

**Chemical Engineering Thermodynamics**  
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**Solution Thermodynamics**

**Lecture - 21**  
**Partial molar properties**

Hello and welcome back. So, we were talking about solution thermodynamics yesterday and in this lecture, we will continue our discussion on solution thermodynamics. But before we do that let us quickly recap what we have done so far on this topic.

(Refer Slide Time: 00:58)

Partial Molar Property:  $\bar{M}_i = \left. \frac{\partial (nM)}{\partial n_i} \right|_{P, T, n_{j \neq i}}$

Fundamental property relation

$$d(nM) = \left. \frac{\partial (nM)}{\partial P} \right|_{T, n_i} dP + \left. \frac{\partial (nM)}{\partial T} \right|_{P, n_i} dT + \sum_i \bar{M}_i dn_i$$

$$d(nG) = (nV)dP - (nS)dT + \sum_i \bar{G}_i dn_i$$

$\bar{G}_i \rightarrow \text{chemical potential}$

$$dG = VdP - SdT + \sum_i \mu_i dx_i$$

closed  $\rightarrow dG = VdP - SdT \quad (dx=0)$

Pure equilibrium ( $T, P, \mu_i$ )

$T^s = T^L$

$P^s = P^L$

$\mu_i^s = \mu_i^L \quad \forall i$

The first thing we have defined for a mixture or a solution is what is known as the Partial Molar Property. Partial Molar Property, this can be any thermodynamic property such as internal energy, enthalpy, entropy, Gibbs free energy etcetera.

And this partial molar property we have indicated it as  $\bar{M}_i$  let us say and this  $\bar{M}_i$  represents the partial molar property for component  $i$  and it is defined as the derivative of the total property  $nM$  with respect to the number of moles of that component  $i$ , when we hold the temperature, pressure and moles of all the other components  $j$  not equal to  $i$  constant. This is how we have defined the partial molar property and we have looked at a few relations for partial molar property.

The first one is that it arises from the definition of a for a or it arises from the fundamental property relation for an open system. So, the fundamental property relation for an open system using this partial molar property is written as  $dM = \sum_i n_i d\bar{M}_i + \bar{V} dP - \bar{S} dT + \sum_i \bar{M}_i dn_i$ . The total change in the property  $M$  will be the derivative of  $M$  with respect to the pressure at constant  $T$  and all the moles are a  $n_i$ 's constant;  $dP$  plus the derivative with respect to the temperature at constant  $P$  and  $n_i$   $dT$  plus the sigma over all the components  $i$  the derivative with respect to each one of those  $n_i$ 's  $dn_i$ .

And notice that the last term essentially of the derivative in the last term essentially is what we call as  $\bar{M}_i$ . This is the fundamental property relation for any thermodynamic property  $M$  and we can use it to write for example, the relation for  $dG$  will be  $\bar{V} dP - \bar{S} dT + \sum_i \bar{G}_i dn_i$  over all  $i$ . The other thing we have defined yesterday is  $\bar{G}_i$  is also known as  $\mu_i$  or the chemical potential; the chemical potential.

In addition to this, if we look at this equation and if I write this equation just for one mole of substance of course,  $dG$  if  $n$  equals 1, then  $dG$  will be  $\bar{V} dP - \bar{S} dT + \sum_i \mu_i dn_i$  for 1 mole  $dn_i$  will be same as  $dx_i$ . This is true for an open system. If the system is closed, then  $dG$  will be simply  $\bar{V} dP - \bar{S} dT$  because for a closed system  $dx$  equals 0. So,  $dG$  will be simply  $\bar{V} dP - \bar{S} dT$  whatever we had earlier for a closed system right.

So, in that sense this particular equation is more general. We can write similar thermodynamic properties for a fundamental property relations for involving other thermodynamic variables, but the Gibbs free energy is of more interest for us in chemical engineering applications. The other thing we might want to mention here is that we have derived a condition for phase equilibrium between two phases, alpha and beta phases.

And it turns out that we said  $T_\alpha$  will be  $T_\beta$ . The pressure in the alpha phase all is equal to the pressure in the beta phase. And finally, the chemical potential for each of the species in the alpha phase needs to be equal to the chemical potential for each of the species in the beta phase for all these species right. This was the criteria for phase equilibrium; we have derived using the chemical potential in the previous lecture.

(Refer Slide Time: 05:54)

$M = \sum x_i \bar{M}_i$  (summability)  
 $M = x_1 \bar{M}_1 + x_2 \bar{M}_2$   
 For example if  $C=2$ , binary mixture  $\pi=1$  phase  
 $F = C - \pi + 2 = 3$   
 $G = G\{T, P, x_1\}$      $M = M\{T, P, x_1\}$   
 $n = n\{T, P, n_1, n_2\}$   
 $\bar{M}_i = \bar{M}_i\{T, P, x_1\}$      $T, P$ , composition

$\bar{M}_i$  need not be same  $M_1$   
 $\bar{M}_2$  need not be same  $M_2$

$M_i$  - pure species  
 $\bar{M}_i$  - species  $i$  partial molar in mixture  
 $M$  - molar prop for the mixture  
 INTENSIVE

Now, in addition to this, we have also derived a few other relations involving the partial molar properties. One of them is what we called as the summability relation  $M$ . It turns out will be equal to  $\sum x_i \bar{M}_i$ . We call this as the summability relation right. What this means is that for a binary system  $M$  will be equal to  $x_1 \bar{M}_1$  plus  $x_2 \bar{M}_2$ .

So, in that sense what we are trying to do is trying to treat the total property in a mixture  $M$  as if it were it is a result of contribution of a part coming from component 1 and another part coming from component 2. And each of these parts from components 1 and 2 is proportional to the partial molar volume or partial molar property coming from 1 and partial molar property coming from 2. So, this total property for the mixture  $M$  is arising from a contribution proportional to  $\bar{M}_1$  from component 1 and a contribution proportional to  $\bar{M}_2$  from component 2 right.

Now, in addition to this remember that because we are talking about a mixture  $\bar{M}_1$  need not be same as  $M_1$  and  $\bar{M}_2$  need not be same as  $M_2$ . When we say just quickly to so that we reiterate the notations, when we say  $M_i$ , it is for the pure species  $i$ . When I say  $\bar{M}_i$ , it is for species  $i$ , but it is a partial molar property in mixture and when I say only  $M$ , it is the molar property for the mixture that contains whatever components there are in that particular mixture. So, that is the notation we are using  $M_i$ ,  $\bar{M}_i$  and  $M$  and in a mixture obviously, with the example we looked at yesterday

in terms of volume  $M_1$  bar need not be same as the pure component value  $M_1$ ;  $M_2$  bar need not be same as the pure component value  $M_2$  etcetera right.

Now, all of these are molar properties. Partial molar property  $M_i$  is the molar property for pure species  $i$ .  $M$  is the molar property for the mixture of components and all of them are molar properties. So, all of them are Intensive variables. They do not depend on the size of the system right. What do they depend on? Well, what they depend on comes from the phase rule.

For example, in case of a binary mixture the number of components is 2. I have a binary mixture and I have one phase number of phases is 1. Then the degrees of freedom is  $C$  minus of  $p_i$  plus 2. So, that is 3. So, I have 3 degrees of freedom and like we talked yesterday. For example, the Gibbs free energy is going to be a function of 3 variables the temperature, the pressure and one of the 2 mole fractions either  $x_1$  or  $x_2$  in case of a binary mixture right. In general the property  $M$  is going to be a function of 3 variables  $T$ ,  $P$  and  $x_1$ . If it is a multi component mixture, it will be dependent on  $M$  minus 1 mole fractions etcetera.

If this be the case if  $M$  is dependent on temperature, pressure and mole fraction; I take the derivative of this with respect to  $n_i$   $n_M$  obviously, will be dependent on the way we indicated it for  $G$  was small  $M$  right  $T$ ,  $P$   $n_1$ ,  $n_2$  right for a binary mixture and so on and if I take the derivative of this with respect to  $n_1$  or  $n_2$ , then what I get is either  $M_1$  bar or  $M_2$  bar. Then, it turns out that  $M_1$  bar is going to be a function again of the three variables right  $T$ ,  $P$  and  $x_1$  or  $T$ ,  $P$  and  $x_2$ .

So, the degrees of freedom does not change. It is a partial molar property, it still remains 3. So,  $M_1$  bar also will be a function of three variables  $T$ ,  $P$  and  $x$  or in general for a multi component mixture, it is going to be a function of the temperature the pressure and composition; it will depend on all of these variables and these are again molar properties. So, they are intensive variables, but then in case of a mixture they will depend on temperature pressure and composition for a pure component of course, they depend only on temperature and pressure.

(Refer Slide Time: 11:03)

Pure species 1  $n = n_1$   $M = M_1 \rightarrow$  (independent of  $n_1$ )  

$$\bar{M}_1 = \left. \frac{\partial (nM)}{\partial n_1} \right|_{P,T} = \left. \frac{\partial (n_1 M_1)}{\partial n_1} \right|_{P,T} = M_1 \left. \frac{\partial n_1}{\partial n_1} \right|_{P,T} = M_1$$

Now, if I ask you what is the partial molar property for a pure species? For a pure species of course,  $M$  let's say I have only 1 component. Pure species, one alone and I am interested in finding  $M_1$  bar right. For pure species  $n$  will be equal to  $n_1$  and  $M$  the molar property will be equal to  $M_1$ ; the molar property of the pure species 1 with the notation we have used. So,  $M_1$  bar, then will be equal to derivative of  $nM$  with respect to  $n_1$ , when I hold temperature, pressure and  $n_2$  here. I only have one component.

So, holding  $n_2$  everything else anyway there is no other species which needs to be held constant. So, it is simply derivative of  $nM$  with respect to  $n_1$  at  $P$  and  $T$  right and since  $n$  is same as  $n_1$  and  $M$  is  $M_1$  which is constant;  $M_1$  itself will not depend on the number of moles, it is a molar property. So, independent that is right that independent of  $n_1$  right because it is an intensive property, it is a molar property for pure species 1. So, it is independent of  $n_1$ .

So, I can write this guy as  $n$  times  $n_1$  times  $M_1$  over  $n_1$  at  $P$  and  $T$  and that  $M_1$  can come out of the derivative and what I have is derivative of  $n_1$  with respect to  $n_1$  at  $P$  and  $T$  and this will be  $M_1$ . So,  $M_1$  bar for pure species is same as the pure species molar property. So, partial molar property will be same as the pure component property if I have only one component in that mixture obviously, right.

(Refer Slide Time: 12:56)

Gibbs-Duhem Equation

$$dM = \left. \frac{\partial M}{\partial P} \right|_{T,x} dP + \left. \frac{\partial M}{\partial T} \right|_{P,x} dT + \sum_i \bar{M}_i dx_i \quad \text{--- (1)}$$

$$M = \sum_i x_i \bar{M}_i \Rightarrow dM = \sum_i x_i d\bar{M}_i + \sum_i \bar{M}_i dx_i \quad \text{--- (2)}$$

$$\left. \frac{\partial M}{\partial P} \right|_{T,x} dP + \left. \frac{\partial M}{\partial T} \right|_{P,x} dT - \sum_i x_i d\bar{M}_i = 0$$

At Const. T & P

$$\sum_i x_i d\bar{M}_i = 0 \quad (\text{@ Const. T \& P})$$

Now, let us talk about another very important relation we commonly use in solution thermodynamics right; we call this as Gibbs-Duhem Equation. It turns out that if I write a fundamental property relation for any molar property M, dM was derivative of M with respect to P at T and x for T and n i. So, it is T and x d P plus derivative of M with respect to T at P and x dT plus sigma over i M i bar d x. I am right? We have also seen that through summability relation M is a sigma over i x i Mi bar. What this means is that if I take a derivative of this dM will be sigma over i x i d Mi bar plus sigma over i Mi bar d x i.

Now, if I use these two relations 1 and 2, I can eliminate the M right and what results is derivative of M with respect to P T x d P plus derivative of M with respect to T P x dT plus the sigma Mi bar dx; I will cancel out will be equal to sigma of i x i d Mi bar. In a more general way, we actually bring it to the other side and write it as negative this will be equal to 0. This particular equation the last equation is known as the Gibbs-Duhem equation.

What it gives us is that this equation must always be satisfied for any changes in temperature, pressure and partial molar property Mi bar. We can restrict this for conditions of constant temperature and pressure which is a more useful way of using Gibbs-Duhem equation. At constant temperature and pressure the first two terms drop

out right and what we are left with is  $\sum x_i d\bar{V}_i$  will be equal to 0 at constant temperature and pressure right.

This is more restricted form of Gibbs-Duhem equation at constant temperature and pressure, but then it is more useful for practical applications let us see what we mean by that right. Let us consider a binary system.

(Refer Slide Time: 15:58)

The image shows a handwritten derivation on a black background. It starts with the volume equation  $V = x_1 \bar{V}_1 + x_2 \bar{V}_2$ . Below it, the Gibbs-Duhem equation is written as  $\sum x_i d\bar{V}_i = 0$  (Gibbs-Duhem equation) at constant temperature and pressure. This is then expanded to  $x_1 d\bar{V}_1 + x_2 d\bar{V}_2 = 0$ . Since it's a binary system,  $x_2 = 1 - x_1$ , so the equation becomes  $x_1 d\bar{V}_1 + (1 - x_1) d\bar{V}_2 = 0$ . Dividing both sides by  $dx_1$  yields  $x_1 \frac{d\bar{V}_1}{dx_1} + (1 - x_1) \frac{d\bar{V}_2}{dx_1} = 0$ . Finally, the relationship  $\frac{d\bar{V}_2}{dx_1} = -\frac{x_1}{1 - x_1} \frac{d\bar{V}_1}{dx_1}$  is boxed in red, with an arrow pointing to the right.

So, the molar volume, it is easy to explain most of this concept in terms of volume because we can easily relate to the volume right. So,  $v$  the molar volume of the mixture  $v$  in a binary mixture by summability relation is  $x_1 v_1$  bar plus  $x_2 v_2$  bar.

So, now if I say at constant  $T$  and  $P$   $\sum x_i d\bar{V}_i$  has to be 0. This is Gibbs-Duhem equation right. So, what this means is  $x_1 d\bar{V}_1$  bar plus  $x_2 d\bar{V}_2$  bar equals 0. This is a binary system. So, we can actually write  $x_2$  in terms of  $x_1$ . So, this is  $x_1 d\bar{V}_1$  bar plus  $(1 - x_1) d\bar{V}_2$  bar is 0. Like we said this is constant temperature and pressure the only way  $v_1$  bar or  $v_2$  bar will change is when  $x$  changes right.

So, essentially when we say  $d\bar{V}_1$  bar, it is change in  $v_1$  bar due to change in  $x$ . So, I can also write this equation as  $x_1 d\bar{V}_1$  bar by  $dx_1$  plus  $(1 - x_1) d\bar{V}_2$  bar over  $dx_1$  equals 0 or in other words,  $\frac{d\bar{V}_2}{dx_1}$  is negative of  $x_1$  by  $(1 - x_1) \frac{d\bar{V}_1}{dx_1}$  or rather  $d\bar{V}_1$  bar by  $dx_1$ .

Now, what this equation gives me is that the change in the molar volume for two v 2 bar is not independent. It is dependent on how v 1 bar changes with x 1, the slope of v 1 bar versus x 1 curve which is dv 1 by dx 1 will determine the slope of v 2 bar versus x 1 curve also via this relation; both of them are not completely independent in that sense.

So, this equation always has to be satisfied which means there are two partial molar properties v 1 bar and v 2 bar cannot independently change by themselves. They are somehow related to one another in this case we are this particular equation. Now, we will hang on to this for the next part of our discussion also. We will come back and revisit this equation. Let us see another important property of a partial molar proper partial molar properties right.

(Refer Slide Time: 18:40)

Binary system  $n = n_1 + n_2$

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

$$nV = n_1 \bar{V}_1 + n_2 \bar{V}_2$$

Add  $\Delta n_1 (\rightarrow 0)$  moles of 1 to this mixture! (at the same T, P)

$$(nV)_{\text{final}} = (n_1 + \Delta n_1) \bar{V}_1 + n_2 \bar{V}_2$$

$$(nV)_{\text{final}} - (nV)_{\text{initial}} = \Delta(nV) = \Delta n_1 \bar{V}_1$$

At pure component limit of 1 i.e.  $x_1 \rightarrow 1$   $x_2 \rightarrow 0$   $n_1 \gg n_2$

$$\Delta(nV) = \Delta n_1 \bar{V}_1 \text{ pure 1}$$

$$\lim_{x_1 \rightarrow 1} \bar{V}_1 = V_1$$

*Similarly*  
 $\lim_{x_2 \rightarrow 1} \bar{V}_2 = V_2$

We said v is we will go back to our example of a binary system right.

Let us look at a binary system. So, v is x 1 v 1 bar plus x 2 v 2 bar; if I write the total volume, then n times v will be n 1 v 1 bar x 1 times n is n 1 plus n 2 v 2 bar. Now, remember that n is n 1 plus n 2. This is a binary system right. Now at this case we decide to add delta n 1 clue very small value delta n 1 moles of 1 to this mixture all right.

We decide to add delta n 1 moles of 1 to this mixture and what happens is there will be a change in volume and v final will be n 1 plus delta n 1 times v 1 bar; v 1 bar and v 2 are all though a functions of composition, we are doing it at the same T and P. Those are not



changing although they are functions of composition, if the change in  $n_1$  is very very small;  $\Delta n_1$  goes to 0. Then,  $v_1$  bar and  $v_2$  bar is essentially the same right.

So,  $n_1$  plus  $\Delta n_1$  times  $v_1$  bar plus  $n_2$  times  $v_2$  bar right and  $v$  final minus  $n v$  initial right; the initial value is right here all right and we final minus  $n v$  initial will be essentially then  $\Delta n_1$  times  $v_1$  bar right. So, let us call this as  $\Delta n v$ . This will be  $\Delta n_1$  times  $v_1$  bar right. So, the change in volume of the mixture is  $\Delta n_1$  times  $v_1$  bar.

Now, at pure component limit of one that is if I take my mixture to be mostly 1, there is very small amount of 2; then  $x_1$  goes to 1,  $x_2$  goes to 0 and this will be the case when  $n_1$  is very large than then  $n_2$  right. If this is the case, I have a mixture which is mostly 1 and very small amount of 2, in this particular mixture. At such a scenario, what if I add  $\Delta n_1$  moles of 1; what would be the change in volume?

It will no doubt be  $\Delta n_1$  times  $v_1$  bar at every location, whatever that  $v_1$  bar value is. But if my mixture is mostly 1 and I add  $\Delta n_1$  moles of 1, then there is no reason to believe that the change will not be proportional to the pure component value of 1. Or in other words,  $\Delta n v$  will be equal to  $\Delta n_1$  times  $v_1$ . At this limit the change in volume because I am adding additional moles of 1 and it is mostly pure component 1 anyway, it will be same as  $\Delta n_1$  times the pure component value for 1.

So, what this tells me is that at this pure component limit, then limit  $x_1$  going to 1  $v_1$  bar should equal to  $v$  for pure 1. You can compare this particular equation here and this equation which is the general case applicable in all the compositions and looking at them, you can tell that they add the pure component limit  $v_1$  bar will be equal to the pure component value for 1 which is  $v_1$ .

Similarly, right limit of at the other pure component limit, when I have mostly 2 at that case  $v_2$  bar will be same as  $v$  for pure 2. So, in general then at the pure component limit, the partial molar property will be same as the molar property for the pure species. That was an easy result to obtain.

(Refer Slide Time: 23:40)

At  $x_1 \rightarrow 0$ ,  $n_1 \ll n_2$   $\Delta(nv) = \Delta n_1 \bar{v}_1$

$\bar{v}_1 \rightarrow ?$

$x_2 \rightarrow 1$ , pure species 2

As  $x_1 \rightarrow 0$  → infinitely dilute 1 or infinite dilution for Component 1.

$\bar{v}_2 \rightarrow \bar{v}_2$

$$\frac{d\bar{v}_1}{dx_1} = -\frac{1-x_1}{x_1} \frac{d\bar{v}_2}{dx_1} \rightarrow 0$$

$$\lim_{x_1 \rightarrow 0} \frac{d\bar{v}_1}{dx_1} = -\lim_{x_1 \rightarrow 0} \frac{1-x_1}{x_1} \frac{d\bar{v}_2}{dx_1} = 0$$

$\bar{v}_1 \rightarrow$  Constant value (independent of  $x$ )

$\bar{v}_1 \rightarrow \infty$  partial molar volume for 1 at infinite dilution.

Let us talk about the other limit. What happens when  $x_1$  goes to 0 which will be the case when  $n_1$  is much smaller than  $n_2$ ? At this limit if I add, now remember this is a general result  $\Delta n v$  is  $\Delta n_1 \bar{v}_1$  right. At  $x_1$  going to 0, if  $n_1$  is much smaller than  $n_2$ ; then, can I say something about  $\bar{v}_1$ ? At the other limit when  $x_1$  was going to 1,  $\bar{v}_1$  was same as pure 1.

At the limit when  $x_1$  goes to 0; can I say something about  $\bar{v}_1$ ? First of all as  $x_1$  goes to 0, we call this as infinitely dilute 1 or infinite dilution for component 1 in the mixture of course ok. To answer this question, what happens to  $\bar{v}_1$ , we resort to using the Gibbs-Duhem equation we had earlier.

What we have obtained earlier in terms of Gibbs-Duhem equation, if you recall is expression between  $d\bar{v}_1$  by  $dx_1$  and  $d\bar{v}_2$  by  $dx_1$  right. So, it turns out that  $d\bar{v}_1$  by  $dx_1$  is negative  $1 - x_1$  by  $x_1$   $d\bar{v}_2$  by  $dx_1$ . As  $x_1$  goes to 0;  $x_2$  goes to 1, it is pure species 2. So, because it is pure species 2  $d\bar{v}_2$  by  $dx_1$  approaches  $\bar{v}_2$  and  $d\bar{v}_2$  by  $dx_1$  approaches 0 right. It does not change; its 0 because you are approaching the pure component limit.

The second term is 0 alright, but the first term also is divided by 0. So, what we do is we apply lhopitals rule for this particular expression; evaluate it and as you will see if I apply lhopitals rule at this limit, it turns out that the limit of  $x_1$  going to 0  $\bar{v}_1$  by  $dx_1$

1 is negative limit  $x_1$  going to 0,  $1 - x_1$  by  $x_1 d v_2$  bar over  $dx_1$  and this limit applying lhopitals rule turns out to be 0.

What this means is that  $v_1$  bar approaches a constant value. That is the only way this derivative can go to 0, when we say constant value, we mean that it is independent of  $x$ . So, at the other limit when  $x_1$  goes to 0,  $v_1$  bar approaches a constant value or it approaches a value which is independent of the composition. Now, we also know that the change in the total volume is  $\Delta n_1$  times  $v_1$  bar  $\Delta n_1$  is finite.

So,  $v_1$  bar also has to be a finite value so that the change in the total volume will be finite which means that  $v_1$  bar will approach some constant finite value. So, I am going to add that term here, constant finite value right. So, then we call that constant finite value  $v_1$  bar infinity or partial molar volume for one at infinite dilution.

So, we have looked at two limits; one is the limit when we approach the pure component value for pure component of 1, at that case  $v_1$  bar is unit  $v_1$  bar is same as  $v_1$ . At the other end when I approach the pure component limit for 2 or infinite dilution for 1, then  $v_1$  bar will be  $v_1$  bar infinity. So, we talked about a molar volumes, but then this discussion is applicable to any thermodynamic property.

(Refer Slide Time: 28:24)

$$\left. \begin{aligned} \lim_{x_i \rightarrow 1} \bar{M}_i &= M_i \\ \lim_{x_i \rightarrow 0} \bar{M}_i &= \bar{M}_i^\infty \end{aligned} \right\} \begin{aligned} \bar{M}_i^\infty \\ \bar{S}_i^\infty \end{aligned}$$

So, let us summarize what we just said about partial molar properties limit of  $x_i$  going to 1  $\bar{M}_i$  bar is  $M_i$ . At the pure component limit the partial molar property is same as the

pure component property. Limit  $x_i$  going to 0 at the infinite dilution limit  $M_i$  bar is a constant value called as the infinite dilution value  $M_i$  bar infinity. So, these are the two important characteristics of a partial molar property. We can use it and say that and in when I say  $H_i$  bar infinity, this is the enthalpy for 1 at infinite dilution when I say  $S_i$  bar infinity, infinite entropy for 1 at infinite dilution limit etcetera.

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Handwritten mathematical derivations on a blackboard background:

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

$$dG = VdP - SdT + \sum_i \bar{G}_i dx_i$$

$$\left. \frac{\partial G}{\partial T} \right|_{P,x} = -S \quad (1)$$

$$\left. \frac{\partial G}{\partial P} \right|_{T,x} = V \quad (2)$$

$$\left. \frac{\partial G}{\partial n_i} \right|_{P,T,n_j} = \bar{G}_i \quad (3)$$

$$\frac{\partial}{\partial n_i} \left[ \left. \frac{\partial G}{\partial T} \right|_{P,x} \right]_{P,T,n_j} = \frac{\partial}{\partial n_i} [-S]_{P,T,n_j}$$

$$\frac{\partial}{\partial T} \left[ \left. \frac{\partial G}{\partial n_i} \right|_{P,T,n_j} \right]_{P,x} = -\bar{S}_i$$

$$\Rightarrow \left. \frac{\partial \bar{G}_i}{\partial T} \right|_{P,x} = -\bar{S}_i \quad (4)$$

$$\left. \frac{\partial \bar{G}_i}{\partial P} \right|_{T,x} = \bar{V}_i \quad (5)$$

Now, we looked at some of the characteristics of partial molar properties. Let us look at a few more important relations amongst partial molar properties themselves. If you recall  $d(nG)$  was  $nV dP$  minus  $nS dT$  plus sigma over  $i$   $\mu_i dn_i$ . We can write it for a size of the system equal to 1 and in that case  $dG$  will be  $VdP$  minus  $SdT$  plus sigma over  $i$   $\bar{G}_i dx_i$  for sake of clarity I am going to use  $\bar{G}_i$  instead of  $\mu_i$ , both of them are identical as you know  $dx_i$  right.

Now, looking at this fundamental property relation for an open system, if I ask what would be the derivative of  $G$  with respect to the temperature, when I hold the pressure and composition all mole fractions of all the components  $P$  and  $x$  constant. Then, we can easily answer that it is negative  $S$  right. Similarly, if I look at this equation and ask the derivative of  $G$  with respect to  $P$  at constant  $T$   $n$   $x$  is  $V$  right. Once  $x$  is constant remember that it means that we are in a condition for the closed system.

So, essentially these were the equations which we actually used for a closed system right. Now I start from here and then the last equation of course, is going to be derivative of  $G$

with respect to  $n_i$  at  $P, T$  and  $n_j$  all the other  $j$ 's that are not equal to  $i$  will be  $\bar{G}_i$ . Now, what I will do is I will take these equations 1, 2 and 3. I will take these equations 1, 2 and 3; let us start with one and three first right and then so, now what we will do is take equation 1 here and take the derivative with respect to  $n_i$ . Derivative with respect to  $n_i$ , Derivative of  $G$ , derivative of  $T$  at  $P$  and  $x$  and with the derivative with respect to  $n_i$  is taken at  $P, T$  and  $n_j$  right and on the right hand side, it will be derivative. So, I am using equation 1 and taking derivative with respect to  $n_i$  on both sides, it will be negative  $S$  at  $P, T$  and  $n_j$  right.

Now, if I look at the right hand side derivative of  $S$  with respect to  $n_i$  at  $P, T$  and  $n_j$ ; obviously, is the definition for partial molar entropy. So, it will be  $\bar{S}_i$  a negative sign that carries. And on the right hand side, what we will do is we will change the order of differentiation. So, it will be derivative of  $G$  with respect to  $n_i$  at  $P, T$  and  $n_j$  and derivative of that with respect to  $T$  at  $P$  and  $x$  and the term within the square parentheses here is essentially  $\bar{G}_i$  as you know.

So, that value will be derivative of  $T \bar{G}_i$  at  $P$  and  $x$  is negative  $\bar{S}_i$  right. This is what I get using equation 1. I can similarly use equation 2 to get derivative of  $\bar{G}_i$  with respect to  $P$  at constant temperature and  $x$  is essentially  $\bar{V}_i$ . This follows from 2; this was from 1 right. So, now, I have equation 4 and equation 5. If you look at equation 4 and 5, in both cases my composition is constant; we are at constant  $x$  right.

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In a mixture of const. composition

$$\left. \frac{\partial \bar{G}_i}{\partial T} \right|_{P, x} = -\bar{S}_i$$

$$\left. \frac{\partial \bar{G}_i}{\partial P} \right|_{T, x} = \bar{V}_i$$

$$\bar{G}_i = \bar{G}_i(T, P, x)$$

$$d\bar{G}_i = \left. \frac{\partial \bar{G}_i}{\partial P} \right|_{T, x} dP + \left. \frac{\partial \bar{G}_i}{\partial T} \right|_{P, x} dT$$

$$d\bar{G}_i = \bar{V}_i dP - \bar{S}_i dT$$


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

$$dG = VdP - SdT \quad (\text{const } x)$$


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$$dU = TdS - PdV$$

$$d\bar{U}_i = Td\bar{S}_i - Pd\bar{V}_i$$

So, if we take that, then it turns out in a mixture of constant composition. Derivative of  $\bar{G}_i$  with respect to  $T$  at  $P$  and of course,  $x$  because it is constant composition anyway, it is negative  $\bar{S}_i$  derivative of  $\bar{G}_i$  with respect to  $P$  at  $T$  and  $x$  is  $\bar{V}_i$  right and in a constant composition mixture. Obviously,  $\bar{G}_i$  will be a function only of two variables  $T$  and  $P$  because  $x$  is already constant.

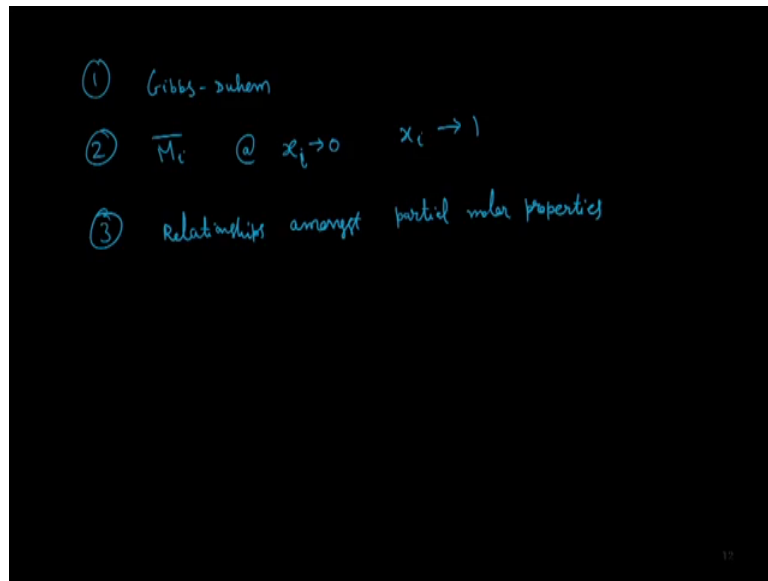
We said in general  $\bar{G}_i$  is a function of  $T$ ,  $P$  and  $x_i$ , but then because it is a constant composition mixture this term drops out and all I have is functionality with respect to  $T$  and  $P$  and if I write the total derivative then  $d\bar{G}_i$  is derivative of  $\bar{G}_i$  with respect to  $P$  at constant temperature and of course,  $x$  is constant  $dP$  plus derivative of  $\bar{G}_i$  with respect to  $T$  at constant  $P$  and  $x$  of course  $dT$ .

The first term here is  $\bar{V}_i$ ; the second term here is negative  $\bar{S}_i$ . So, what we end up with is  $d\bar{G}_i = \bar{V}_i dP - \bar{S}_i dT$ . On the other hand, if in a constant composition mixture if I write the equation fundamental property relation for the open system; then,  $dG = VdP - SdT + \sum \mu_i dx_i$  and in case of constant composition  $dx_i$  will go to 0. So, what I will have is essentially  $dG = VdP - SdT$ . This is constant composition  $x$ .

So, now, I have two relations; one on the left hand side relating partial molar properties to changes in temperature and pressure and another on the right hand side, relating the total property to changes in temperature and pressure and if you look at the structure of these 2 equations. They are identical for the total property  $dG = VdP - SdT$  and for the partial molar property  $d\bar{G}_i = \bar{V}_i dP - \bar{S}_i dT$  right.

So, partial molar properties are related by analogous equations to that of the total properties in a constant composition mixture in. I can also write the other thermodynamic properties right. For example,  $dU = TdS - PdV$  in a constant composition mixture  $d\bar{U}_i = Td\bar{S}_i - Pd\bar{V}_i$ .

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What we have done today is looked at what we call as the Gibbs-Duhem equation and you already see in its application in obtaining the partial molar property at the infinite dilution. We also looked at the values of the partial molar properties at the two limits  $x_i$  going to 0; or  $x_i$  going to 0 and  $x_i$  going to 1. And finally, we looked at the relationships between the partial molar properties themselves; relationships amongst the partial molar properties. So, we are trying to build a thermodynamic framework to handle solutions or a mixture of chemical species. We looked at partial properties, several relationships that relate these partial molar properties amongst themselves.

And then, we looked at what is known as the summability relation which relates the partial molar property to the property of the mixture and we looked at Gibbs-Duhem equation which essentially talks about how the partial molar properties vary with respect to composition or the relationship amongst variation in the partial molar properties of different species.

And so, we will end our discussion there today. When we come back, we will carry forward this ideas of partial molar properties and solution thermodynamics so that we can apply them to chemical engineering problems.

Thank you.