 - 1 + 2 = \textcircled{3}$

$G = G\{T, P, \underset{x_2}{\cancel{x_1}}\}$ $x_1 + x_2 = 1$

$F = \textcircled{4}$ 3 Components, 1 phase

$G = G\{T, P, x_1, x_2\}$ $x_1 + x_2 + x_3 = 1$

$G = G\{T, P, x_1, x_2, \ldots, x_{m-1}\}$ m Components

Now, recall that the Gibbs free energy the total Gibbs free energy is n v d P minus n s d T. This is applicable for a closed system single phase, but if we have a single phase homogenous single phase system and it is closed, then this particular expression is applicable is what we said. Now, if we have a single phase system and the system itself is closed, then the number of moles for all the chemical species are same right; they are not changing.

So, this expression just considers the change either in the temperature or pressure of the system, but not in the number of moles of the system because there is only one phase and it is closed. The moles whatever are present in that vessel are always present right. I have a vessel like this closed vessel I have something inside this vessel, all that is changing is the temperature or pressure the number of moles cannot change once it is closed and it is in a single phase.

So, this equation in that sense is actually applicable not just for a closed single phase system, but it is applicable when we say closed single phase system, it will also be applicable for a system where constant; where the composition is constant. So, this system actually or this particular equation actually is also applicable for a system with constant composition. I can have a mixture inside this, but as long as it is closed and it is in a single phase even that mixture can be or the change in Gibbs free energy of that mixture can be expressed by this particular expression because the mixture is at a constant composition.

Now, what happens if it is not a closed system, if it is an open system and the system is allowed to exchange matter with the surroundings. I can add some number of moles for one of the chemical species or for both the chemical species. It is a mixture of chemical species and how do we express the change in Gibbs free energy for such a system. So, to answer that question let us revisit the phase rule. The phase rule says the number of degrees of freedom F is the number of chemical components minus the number of phases plus 2 right.

Now, if I have a single phase system with two chemical species, then the number of degrees of freedom is going to be 3 right. So, I need to fix 3 intensive variables to completely fix the state of system at equilibrium right. This is for 2 components and single phase. I have a mixture of two components. So, we can think of this as the Gibbs free energy, it can be any thermodynamic variable. Let us say it is a Gibbs free energy is a function of temperature pressure.

We need three variables; one is temperature, the second one is pressure and the third one can be mole fraction of one of the components right. Note that when I say mole fraction of one of the components, I can choose either x 1 or x 2; once I choose x 1 since the two mole fractions should add to 1, x 2 is automatically fixed. So, I could have said T, P, x 1 or I could have said T, P and x 2; it does not matter, I can choose any one of the 2 mole fractions if they are equivalent.

So, the Gibbs free energy or in fact, any thermodynamic property is a function of three variables in this case we chose it to be T, P and x 1. Now, if I have a mixture of three components and one phase; I am still talking about a single phase system, but then I have three components then F is obviously, going to be 4. As you can see and the Gibbs free energy is going to be a function of 4 variables that would be the temperature pressure x 1 and let us say x 2, the mole fractions of two of the components. The third component obviously is fixed because x 1 plus x 2 plus x 3 is 1; the mole fraction of the third component is going to be fixed. I can choose any two of these 3 variables x 1, x 2 and x 3. In this case we are writing it as a function of x 1 and x 2. So, similarly we can keep extending this.

So, in general Gibbs free energy in a multi component system is going to be a function of T, P, x 1, x 2 all the way through x n minus 1 if there are M components; then, I need a M minus mole fractions and temperature and pressures. So, that would be a total of M plus 1 variables So, to fix the state of the system, I need M plus 1 variables and this is how I can write the functionality for Gibbs free energy. Now, let us carry that a little forward that is the Gibbs free energy G which is a molar value.

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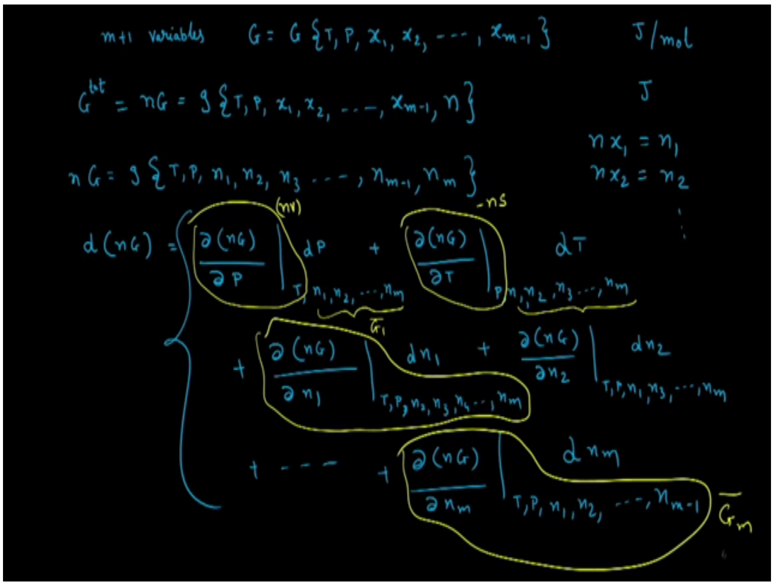

m+1 variables $G = G\{T, P, x_1, x_2, ---, x_{m-1}\}$ J/mol

$G^{tot} = nG = g\{T, P, x_1, x_2, ---, x_{m-1}, n\}$ J

$nx_1 = n_1$

$nx_2 = n_2$

$nG = g\{T, P, n_1, n_2, n_3 ---, n_{m-1}, n_m\}$

$$d(nG) = \left\{ \begin{array}{l} \overset{(nV)}{\left.\frac{\partial(nG)}{\partial P}\right|_{T, \underbrace{n_1, n_2, \cdots, n_m}_{\bar{G}_1}}} dP + \overset{-nS}{\left.\frac{\partial(nG)}{\partial T}\right|_{P, \underbrace{n_1, n_2, n_3 \cdots, n_m}}} dT \\ + \left.\frac{\partial(nG)}{\partial n_1}\right|_{T, P, n_2, n_3, n_4 \cdots, n_m} dn_1 + \left.\frac{\partial(nG)}{\partial n_2}\right|_{T, P, n_1, n_3, \cdots, n_m} dn_2 \\ + --- + \left.\frac{\partial(nG)}{\partial n_m}\right|_{T, P, n_1, n_2, ---, n_{m-1}} dn_m \quad \bar{G}_m \end{array} \right.$$

And it is a function of M plus 1 variables and we are conveniently writing it as G equal to a functionality expressed in terms of T, P, x 1 x 2 so on all the way through x m minus 1.

Now, if I ask a question, what is the functionality for the total Gibbs free energy not the molar Gibbs free energy? Molar Gibbs free energy is an intensive property; the units are something like joules per mole what I want is the total Gibbs free energy j; well obviously, the total Gibbs free energy is an extensive property. It depends on the size of the system do I have 5 moles; do I have 10 moles in the system that is going to determine the total Gibbs free energy. So, the size of the system matter. So, then it is going to be a function of nG that is the total Gibbs free energy right.

So, we will let us write it as G total is nG. It is going to be a functionality expressed in terms of temperature, pressure, x 1, x 2 all the way through x m minus 1 and n the total size of the system; n number of moles or equivalently once I have n and x 1, n times x 1 is obviously, the number of moles for 1 n times x 2 is obviously, the number of moles for 2 and so on. This functionality can be equivalently expressed as it is a function of T, P, n 1, n 2, n 3 so on nm minus 1 and the last value, I can either write as n or I can write the number of moles for the last component as nm, both of them are equivalent functionalities right.

So, then the total Gibbs free energy nG is a function of these variables; M moles temperature and pressure. Now if I want to take the derivative total derivative of this total Gibbs free energy d nG is going to be the derivative of G or nG right both of them are same, with respect to the pressure. When you hold the temperature and all the moles constant times dP plus the derivative of the total Gibbs free energy with respect due to the temperature and you hold pressure n 1 n 2 n 3 nm constant times dT plus the derivative of nG with respect to n 1 right.

When I hold the temperature pressure and all the remaining moles except 1 because I am taking the derivative with respect to 1, I have to hold all the remaining moles constant. In this case, they turn out to be n 2, n 3, n 4 so on nm dn 1 plus the derivative of n G with respect to now first component to n 2; when I hold temperature pressure n 1 n 3 all the way through nm except everything except n 2 times dn 2 plus so on and the last one would be derivative of n G with respect to nm.

When I hold temperature pressure n 1, n 2 and m minus 1 d nm; this would be the total derivative d nG. Now here I am allowing n 1, n 2, n 3 etcetera to change which means the system can exchange the number of moles of any of those chemical species with the surroundings. So, it would be an open system. So, this would be the total change in the total Gibbs free energy of the system of an open system actually right.

Now, let us write it here. When I have n 1, n 2, n 3 and looking at the first term when I have all of these constant all the number of moles constants, then it is as good as a closed system because I am not exchanging moles with the surroundings. So, it is as good as a closed system and for a closed system derivative of n G. It is just for this particular term that derivative is n v. If you recall it is n v right. We said this is for a closed system.

So, if I write the derivative of n G with respect to P at constant temperature, then it would be n v right. This is true for a closed system. Similarly, derivative of n G with respect to T at constant pressure is going to be minus n s right. This is true for a closed system with constant composition. So, I can substitute derivative of nG with respect to P at constant temperature with n v; then of course, all the other moles are constant in which case, it turns out to be a closed system of constant composition. Again, even for the second term all the moles from n 1 through nm are constant.

So, it again is a closed system at constant composition. So, this derivative term here would be minus n s right and if you recall the definition of partial molar property derivative of nG with respect to n 1, when you hold temperature pressure and moles of all the other chemical components constant except n 1; then this term is what we call as partial molar property, in this case it is partial molar Gibbs free energy G 1 bar. Similarly this one would be partial molar Gibbs free energy G m bar etcetera.

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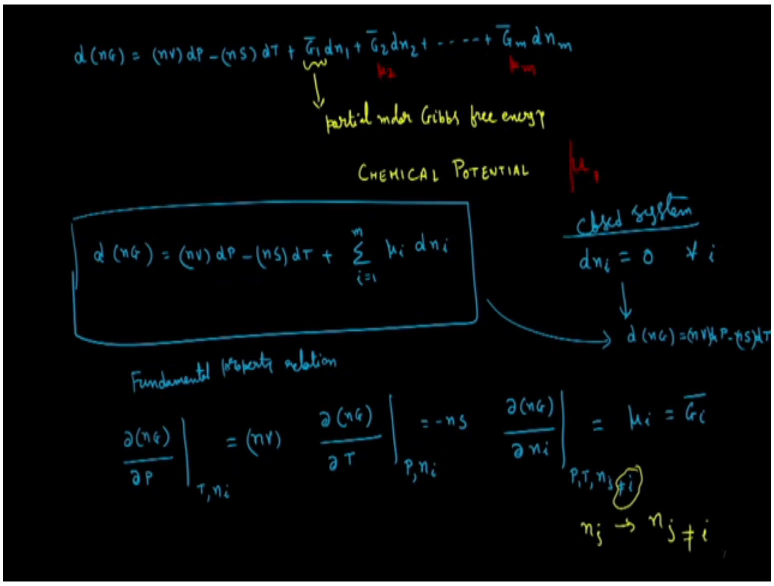

$$d(nG) = (nV)\,dP - (nS)\,dT + \underbrace{\bar{G}_1}_{} dn_1 + \underset{\mu_2}{\bar{G}_2} dn_2 + \cdots + \underset{\mu_m}{\bar{G}_m} dn_m$$

partial molar Gibbs free energy

CHEMICAL POTENTIAL μ_1

$$\boxed{d(nG) = (nV)\,dP - (nS)\,dT + \sum_{i=1}^{m} \mu_i\, dn_i}$$

Fundamental property relation

closed system

$dn_i = 0 \quad \forall i$

$d(nG) = (nV)dP - (nS)dT$

$$\left.\frac{\partial(nG)}{\partial P}\right|_{T,n_i} = (nV) \qquad \left.\frac{\partial(nG)}{\partial T}\right|_{P,n_i} = -nS \qquad \left.\frac{\partial(nG)}{\partial n_i}\right|_{P,T,n_{j \neq i}} = \mu_i = \bar{G}_i$$

$n_j \rightarrow n_{j \neq i}$

So, now I am going to make this substitution. So, that the derivatives look a little simpler and I will rewrite this equation d nG is going to be equal to n v dP minus n s dT plus G 1 bar dn 1 plus G 2 bar dn 2 plus all the way through G M bar d nm right and partial molar Gibbs free energy is a quantity that appears so often in chemical engineering thermodynamics, we will give it a special name. We are going to call this partial molar Gibbs free energy as Chemical Potential. It is a very important aerodynamics for separation processes for chemical reactions etcetera. So, we give it a special name we will call it as Chemical Potential and denote it by a Greek letter mu and because it is for

1, we call it as mu 1. The over bar is not required it automatically mu 1 itself is partial molar Gibbs free energy or chemical potential.

Similarly this is mu 2. This is mu m etcetera. So, if I were to write this expression in terms of chemical potentials, it would be d nG is going to be equal to n v dP minus n s dT plus summation over all these species i going from 1 through m; mu i the chemical potential of that particular species i d n i. So, this is a fundamental property relation for the role of Gibbs free energy of the system of an open system right. If the system is closed of course, if you look at this equation if the system is closed, then d n i for all i is 0 right because it is closed. The number of moles for all the species are constant; d n i would be 0. The last term drops out and this equation reduces to.

This is for a closed system all right. For a closed system d n i is 0 for all i and this equation would reduce to d of n G is n v dP minus n s dT which is what we already know right. So, it will go back to its form for the closed system. So, this equation in that sense is more general. It is applicable for both open and closed systems. For a closed system, the last term going to be 0 of course right. This is called as the Fundamental property relation and in fact, we can write all the derivatives we talked so far by looking at this fundamental property relation, if I were to take the derivative of nG with respect to P holding the temperature and all n i is constant. Then, holding temperature and all n i is constant will cancel out the second and the third terms; all I have left is the first term. So, this will be n v.

Similarly, I can look at this equation and easily write that the derivative of nG with respect to temperature, holding pressure constant will cancel out the first term. Holding a n i is constant and will cancel out everything in the third term. So, this will be equal to negative n s. Similarly, derivative of nG with respect to n i and remember when I say ni, this is a summation over a number of chemical components. When I say i, it is only one chemical component. So, I need to hold P T and n j not equal to i. All other components which are not; I need to be held or the moles for all those components need to be held constant. This would be equal to mu i which of course, is what we know the definition for partial molar Gibbs free energy G I bar etcetera.

So, from now onward when we write these derivatives for partial molar properties when I say mu i, we are going to ignore this particular expression right. We will simply call it as nj and by nj we automatically mean that nj not equal to i. So, that will make the notation a little easier. So, the partial molar Gibbs free energy then is same as the chemical potential which is the derivative of total Gibbs free energy with respect to ni at P T and n n j right. So, now, having said that let us look at the importance of chemical potential; chemical potential for phase equilibrium and then certain relationships between various partial molar properties right.

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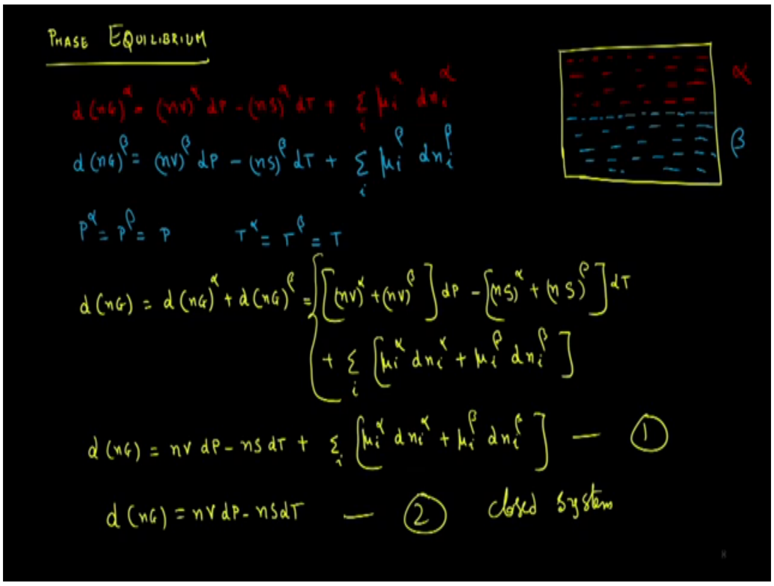

PHASE EQUILIBRIUM

$$d(nG)^{\alpha} = (nV)^{\alpha} dP - (nS)^{\alpha} dT + \sum_i \mu_i^{\alpha} dn_i^{\alpha}$$

$$d(nG)^{\beta} = (nV)^{\beta} dP - (nS)^{\beta} dT + \sum_i \mu_i^{\beta} dn_i^{\beta}$$

$$P^{\alpha} = P^{\beta} = P \qquad T^{\alpha} = T^{\beta} = T$$

$$d(nG) = d(nG)^{\alpha} + d(nG)^{\beta} = \left\{ \begin{aligned} & \left[(nV)^{\alpha} + (nV)^{\beta}\right] dP - \left[(nS)^{\alpha} + (nS)^{\beta}\right] dT \\ & + \sum_i \left[\mu_i^{\alpha} dn_i^{\alpha} + \mu_i^{\beta} dn_i^{\beta}\right] \end{aligned} \right.$$

$$d(nG) = nV\,dP - nS\,dT + \sum_i \left[\mu_i^{\alpha} dn_i^{\alpha} + \mu_i^{\beta} dn_i^{\beta}\right] \quad — \text{①}$$

$$d(nG) = nV\,dP - nS\,dT \quad — \text{②} \quad \text{closed system}$$

Let us first look at the phase equilibrium part. Now let us talk about a system that is closed. It has two phases any two phases; it can be a vapour and a liquid phase. So, let us talk it vapour liquid equilibrium, but then this is extendable to any equilibrium. So, I have some liquid mixture here and a corresponding vapour mixture above the liquid mixture. For generality let us call this as the alpha phase and this as the beta phase. Let us give it a different color.

So, we have alpha phase on the top and beta phase on the bottom. Now, for this particular scenario, let us write the expression for the total Gibbs free energy change of the alpha phase and the total Gibbs free energy of the beta phase. For the alpha phase d n G for alpha is going to be equal to n v alpha dP minus n s alpha dT plus sigma over i mu i alpha d n i alpha. This is the expression for the total Gibbs free energy of the alpha phase right.

Now, the let us say that these two phases are in equilibrium right and when we have these two phase mixture, they are free to exchange the total vessel is closed, but a particular phase is open because it is free to exchange matter with the other phase. So, for example, some moles from the alpha phase can be transferred to beta phase for a component i; some moles for beta phase can go through alpha phase.

So, each phase in itself is an open system, but both phases put together are inside the closed vessel and they constitute a closed system right. And what we have written here is the total Gibbs free energy for the alpha phase. I can also write the total Gibbs free energy for the beta phase d nG beta is going to be equal to n v beta d P minus n s beta dT plus sigma over i mu i beta d n i beta right..

Now, notice that we have not used a subscript for P and for T. So, the implicit assumption in here is that they are inside the container both of them are in equilibrium. So, the temperature and pressure for both the phases is same. So, we are simply going to use P instead of P alpha or P beta T instead of T alpha or T beta. So, these are the expressions for alpha and beta phases now.

For the total closed vessel, for both the phases put together right the Gibbs free energy d nG is going to be the summation of the Gibbs free energies of the alpha phase and the beta phase right and its going to be n v alpha phase plus n v beta phase dP minus ns for the alpha phase right ns for the beta phase dT plus mu i for the alpha phase d n i alpha plus mu i for the beta phase d n i beta and summation of this over all the components i. When I say all the components i, it is from i equal to 1 to m; where, m is the number of components in this particular system.

So, this is the expression for d of n G the system itself is closed right. So, because the system is closed the total volume of the system is not going to change. Now, the system itself is closed right. Then, I look at the first term in this particular scenario nv of alpha phase plus nv of beta phase is the total volume of the alpha phase plus total volume of the beta phase, when we add these two volumes what we get is the volume of the system we can simply call it as nv right.

So, d of nG is going to be equal to nv; where, n is the total volume of the system that for the alpha phase plus that for the beta phase dP minus as for the alpha phase plus as for the beta phase is the role entropy ns dT plus sigma over i this term stays as such d n i alpha plus d n i beta d n i beta right. Now, because the system is closed right d of n G is for a constant composition system, when we put both the phases together this equation should hold. So, this was the first equation and this is the second equation, this is true for any closed system. Once the system is closed both the phases put together are closed, they are not exchanging outside the yellow box.

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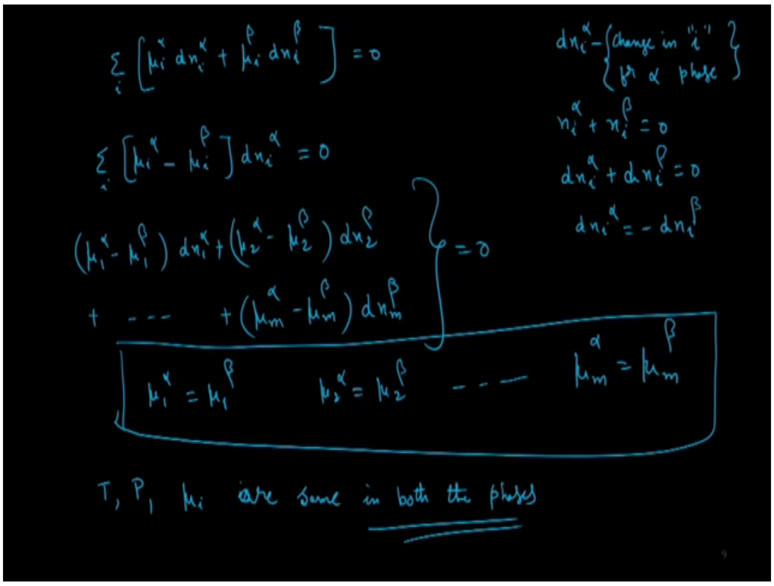

$$\sum_i \left[\mu_i^\alpha dn_i^\alpha + \mu_i^\beta dn_i^\beta\right] = 0$$

$$\sum_i \left[\mu_i^\alpha - \mu_i^\beta\right] dn_i^\alpha = 0$$

$$\left.\begin{aligned}(\mu_1^\alpha - \mu_1^\beta)\, dn_1^\alpha + (\mu_2^\alpha - \mu_2^\beta)\, dn_2^\beta \\ + \cdots + (\mu_m^\alpha - \mu_m^\beta)\, dn_m^\beta\end{aligned}\right\} = 0$$

$$\boxed{\mu_1^\alpha = \mu_1^\beta \qquad \mu_2^\alpha = \mu_2^\beta \qquad \cdots \qquad \mu_m^\alpha = \mu_m^\beta}$$

dn_i^α – {change in "i" for α phase}

$$n_i^\alpha + n_i^\beta = 0$$

$$dn_i^\alpha + dn_i^\beta = 0$$

$$dn_i^\alpha = -dn_i^\beta$$

T, P, μ_i are same in both the phases

So, the second equation has to hold from equations 1 and 2, it is obvious that sigma over i mu i d n i for the alpha phase plus mu i d n i for the beta phase should equal to 0. Now, if you think about it; d n i alpha is the number of change in i for alpha phase which means the number how many moles have changed from the alpha phase and because n i alpha is automatically means that d n i alpha plus d n i beta equals 0. So, the number of moles that have disappeared from one phase have to appear in the other phase or in other words, d n i alpha is negative of d n i beta.

So, if I take that, then this equation reduces to mu i alpha minus mu i beta d n i alpha is equal to 0 right. So, let me extend that a little bit. This would be mu i alpha minus mu i beta or mu 1 alpha plus mu 1 beta times d n 1 alpha plus mu 2 alpha minus mu 2 beta times d n 2 beta plus so on all the way through the mth component mu m alpha minus mu m beta times d n m beta; this needs to be equal to 0.

Now, each of these components n 1 alpha n 2 alpha etcetera are independent and arbitrary. We can choose the number of moles for any of the species arbitrarily and they are independent of each other and because of that reason the only way this expression is going to go to 0 is if each of the terms goes to 0 or in other words, mu 1 alpha has to be equal to mu 1 beta; mu 2 alpha has to be equal to mu 2 beta and so on all the way through the m component mu m alpha has to be equal to mu m beta.

So, in that sense if the phases are in equilibrium, then it turns out that the chemical potential for each of the species 1 2 3 all the way through m have to be equal in both the phases alpha and beta. In addition of course, we already considered that the temperature and pressure in both the phases are same. So, the criteria for equilibrium then is that the temperature, pressure and the chemical potential mu i for all species i is or are same in both the phases right.

This is the criteria for equilibrium and now we see why this is such an important variable for chemical engineering applications right. Chemical potential turns out to be an important variable which decides on how much phase dry or mass transfer we can achieve from one phase to another. We will come back to that discussion later on, but for now let us move on with the partial molar properties.

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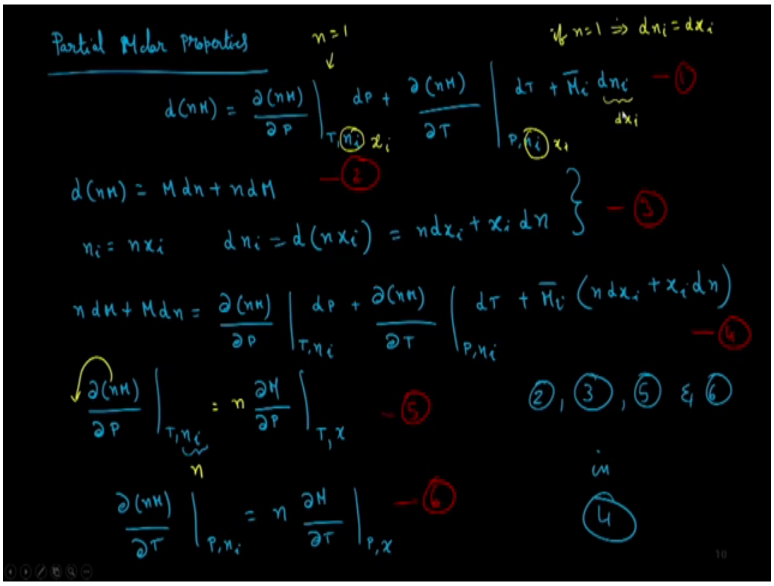

Partial Molar Properties

$n=1$ ↓

if $n=1 \Rightarrow dn_i = dx_i$

$$d(nM) = \left.\frac{\partial(nM)}{\partial P}\right|_{T,n_i\ x_i} dP + \left.\frac{\partial(nM)}{\partial T}\right|_{P,n_i\ x_i} dT + \bar{M}_i \underbrace{dn_i}_{dx_i} \quad -①$$

$$d(nM) = M\,dn + n\,dM \quad -②$$

$$\left.\begin{array}{ll} n_i = nx_i & dn_i = d(nx_i) = n\,dx_i + x_i\,dn \end{array}\right\} -③$$

$$n\,dM + M\,dn = \left.\frac{\partial(nM)}{\partial P}\right|_{T,n_i} dP + \left.\frac{\partial(nM)}{\partial T}\right|_{P,n_i} dT + \bar{M}_i\,(n\,dx_i + x_i\,dn) \quad -④$$

$$\left.\frac{\partial(nM)}{\partial P}\right|_{\underbrace{T,n_i}_{n}} = n\left.\frac{\partial M}{\partial P}\right|_{T,x} \quad -⑤$$

$$\left.\frac{\partial(nM)}{\partial T}\right|_{P,n_i} = n\left.\frac{\partial M}{\partial T}\right|_{P,x} \quad -⑥$$

②, ③, ⑤ & ⑥

in

④

So, we looked at what partial molar volume is in detail and then, we extended that discussion to various partial molar properties such as Gibbs free energy, enthalpy, internal energy etcetera and it turns out there is a common thread that binds all these our partial molar properties. If you recall the discussion we had for the total Gibbs free energy, we can write a similar expression for the any total thermodynamic property d of n M, it would be the partial derivative of M with respect to the pressure when we hold temperature and ni constant times dP, the partial derivative of M with respect to the temperature.

When I hold pressure and ni constant times dT plus the partial derivative or summation of the partial derivatives of nm with respect to ni, when I hold pt and nj constant right d n i and the last term is what we call as the partial molar property M i. So, I am going to replace the last term with M i bar just to make it simpler to handle, it is M i bar d n i. Now d of nM is M times d n plus n times dM.

And similarly, if I write ni is the total number of moles multiplied with the mole fraction then d n i is going to be d of n times x i or n times d x i plus x i times dn. Now, let me put these two expansions in the previous equation. So, that what we get is n times dm plus M times dn is the derivative of nm with respect to P temperature ni dP plus derivative nm T pressure n i dT plus M i bar n d x i plus x i d right.

So, we will take this equation here and try to rearrange the terms a little bit; what we get is d M minus the derivative of nM with respect to P at T and n i write and when I hold all the n i ok, let us make one other. Now the derivative of nm with respect to P and I hold all the n is constant, it automatically means the total number of moles n is constant. So, this can come out of this derivative. So, this will be n times the derivative of M with respect to P and because all ns are constant I can also claim that the mole fraction x is constant.

Similarly, for the second term derivative of nm over T at P and n i will be n times derivative of M with respect to T at P and x. So, I am going to make let us number them so that it is easy this is 1 2 3 4 5 and 6. So, what I will do is, I will substitute 2 3 5 and 6 and 4. I will make this substitution and do a little bit of rearrangement of the terms etcetera.

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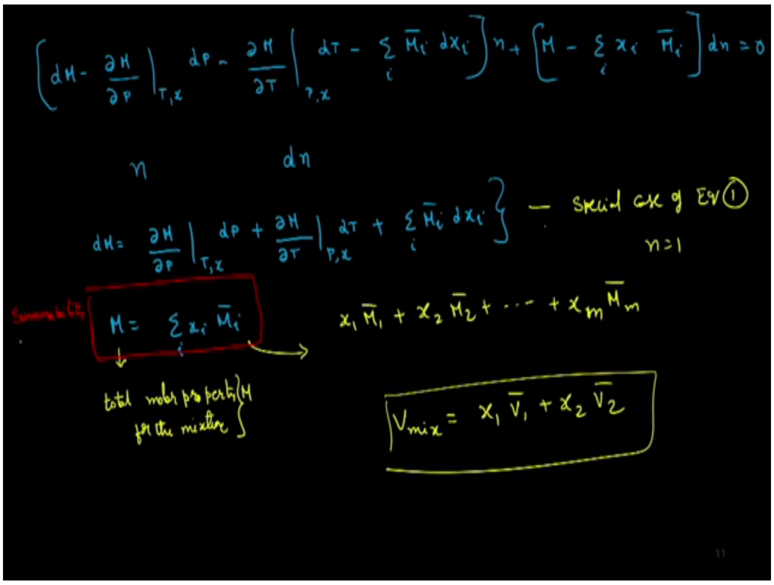

$$\left[dM - \frac{\partial M}{\partial P}\Big|_{T,x} dP - \frac{\partial M}{\partial T}\Big|_{P,x} dT - \sum_i \bar{M}_i\, dx_i\right] n + \left[M - \sum_i x_i \bar{M}_i\right] dn = 0$$

n dn

$$\left.dM = \frac{\partial M}{\partial P}\Big|_{T,x} dP + \frac{\partial M}{\partial T}\Big|_{P,x} dT + \sum_i \bar{M}_i\, dx_i \right\}$$ — Special case of Eq ① $n=1$

Summability $\boxed{M = \sum_i x_i \bar{M}_i} \rightarrow x_1\bar{M}_1 + x_2\bar{M}_2 + \dots + x_m\bar{M}_m$

total molar property (M for the mixture)

$$\boxed{V_{mix} = x_1\bar{V}_1 + x_2\bar{V}_2}$$

And if you do that I will leave it for you to do it. If you do that what we will end up with is dM minus derivative of M with respect to P T x dP minus derivative of M with respect to T P x dT minus sigma over i M i bar d x i multiplied with plus M minus sigma over i x i d mi bar multiplied with the d n i or d n equals 0.

So, we rearrange the terms and made those substitutions to get this equation and once we are at this stage, if you look at it what this tells me is that sum of two turns needs to be 0. If you look at this equation there are two terms in this equation; the first term is multiplied with n, the size of the system and the second term is multiplied with d n or the change in size of the system. Both these quantities n and d n are arbitrary. I can choose any size of the system and I can choose decide to change that size by any amount I wish to d n and both of them are independent and arbitrary in that sense.

And the only way this particular equation will be applicable, then for all the scenarios is if each of the terms inside the parenthesis is going to go to 0 and if that happens the first term is an equation which we already know the total molar property M is going to be the derivatives of the partial properties dx dP oh sorry is going to be the total molar property M is going to be the derivative of M with respect to P at T n constant T n x dP derivative of M with respect to T at constant P and x dT plus sigma mi bar d x i overall i. The second equation is M is sigma x i M i bar again over all i.

Now this first equation here is actually a special case of the equation we already know right. Now, if you take this equation 1 and you make the total size of the system n equal to 1 right; in equation 1 here if I put n equal to 1, what we get is dm on the left hand side dm over dP dou M over dou P at constant T and n i; if all ni's are constant, it automatically means the mole fraction of all is also is constant right.

So, it is same as dou n by dou P at T and xd P dou M by dou T at P and x dT plus sigma M i bar and when the size of the system is 1; d n i equals dx i. If the total number of moles is 1 right. So, the last term will be d x i. So, this equation 1 essentially reduces to what we have here; this is a special case of 1, when the size of the system is 1 right and the second equation however, is an outcome of this whole exercise. It says that the total molar property M is equal to summation of the partial molar properties weighted with the respective mole fractions x m M m bar.

So, you weight all the partial molar properties with their respective mole fractions add them that will give the total molar property for the mixture. This is an important outcome. So, when we mix the components the partial molar volumes are not additive right, but then what are additive is the partial molar volumes. If we know the partial molar volume, then we can say that the total volume for the molar volume for the mixture is going to be x 1 v 1 bar plus x 2 v 2 bar. For a special case v 1 bar might be same as v 1; v 2 bar might be same as v 2 etcetera, but irrespective of whether it is true or not, this particular expression is always true for a binary mixture.

Not just volume for any molar property M not just for binary mixture, but for even multi component mixtures, M will always be equal to sigma x i M i bar and we call this relation as Summability. We are summing the partial molar properties with respective or weighted with their respective mole fractions and we call this as Summability relation. So, that is the take home message for todays lecture. We will hold on to that and when we come back in the next class, we will talk more about solution thermodynamics.

Thank you.