Course on Phase Equilibrium Thermodynamics
By Professor Gargi Das
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Lecture No 33
Partial Molar Properties

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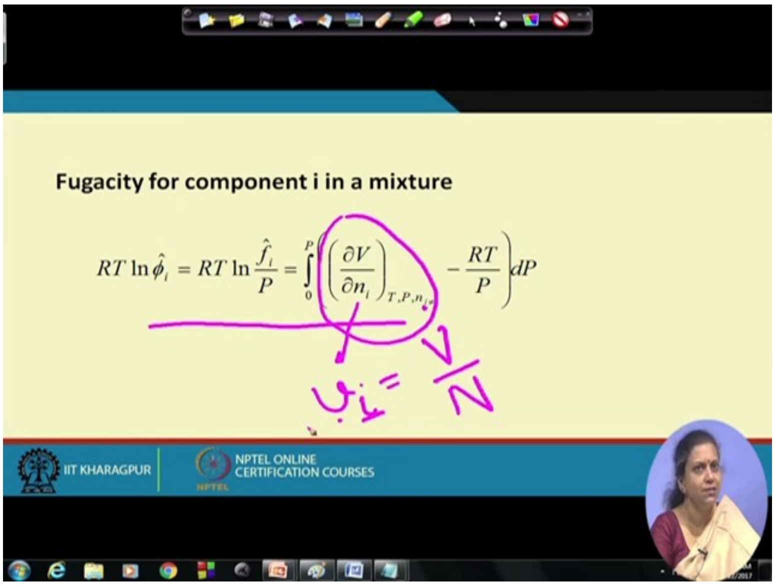

Fugacity for component i in a mixture

$$RT\ln\hat{\phi}_i = RT\ln\frac{\hat{f}_i}{P} = \int_0^P\left(\left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}} - \frac{RT}{P}\right)dP$$

So I start from the point where I had left in the last class in the last class I had left in this particular slide I had left in this particular slide where I was trying to define fugacity for component i in a mixture and I had also mentioned what is the importance of finding out the fugacity of a particular component in a mixture rather than finding out fugacity of the total mixture and when we were trying to find out what did we find?

We found out that we got stuck up in this particular property, what is this particular property? Is this property the can this be defined as the molar volume of component i which is just the volume of component i divided by total number of moles of component i or in other words suppose I add this component i with when i is in a mixture of j, will the contribution of i be the same as if I add i to a large portion of component i itself.

So therefore in order to understand these things and I would also like to mention you all these things I am mentioning in terms of volume the same things are applicable for other extensive properties as well, right? So therefore in order to understand this, what people did? They tried with different solutions or rather different proportions of water and ethanol to form a water ethanol mixture and what did they observe?

They found that when they added one mole of water to a large volume of water, what was the increasing volume?

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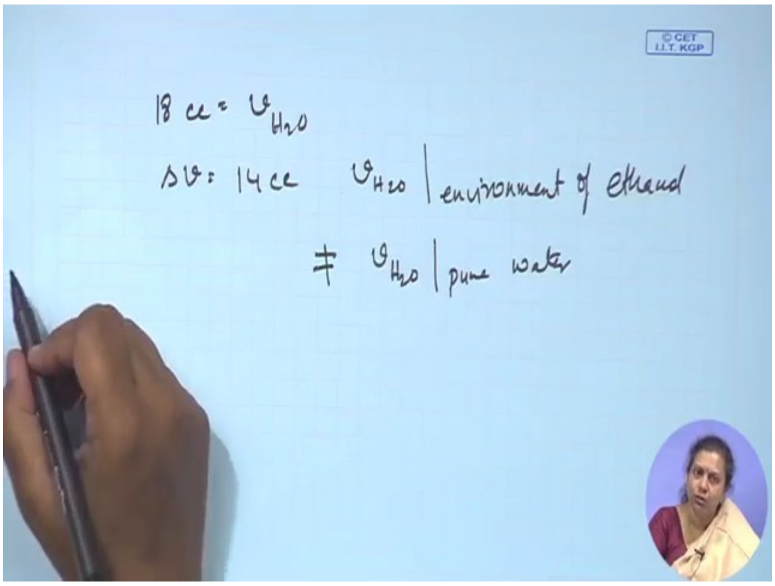

18 cc = v_{H_2O}

Δv = 14 cc $\quad v_{H_2O} \mid$ environment of ethanol

$\neq v_{H_2O} \mid$ pure water

It was 18 cc and all of us know that 18 cc it is the molar volume of water then what they did? They added the same one mole of water to a large volume of Ethanol and what did they see? They found that in that particular case the increment in volume was not 18 cc it was 14 cc. So then what did it deduce it meant that the volume occupied by water by one mole of water in an environment of ethanol is not the same as the molar volume of water in pure water in fact they found out that whenever this one mole of water was added to different compositions of the ethanol water mixture they found that the increase in volume was by different amounts.

So therefore that automatically implied that the contribution of any particular component i to the total property of the component or rather total property of the component in the mixture is cannot be evaluated in a straightforward manner just by its molar property. So therefore we need a different set of properties to define or to identify the contribution of component property to the total property, right?

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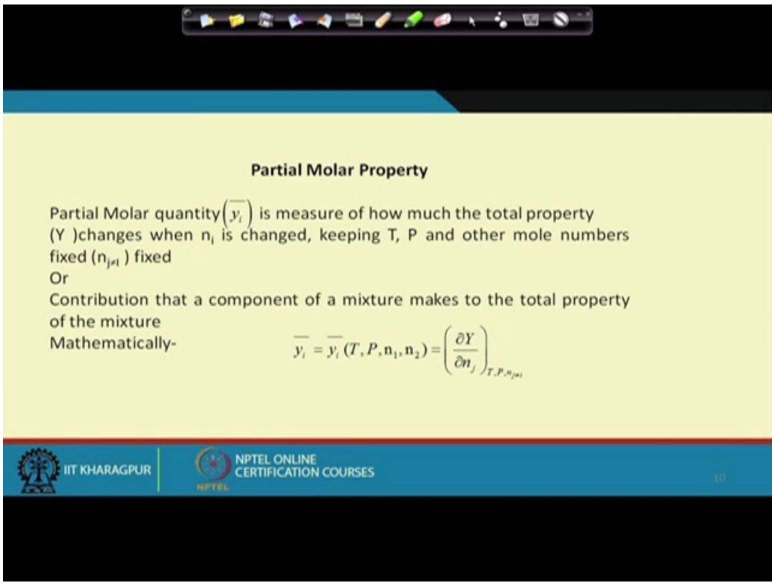

Partial Molar Property

Partial Molar quantity ($\bar{y}_i$) is measure of how much the total property (Y)changes when n_i is changed, keeping T, P and other mole numbers fixed ($n_{j\neq i}$) fixed

Or

Contribution that a component of a mixture makes to the total property of the mixture

Mathematically- $\bar{y}_i = \bar{y}_i(T,P,n_1,n_2) = \left(\frac{\partial Y}{\partial n_i}\right)_{T,P,n_{j\neq i}}$

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And these set of properties they were defined as the partial molar properties. What are these partial molar properties, let us see? They are a measure of how much the total property changes when the moles of component i is added keeping temperature pressure and other mole numbers fixed.

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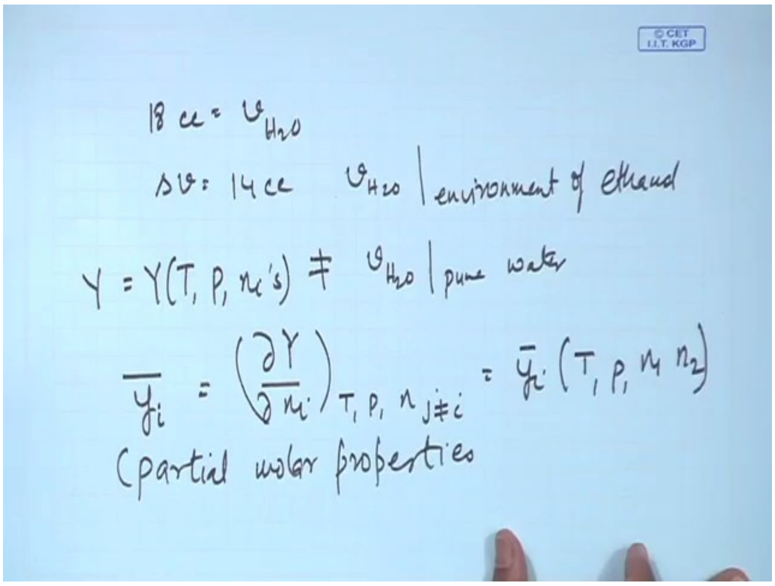

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18 cc = v_{H_2O}

Δv = 14 cc $\quad v_{H_2O}\big|$ environment of ethanol

$Y = Y(T, P, n_i\text{'s}) \neq v_{H_2O}\big|$ pure water

$$\bar{y}_i = \left(\frac{\partial Y}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \bar{y}_i(T, P, n_1\, n_2)$$

(partial molar properties

So therefore the partial molar property was defined as, suppose my total property is Y this Y it is a function of say T, P and mole numbers ni’s, right, right? And for the time being I just assume binary mixture’s simply because it will be easy for you to understand that. Remember one thing whatever we are doing far binary mixtures will be equally applicable to any number of components n of multi-component mixtures number 1. Number 2 most of the discussions will be in terms of volume simply because it is easy to measure and easy to imagine and easy to understand, whatever I discuss will be equally applicable to partial molar properties of all extensive functions, right?

So therefore suppose Y is an extensive property then we find that del Y del ni at constant T, P nj not equal to i this is nothing but the molar property of y which is signified as the component is specified and to differentiate it from molar properties a bar is put on the top and therefore these are termed as partial molar properties which identify the contribution that a component of the mixture makes to the total property of the mixture, right?

So therefore this is basically fused again if we start its understanding it in terms of volume it means that suppose we add one mole of component a to a very large volume of the solution such that the composition of the solution remains unchanged under that condition the contribution to volume which this particular one mole of component a makes is the partial molar volume of component a in mixture a and b, remember one thing partial molar volume it has to be a function of composition it has to be a function of the identity of the other components because a will behave differently when it is in a solution with b. It will be able differently when it is in solution of c and so on and so forth depending on how friendly b, c etc are with a.

So therefore it is important to remember that yi bar it is a function of temperature pressure and suppose there is just 2 components it is a function of n1 and it is a function of n2. So therefore what do we find here? We find here that in the process when we shifted from pure components to mixtures what did we do? For pure component we had total properties we had molar properties I had very categorically mentioned to you total properties means capital letters, molar properties means small case letters why did I enforce?

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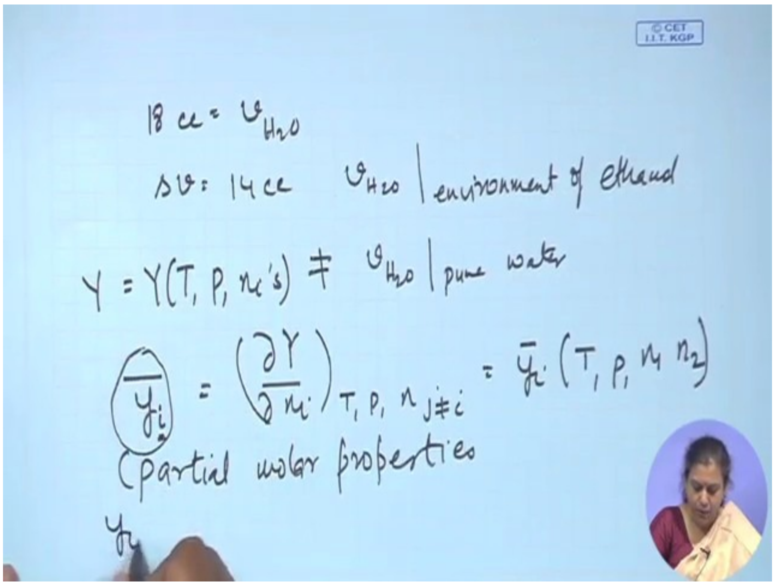

$18\,cc = v_{H_2O}$

$\Delta v = 14\,cc \quad v_{H_2O}\big|_{\text{environment of ethanol}}$

$Y = Y(T, P, n_i\text{'s}) \neq v_{H_2O}\big|_{\text{pure water}}$

$\boxed{\bar{y}_i} = \left(\frac{\partial Y}{\partial n_i}\right)_{T, P, n_{j \neq i}} = \bar{y}_i(T, P, n_1 n_2)$

(partial molar properties

y_i

It is going to be clear you are going to come across more sets of properties and unless the nomenclatures are defined we get confused at the end. So therefore now we have come across partial molar properties which are exhibited only in solutions how do we denote them? We denote them by denoting the component as the subscripts every time whenever I am mentioning the components they are subscripts you must be remembering phases are superscripts and components are subscripts and there is a bar over there over the top which differentiates this from the molar property of component i, right?

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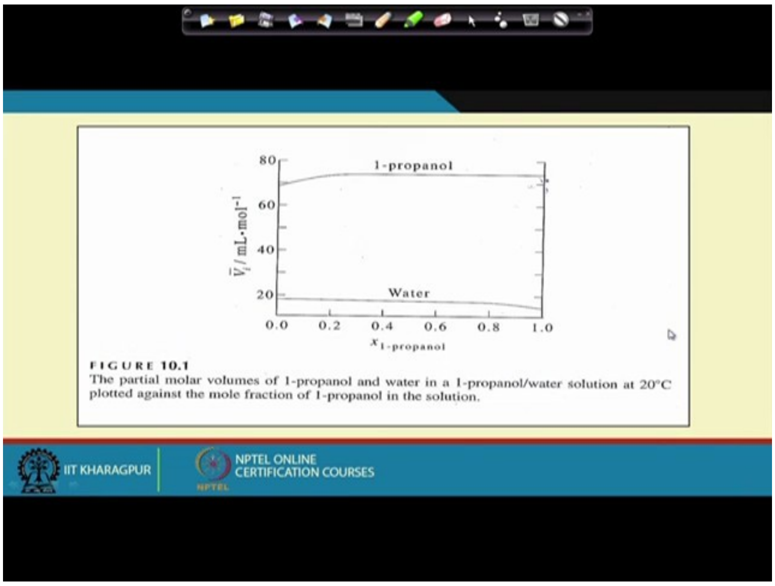

FIGURE 10.1
The partial molar volumes of 1-propanol and water in a 1-propanol/water solution at 20°C plotted against the mole fraction of 1-propanol in the solution.

So therefore first thing once we define a property let us see what are the different characteristics of the properties? How does it differ from the normal molar properties? We find, here is something interesting just to show you that in what way the it is just a typical example to show you that how the importance of partial molar properties? What have we done? We have taken a mixture of 1 propanol and water.

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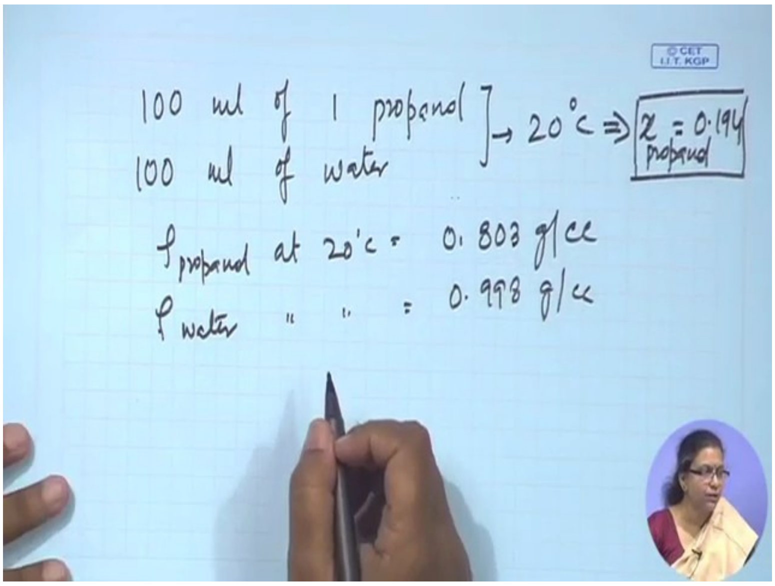

$$\left.\begin{array}{l}100 \text{ ml of 1 propanol} \\ 100 \text{ ml of water}\end{array}\right] \rightarrow 20^\circ C \Rightarrow \boxed{x_{\text{propanol}} = 0.194}$$

ρ_{propanol} at $20^\circ c$ = 0.803 g/cc

ρ_{water} " " = 0.998 g/cc

We know we have taken hundred millilitres of 1 propanol and we have also taken hundred millilitres of water, right? We know and the entire thing was taken at 20 degrees centigrade we know rho propanol the density of propanol at 20 degrees centigrade this is nothing but equal to 0.803 gram per cc. rho water that is also known to you this is nothing but equal to 0.998 grams per cc, right? Now with these rho’s if we calculate and using the molecular weights, we find this hundred mole of 1 propanol in hundred mole of water this corresponds to x propanol of 0.194, right?

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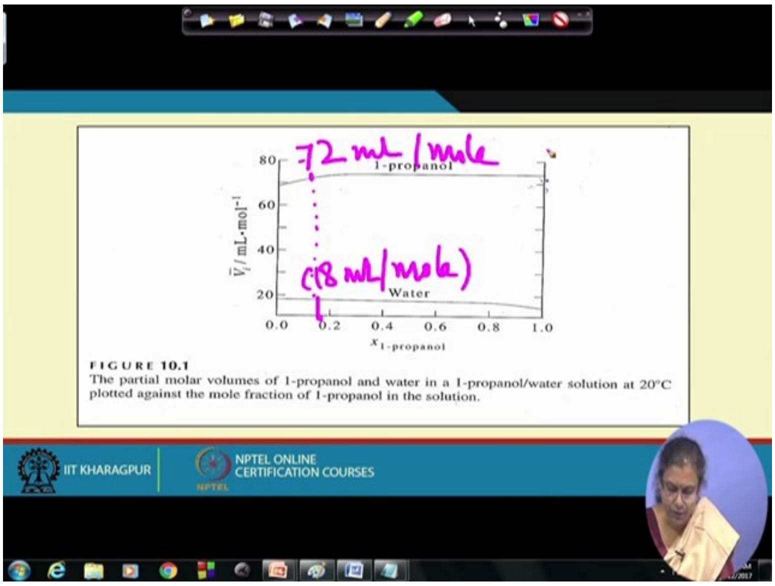

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The partial molar volumes of 1-propanol and water in a 1-propanol/water solution at 20°C plotted against the mole fraction of 1-propanol in the solution.

So therefore if that is the case let us come to 0.194 from here if we go straight up we can find out the volume of the partial molar volume of water we find that this is more or less 18 millilitre per mole, right? Then we keep on continuing straight up till we touch the partial molar volume of propanol versus x propanol curve I could not draw it straight but if we continue then in this particular case we find that more or less the intersection this is at 72 millilitres per mole, fine. So therefore from here what did we know?

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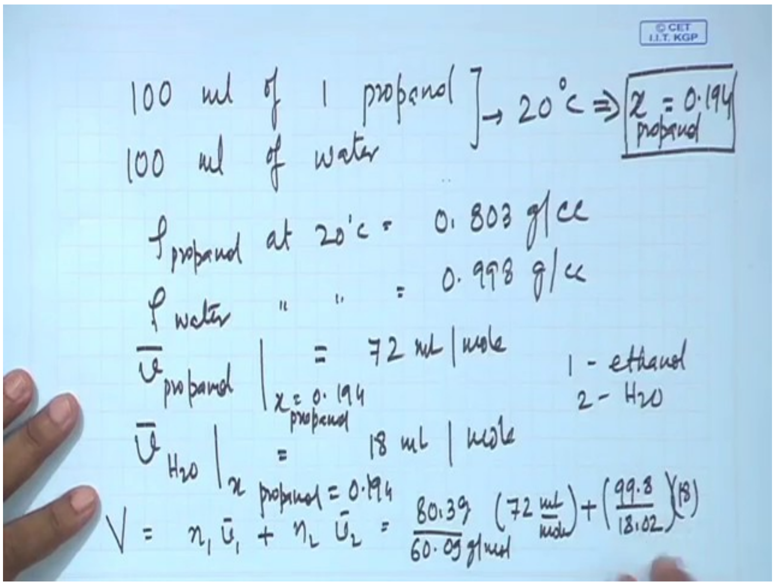

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ρ_{propanol} at $20^\circ c$ = 0.803 g/cc

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$\bar{v}_{\text{propanol}} \Big|_{x_{\text{propanol}} = 0.194} = 72 \text{ ml} | \text{mole}$

1 - ethanol

2 - H_2O

$\bar{v}_{H_2O} \Big|_{x_{\text{propanol}} = 0.194} = 18 \text{ ml} | \text{mole}$

$$V = n_1 \bar{v}_1 + n_2 \bar{v}_2 = \frac{80.39}{60.09 \text{ g/mol}} \left(72 \frac{\text{ml}}{\text{mole}}\right) + \left(\frac{99.8}{18.02}\right)(18)$$

We knew we have come to know that the partial molar volume of propanol at x equals to 0.194 this is equal to 72 millilitres per mole or 72 cc per mole and v bar water at x propanol equals to 0.194 this is equals to 18 millilitres per mole, right? Now then can you calculate the total volume of the solution it is nothing but equals to n1v1 bar or rather suppose say 1 is I write it down suppose say 1 is ethanol 2 is water it will just make my writing faster that is the only thing plus n2v2 bar, what is n1 equals to?

If you just substitute n1 you find it is nothing but equals to 80.3 by 60.09 this is grams this is grams per mole into 72 millilitres per mole plus what is n2 equals to 99.8 grams by 18.02 grams per mole into 18 litres per mole just do the calculation and see what is the result you get?

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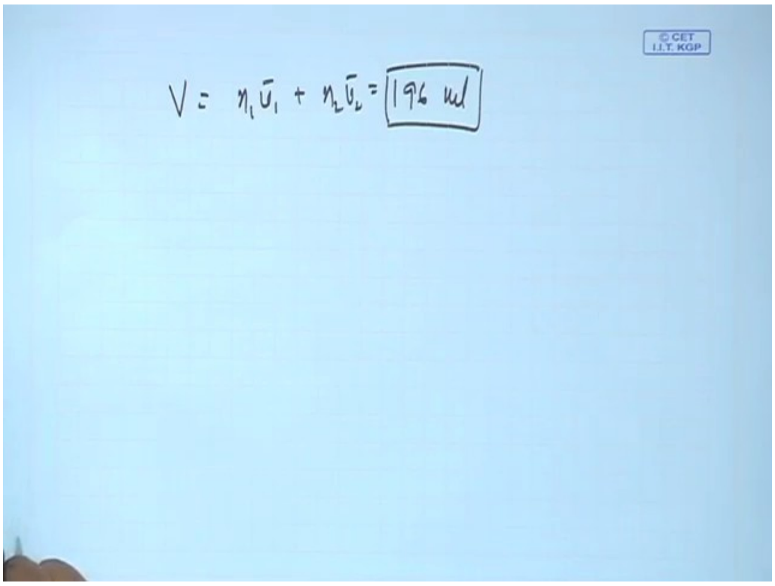

$$V = n_1\bar{v}_1 + n_2\bar{v}_2 = \boxed{196\ ml}$$

We find that from here we get the total volume you can take up the calculation and you can do it yourself we find this gives you 196 millilitres. So you have started with hundred plus hundred 200 millilitres and this was the volume of the liquid before mixing; now the solution is 196 millilitres, okay. So this was just to show you that well, the importance of partial molar properties we cannot just use molar properties and add them up for normal circumstances there are situations where we can do it, we will be doing those solutions are known as ideal solutions we will be dealing them at the end after we have understood solutions, after we have understood how difficult or how complex the behaviour of solution can be and the need for simplifying the situation for practical calculations.

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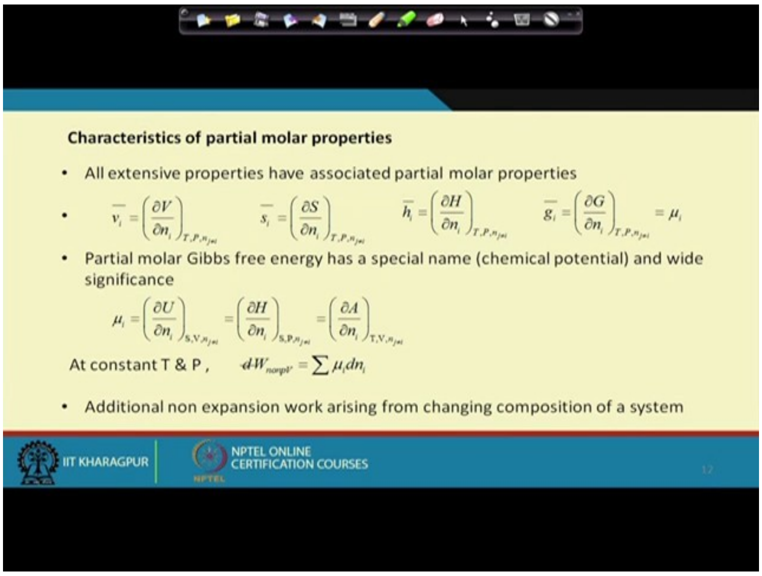

Characteristics of partial molar properties

- All extensive properties have associated partial molar properties
- $\bar{v}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}}$ $\bar{s}_i = \left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_{j\neq i}}$ $\bar{h}_i = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_{j\neq i}}$ $\bar{g}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \mu_i$
- Partial molar Gibbs free energy has a special name (chemical potential) and wide significance

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{j\neq i}} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j\neq i}}$$

At constant T & P , $đW_{non pV} = \sum \mu_i dn_i$

- Additional non expansion work arising from changing composition of a system

For the time being we continue our discussions more on partial molar properties, right? Now just like I have been discussing the properties the volume characteristics let us see the general characteristics of partial molar properties.

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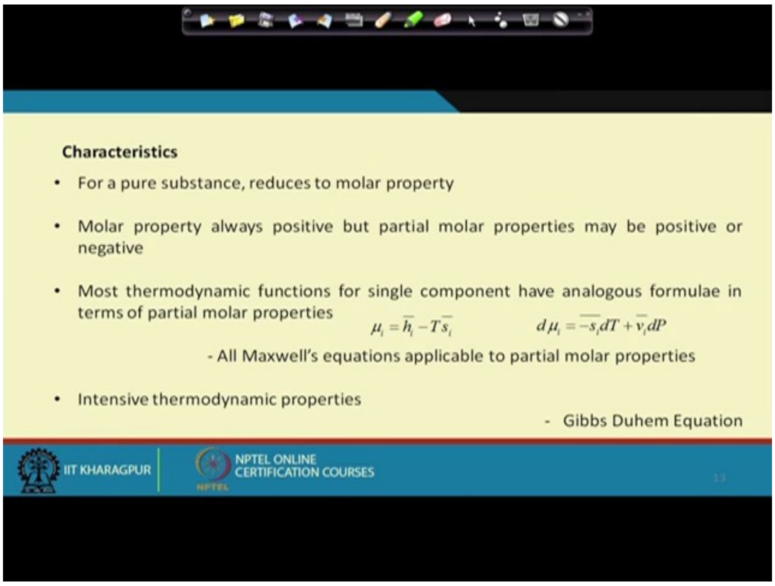

Characteristics

- For a pure substance, reduces to molar property
- Molar property always positive but partial molar properties may be positive or negative
- Most thermodynamic functions for single component have analogous formulae in terms of partial molar properties $\mu_i = \bar{h}_i - T\bar{s}_i$ $d\mu_i = -\bar{s}_i dT + \bar{v}_i dP$
  - All Maxwell's equations applicable to partial molar properties
- Intensive thermodynamic properties
  - Gibbs Duhem Equation

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The first thing is the thing I have written quite at the end but this differentiates the partial molar and molar properties this is something very important we know molar properties are always positive we can never have a negative molar property under some circumstances partial molar properties may be negative as well.

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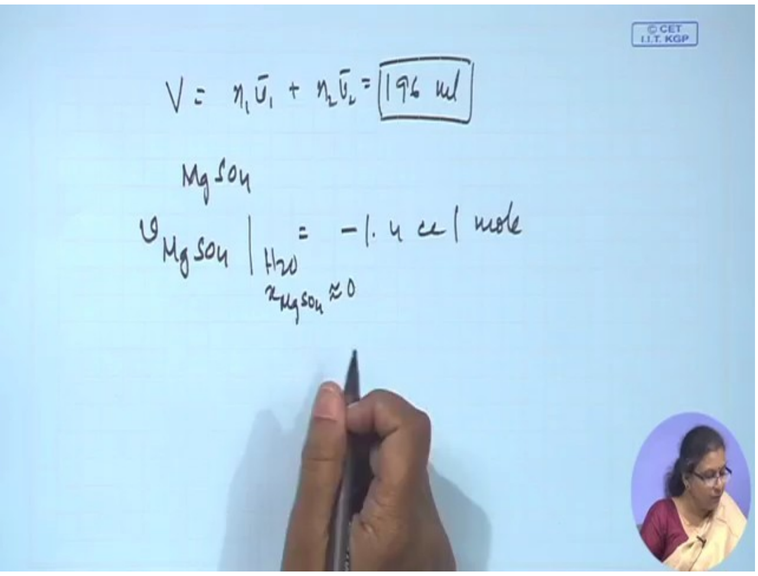

$$V = n_1\bar{v}_1 + n_2\bar{v}_2 = \boxed{196\ ml}$$

$MgSO_4$

$$v_{MgSO_4}\Big|_{H_2O,\ x_{MgSO_4} \approx 0} = -1.4\ cc/mole$$

A typical example when does it happen? When you start with or rather when you add some component in a solution and the volume actually contracts for example suppose you add some magnesium sulphate to water we find that the molar volume of $vMgSO_4$ in almost pure water this is minus 1.4 grams per cc, possibly I do not remember the exact value it is probably minus 1.4 cc per mole.

So when we add magnesium sulphate in a magnesium sulphate solution at say $xMgSO_4$ is almost equal to 0 that means you are added to pure water, we find that when we are adding this one mole of magnesium sulphate to a large volume of water it actually causes a decrease in the volume of water. Now this happens just because the open structure of water breaks up and therefore the ions they become hydrated and therefore they collapse this is entirely a different story it deals with the molecular levels we need not know it. It is just sufficient for us to know that while molar volumes are always positive partial molar volumes maybe positive may be negative this is number 1 thing.

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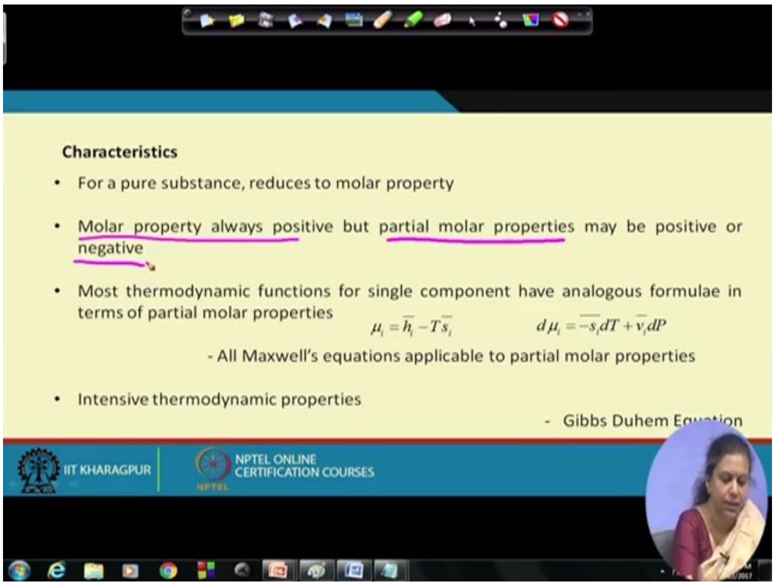

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  - All Maxwell's equations applicable to partial molar properties
- Intensive thermodynamic properties

  - Gibbs Duhem Equation

And for a closed substance the partial molar volume it reduces to the molar property this is number 1.

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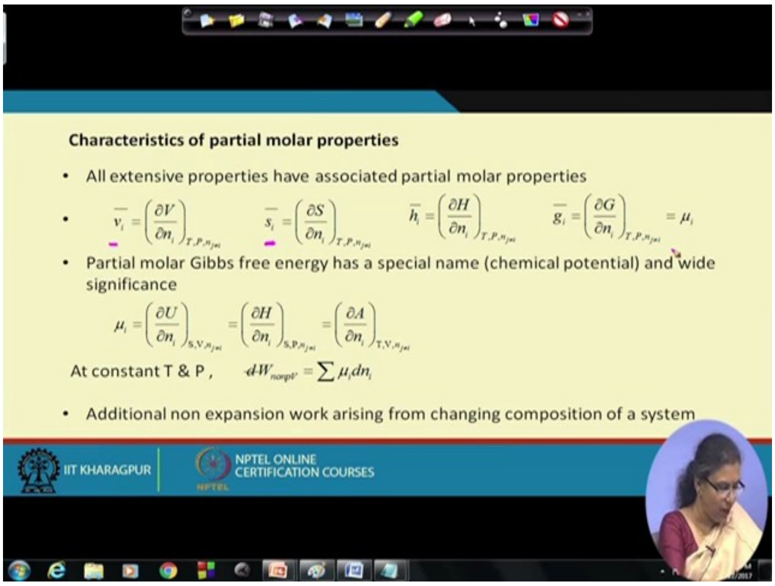

Characteristics of partial molar properties

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At constant T & P , $dW_{non pV} = \sum \mu_i dn_i$

- Additional non expansion work arising from changing composition of a system

Number 2 just like we have defined all extensive properties have associated partial molar properties for example we have already dealt with partial molar volume, fine. Same way we can deal with partial molar entropy we can have all sorts of partial molar properties just in the same way as we have a large number of your for each and every extensive property and it is important to know that the relationships which we have proposed for total properties and for partial properties the same equations also holds for partial molar properties as well.

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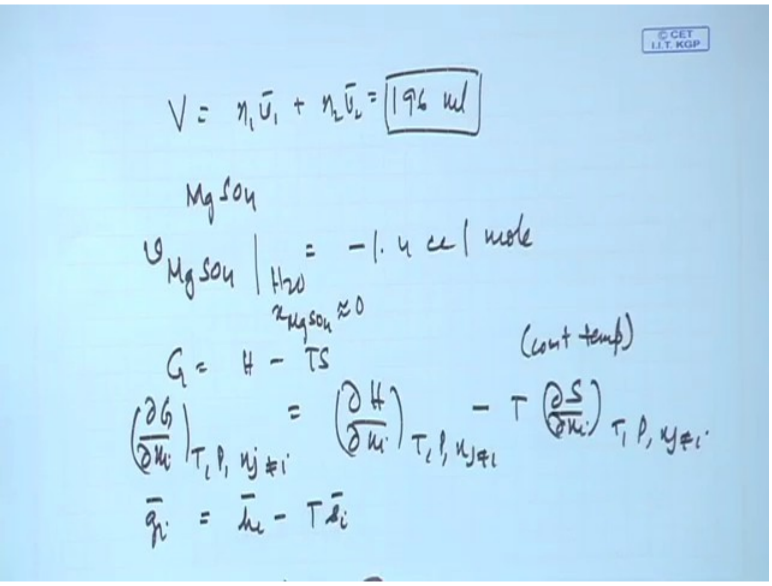

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$MgSO_4$

$\bar{v}_{MgSO_4}\big|_{H_2O} = -1.4\ cc/mole$

$x_{MgSO_4} \approx 0$

(const temp)

$G = H - TS$

$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_{j\neq i}} - T\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_{j\neq i}}$

$\bar{g}_i = \bar{h}_i - T\bar{s}_i$

Let us see, all of us know G equals to H minus TS, fine. Now suppose I differentiate this with respect to say Ni keeping T, P, nj constant, right? What is this? Del H del ni T. P nj not equals to I minus T, since we are doing the whole thing at constant temperature you must remember the conditions constant temperature pressure and composition this is del S del ni T, P nj not equals to i. So what is this? This is nothing but gi bar this will be nothing but hi bar minus T si bar. So we have got this equation.

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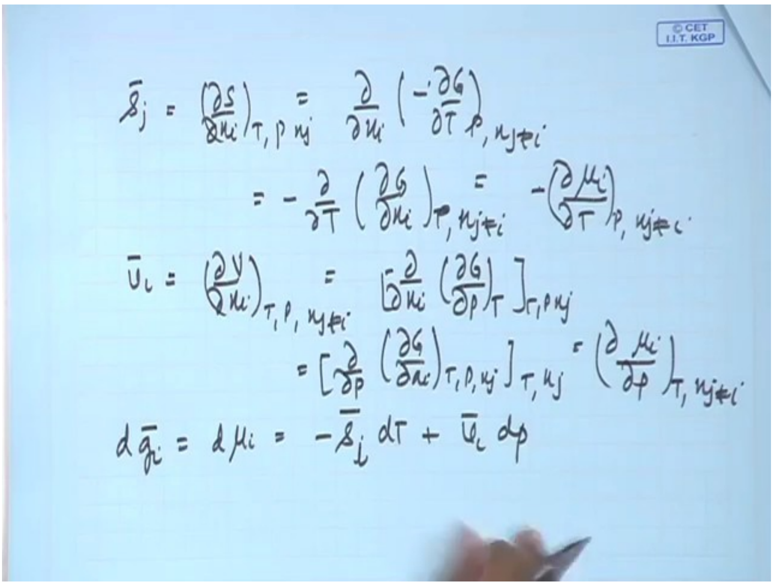

$$\bar{s}_j = \left(\frac{\partial S}{\partial n_i}\right)_{T,P\,n_j} = \frac{\partial}{\partial n_i}\left(-\frac{\partial G}{\partial T}\right)_{P,n_{j\neq i}}$$

$$= -\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial n_i}\right)_{P,n_{j\neq i}} = -\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_{j\neq i}}$$

$$\bar{v}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \left[\frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial P}\right)_T\right]_{T,P\,n_j}$$

$$= \left[\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}\right]_{T,n_j} = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_{j\neq i}}$$

$$d\bar{g}_i = d\mu_i = -\bar{s}_i\,dT + \bar{v}_i\,dp$$

Again suppose we remember that the cross second partial derivatives are equal, what is this sj bar? This is nothing but del S just now as it is written this is T, P nj, fine. What is this? This is nothing but equal to del del ni of minus del G del T at constant P, nj not equal to i , what is this term? This is nothing but minus sj so therefore this can we not write it down as minus del del T of del G del ni P, nj not equals to i, what is this equal to? This is nothing but equal to minus del mui del T at constant P, nj, fine.

So therefore in the same way we can show that vi bar this is nothing but equal to your del v del ni T,P nj not equal to i, what is this equal to? Del del ni del G del P at constant T this whole thing at constant T, P nj again we can change the order of differentiation we get del del P of del G del ni constant T, P, nj this whole thing at constant T, nj and then what is this equal to? This is nothing but equal to del mui del P at constant T, nj.

So from here what do I get? I get dgi bar this is nothing but again this is nothing but the chemical potential this is minus si bar dT plus vi bar dp. So in this particular way what do we find? We find that we can develop an identical set of equations just like we have we had done for total properties as well as for molar properties we can go on in this particular way and finally in this particular process what do we find?

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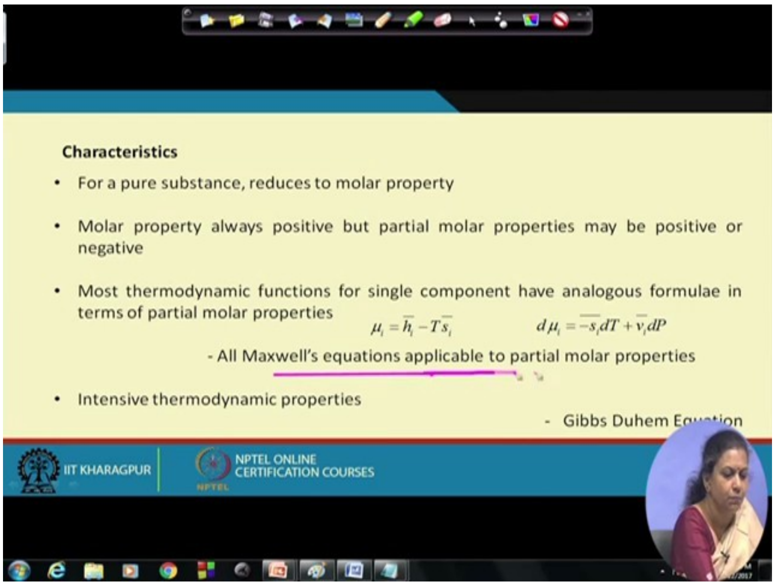

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  - All Maxwell's equations applicable to partial molar properties
- Intensive thermodynamic properties

  - Gibbs Duhem Equation

We find that in this particular process we can arrive at a set of Maxwell's equations in terms of partial molar properties, right? After this what is the next thing? This is the next firstly I found out the difference between molar and partial molar properties the second thing is we found out that all extensive properties have the corresponding partial molar properties and all these partial molar properties they have the same relationships with one another just like the way the molar properties and the total properties were having. What is the next thing that that can be, what are the other properties that we can define? The other properties are that a very, all of these are intensive properties.

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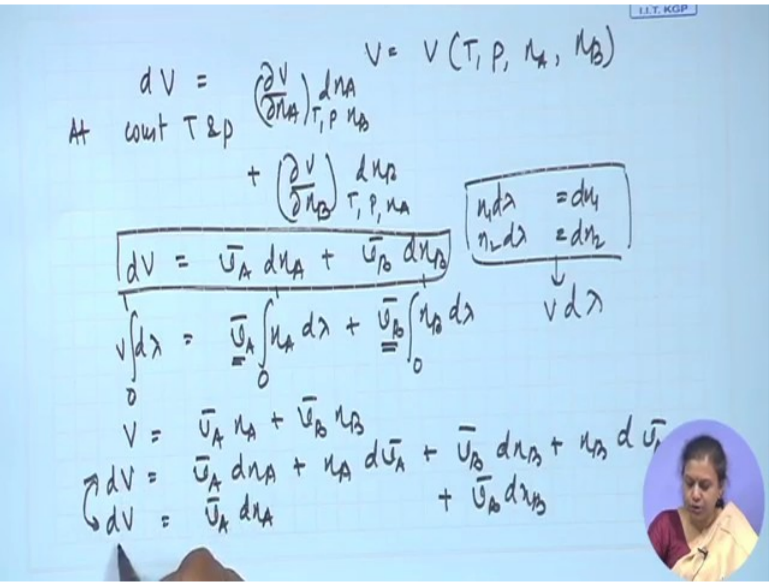
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$V = V(T, P, n_A, n_B)$

At const T & p

$$dV = \left(\frac{\partial V}{\partial n_A}\right)_{T,P,n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{T,P,n_A} dn_B$$

$$\boxed{dV = \bar{v}_A\, dn_A + \bar{v}_B\, dn_B}$$

$$\boxed{\begin{array}{ll} n_1 d\lambda & = dn_1 \\ n_2 d\lambda & = dn_2 \end{array}} \rightarrow V d\lambda$$

$$V\int_0^1 d\lambda = \bar{v}_A \int_0^1 n_A\, d\lambda + \bar{v}_B \int_0^1 n_B\, d\lambda$$

$$V = \bar{v}_A n_A + \bar{v}_B n_B$$

$$dV = \bar{v}_A\, dn_A + n_A\, d\bar{v}_A + \bar{v}_B\, dn_B + n_B\, d\bar{v}_B$$

$$dV = \bar{v}_A\, dn_A + \bar{v}_B\, dn_B$$

Now since they are intensive properties we can come across or we can deduce a very important equation which is known as the Gibbs Duhem equation in terms of partial properties. Now let us define this equation before we stop for a break and go to the next class. Let us start from the basic equation. What is the equation let us see?

We know that what is dV suppose we know for the volume of a mixture this is a function of TP, I have just 2 components A and B, so it is a function of TP and nV. So at constant T and P what is dV equals to? It is nothing but del v del nA constant TP, nB into dnA plus del v del nB constant TP nA into dnB, agreed? Or in other words what is this equal to? This is equals to vA bar dnA plus vB bar dnB, fine. Now suppose I keep on increasing the size of this particular sample such that the volume increases but the composition does not change.

How can I do it? I just increase the size uniformly by a scale parameter lambda say such that we find that dn1 this will be equal to n1 into d lambda similarly I keep on adding dn2 moles such that this becomes n2d lambda so what am I doing in the process? I am increasing the entire volume of the of that particular system keeping the composition constant. So what am I doing? I am adding n1d lambda moles of 1, I am adding n2d lambda moles of 2 such that when I add these 2 my volume becomes v into d lambda, right?

Because I am just adding I am just increasing the volume without changing the composition. So therefore in this particular case I can, so dV I can write it down as vd lambda this is equals to vA bar nAd lambda plus vB bar nbd lambda, agreed? Now we need to remember that as I vary lambda from 0 to 1 I am going from 0 volumes, I am just adding both the components in the similar same proportion such that I attain volume V.

So therefore as lambda is varying from 0 to 1, I am getting the volume of my solutions changing from 0 volume to the total volume and during this process how am I doing this? I am adding nA d lambda of component A and nBd lambda of component 2, right? And so therefore I can write the equations in this particular form. Now as I changed lambda from 0 to 1, I can differentiate this from 0 to 1, I can differentiate this from 0 to 1.

Remember one thing I am not changing the composition of the mixture, so therefore my vA bar ad vB bar remains constant as the volume of the mixture is increasing this is important. So therefore from here what do I get? I get vA bar nA plus vB bar nB, fine. So what have I done? I have increased the solution volume simply by adding or rather simply by keeping the composition of the solution constant now suppose I differentiate this equation what do I get?

On differentiating this equation I would be getting vA bar dnA plus nA dvA bar plus vB bar dnB plus nB dv bar and remember with what had I started? I had started from this equation, what was this equation? It was vA bar dnA plus vB bar dnB what have I done? In both the cases I am trying to compute the change in volume by dV amount and I know that volume is a property of the system so therefore these 2 equations they should be equivalent.

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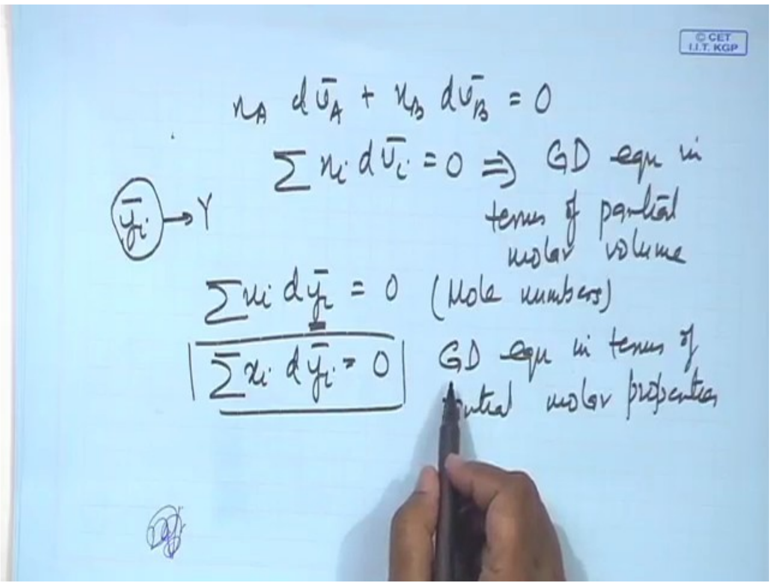

$$n_A\, d\bar{v}_A + n_B\, d\bar{v}_B = 0$$

$$\sum n_i\, d\bar{v}_i = 0 \Rightarrow$$ GD eqn in terms of partial molar volume

$\bar{y}_i \rightarrow Y$

$$\sum n_i\, d\bar{y}_i = 0$$ (Mole numbers)

$$\boxed{\sum x_i\, d\bar{y}_i = 0}$$ GD eqn in terms of partial molar properties

If these 2 equations have to be equivalent then what does it reduce to? It automatically tells you nA dvA bar plus nB dvB bar should be equal to 0, so if I am going for not 2 components but more than 2 components what do I get? I get ni dvbi bar equals to 0 and this particular equation is known as Gibbs Duhem equation this has been derived in terms of partial molar volume but the same derivation that I have done can be applicable for any other partial molar properties as well.

So therefore generalizing this equation, can I not write it down as? Suppose again my yi bar is a partial molar property of total property Y then can I not write it down in this particular form? Where yi bar is the partial molar property of any extensive property i and this also can be rewritten this is in terms of mole numbers we can also rewrite this equation in terms of mole fractions which give us this particular equation. So this is the generalized Gibbs Duhem equation in terms of partial molar properties and this I would like to say is a very important finding or a very important derivation of thermodynamics this is used for a large number of situations we are going to discuss the importance of Gibbs Duhem equation in the next class after I discuss little more about partial molar properties.