Course on Phase Equilibrium Thermodynamics
By Professor Gargi Das
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Lecture No 34
Partial Molar Properties(Contd.)

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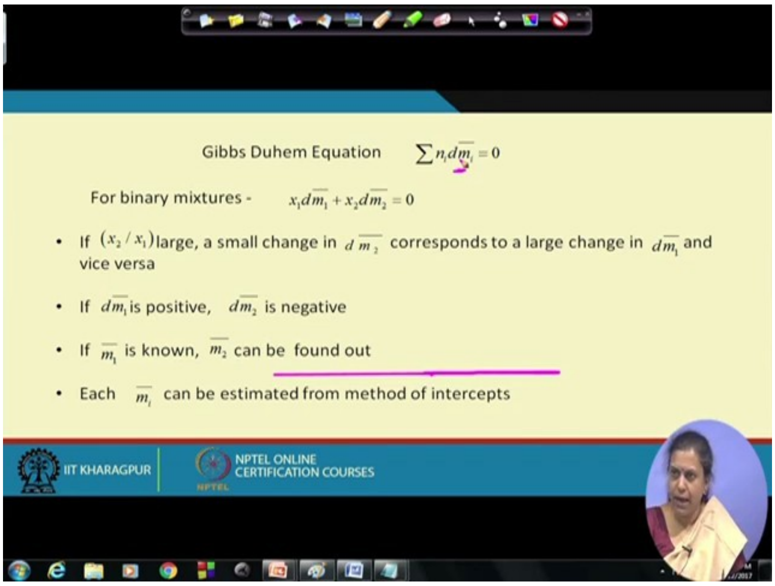

Gibbs Duhem Equation $\sum n_i d\overline{m_i} = 0$

For binary mixtures - $x_1 d\overline{m_1} + x_2 d\overline{m_2} = 0$

- If (x_2 / x_1) large, a small change in $d\overline{m_2}$ corresponds to a large change in $d\overline{m_1}$ and vice versa
- If $d\overline{m_1}$ is positive, $d\overline{m_2}$ is negative
- If $\overline{m_1}$ is known, $\overline{m_2}$ can be found out
- Each $\overline{m_i}$ can be estimated from method of intercepts

Well, to continue with our discussion on partial molar properties I ended the last class by deriving in this particular equation when I had derived the Gibbs Duhem equations in terms of the partial molar properties. as I mentioned this particular equation is something very important, before anything else I would like to discuss the importance of the Gibbs Duhem equation of course in this particle case I had denoted my property with the value of m just keep in mind that what I was telling in terms of n the same thing I have shown in terms of m here mi bar is my partial molar property.

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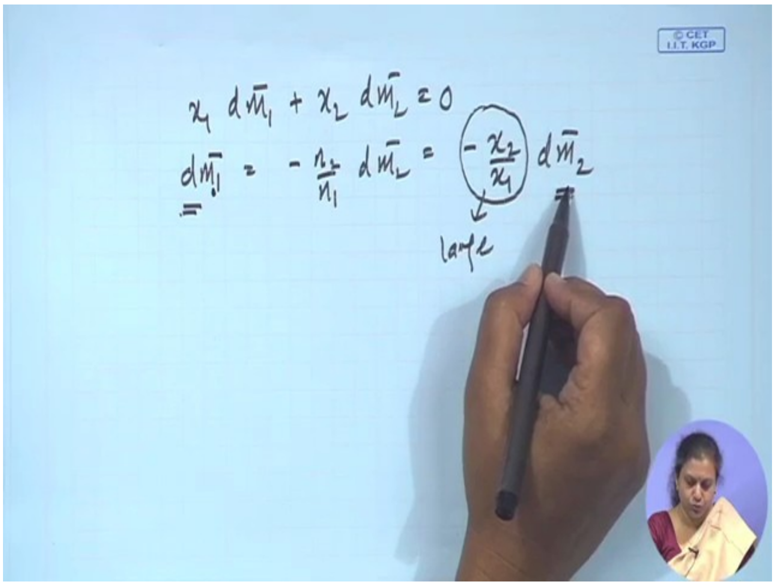

$$x_1\, d\bar{m}_1 + x_2\, d\bar{m}_2 = 0$$

$$\underline{d\bar{m}_1} = -\frac{n_2}{n_1}\, d\bar{m}_2 = \underset{\text{large}}{\left(-\frac{x_2}{x_1}\right)}\, \underline{d\bar{m}_2}$$

Now from this particular equation a large number of things that we can see for example let us start with a binary mixture, what is it? x1 for a binary mixture plus x2 dm2 bar equals to 0 I can also write it down as dm1 bar equals to minus n2 by n1 dm2 bar which is nothing but equal to minus x2 by x1 dm2 bar. So from this what do we find? We find that if x2 by x1 is large then a small change in this will correspond to a large change in this number 1, right?

So therefore we find that the changes in the partial molar properties they are not independent they are dependent upon the mole fractions. So therefore we find that if x2 by x, so therefore if I have a large proportion of x2 then a small change in dm2 is going to bring a large change in dm1, number 1. Number 2 what do we find? X2 by x1 is always positive so therefore an increase in the partial molar property of component 1 reached to a correspond decrease in the partial molar properties of component 2.

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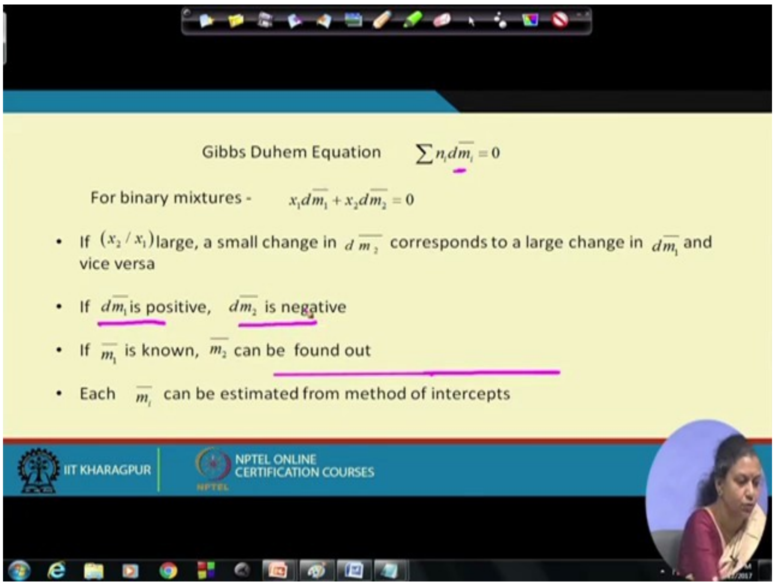

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Or in other words as I have mentioned here dm1 is positive dm2 can be negative, fine. And the most important thing is that it is very difficult to find out the partial molar properties.

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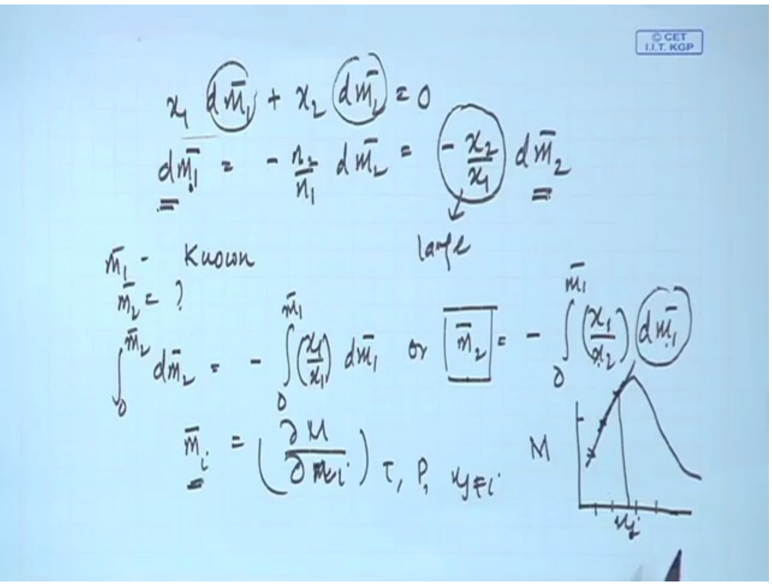

$$x_1 \, d\bar{m}_1 + x_2 \, d\bar{m}_2 = 0$$

$$d\bar{m}_1 = -\frac{n_2}{n_1} d\bar{m}_2 = \left(-\frac{x_2}{x_1}\right) d\bar{m}_2$$

large

$\bar{m}_1$ - Known

$\bar{m}_2 = ?$

$$\int_0^{\bar{m}_2} d\bar{m}_2 = -\int_0^{\bar{m}_1} \left(\frac{x_1}{x_1}\right) d\bar{m}_1 \quad \text{or} \quad \boxed{\bar{m}_2} = -\int_0^{\bar{m}_1} \left(\frac{x_1}{x_2}\right) d\bar{m}_1$$

$$\bar{m}_i = \left(\frac{\partial M}{\partial n_i}\right)_{T, P, n_{j \neq i}}$$

So therefore this equation gives us a way by which if I know the variation of dm1, I would be in a position to find out dm2 on integration it will give me m2 bar for any particular composition x2, right? So therefore how do we go about doing this, suppose my m1 bar is known say, right? I would like to find out my m2 bar I do not have a very straightforward experimental way to find this out.

So therefore can I not write it down as dm2 bar this is equals to minus integral x1 by x2 dm1 bar from 0 to m1 bar or in other words from this integration what do I get? This is equals to minus integral 0 to m1 bar x1 by x2 dm1 bar. So therefore from here what do I get? From here I get that if I know dm1 bar how it varies with composition? I shall be in a position to find out m2 bar and the important thing is for each m2 bar it can be estimated from the method of intercepts.

Firstly just apparently if you just look at the expression, what is mbar mi bar this is delM, Del ni at T, P, nj, fine. So therefore it automatically implies that if you have any particular graph where your total property M that varies with the mole numbers ni say suppose it has a graph of this sort, suppose M equals to volume so suppose what I do? I keep on adding for component i or for component a say I keep on adding moles of a, say 1 mole 2 moles 3 moles 4 moles I keep on adding and for each particular addition I start finding out the increase in volume, right?

Accordingly I can find out different points on this curve I can construct this particular curve. Now if I want to find out the partial molar volume at some particular compositions say at this particular composition what do I do? I I can simply draw a tangent and find the slope of this curve but finding out the slope of this curve in this particular way it is not at all a very easy technique, okay.

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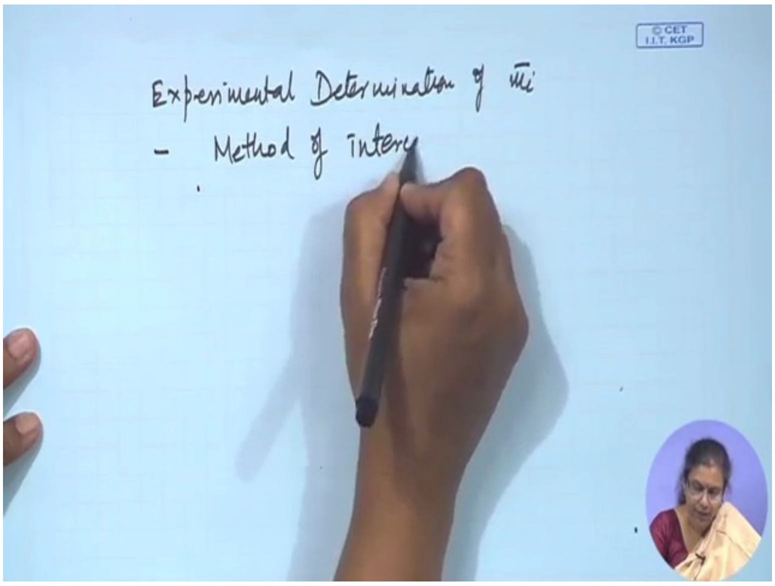

Experimental Determination of $\bar{m}_i$

- Method of Interc

It leads to a large number of errors, so therefore the proper way or much more accurate way of finding out the partial molar properties the experimental determination that is usually done determination of mi bar the usual method is known as the method of intercepts. Let us see what is this method first? And then we will see how it works?

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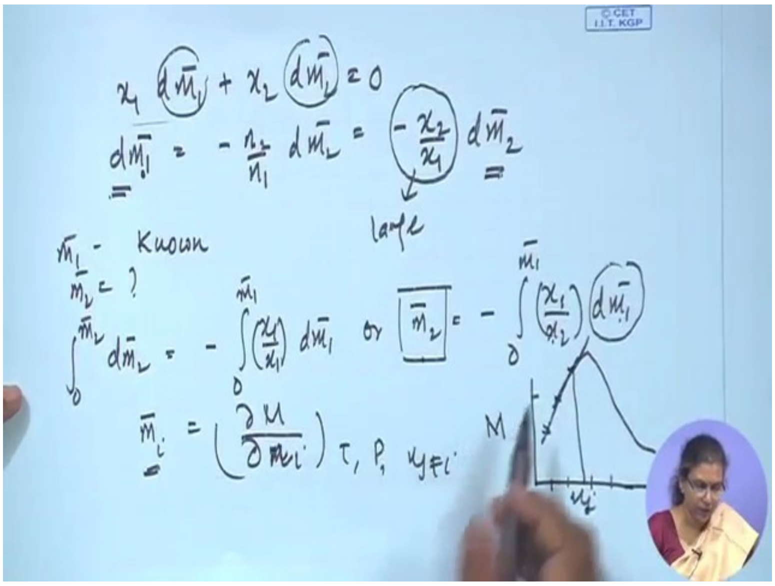

$$x_1\, d\bar{m}_1 + x_2\, d\bar{m}_2 = 0$$

$$d\bar{m}_1 = -\frac{n_2}{n_1}\, d\bar{m}_2 = \left(-\frac{x_2}{x_1}\right) d\bar{m}_2$$

large

$\bar{m}_1$ - Known

$\bar{m}_2 = ?$

$$\int_0^{\bar{m}_2} d\bar{m}_2 = -\int_0^{\bar{m}_1} \left(\frac{x_1}{x_1}\right) d\bar{m}_1 \quad \text{or} \quad \boxed{\bar{m}_2} = -\int_0^{\bar{m}_1} \left(\frac{x_1}{x_2}\right) d\bar{m}_1$$

$$\bar{m}_i = \left(\frac{\partial M}{\partial n_i}\right)_{T, P, n_{j \neq i}}$$

Now definitely you must remember that direct numerical differentiation just I was telling this can be done that but this is not very accurate so therefore this method of intercepts has been adopted.

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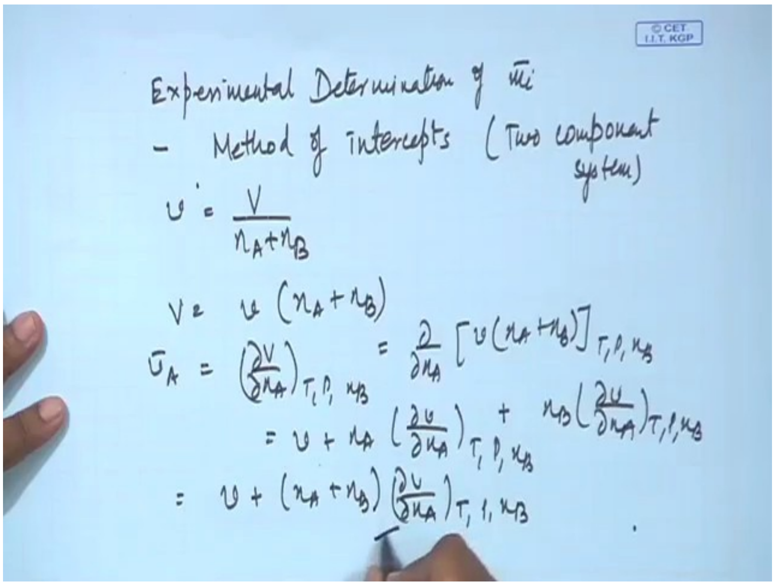

Experimental Determination of $\bar{m}_i$

- Method of intercepts (Two component system)

$$v = \frac{V}{n_A + n_B}$$

$$V = v\,(n_A + n_B)$$

$$\bar{v}_A = \left(\frac{\partial V}{\partial n_A}\right)_{T, P, n_B} = \frac{\partial}{\partial n_A}\left[v\,(n_A + n_B)\right]_{T, P, n_B}$$

$$= v + n_A \left(\frac{\partial v}{\partial n_A}\right)_{T, P, n_B} + n_B \left(\frac{\partial v}{\partial n_A}\right)_{T, P, n_B}$$

$$= v + (n_A + n_B)\left(\frac{\partial v}{\partial n_A}\right)_{T, P, n_B}$$

Now what is this method of intercepts? We know that the molar volume of a mixture, what is this? This is nothing but the, again we use it for a 2 component system say component A and component B, what is V? This is equals to nA plus nB I can write it down or in other words I can write it down as v into nA plus nB, agreed? What is vA bar equals to by definition? It is Del V delnA at constant T, P nB in this particular case.

So this should be equal to differentiation of this, so therefore this should be del del nA of v into nA plus nB at constant T, P nB. On differentiating what does this give you? This gives you v plus nA del v del nA T, P nB plus nB del V del nA T, P nB, right? Because del nA del nB gives you 0. So there what is this? This is equals to v plus nA plus nB that is the total number of moles into del v del nA at T, P nB, agreed? Now from chain rule let us if we can simplify this a little more further.

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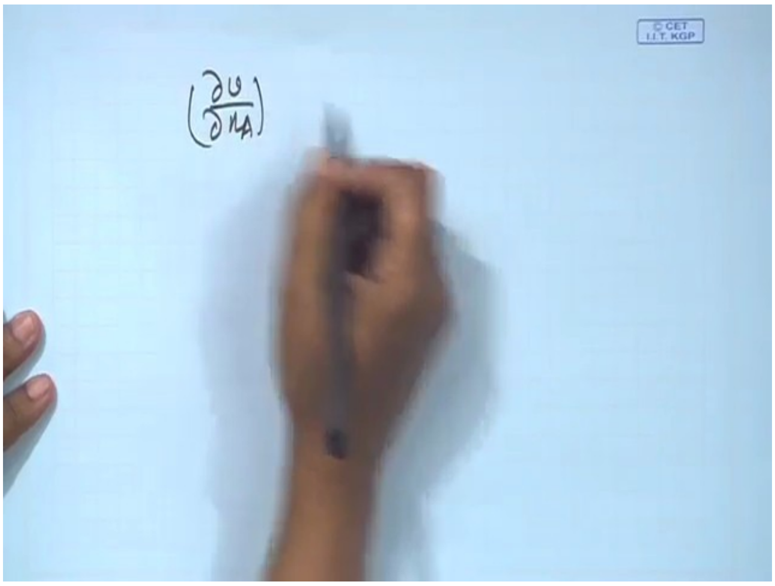

What is this let us see? Del v Del nA at constant what have we done?

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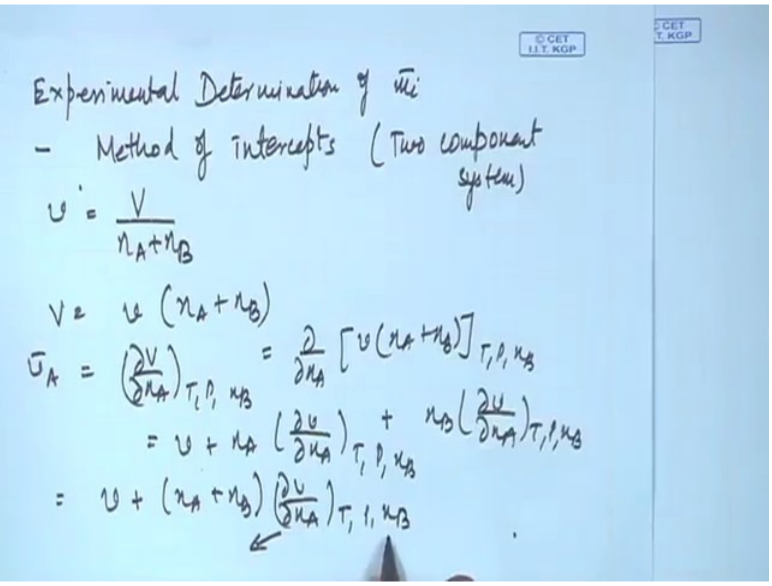


Experimental Determination of $\bar{v}_i$

- Method of intercepts (Two component system)

$$v = \frac{V}{n_A+n_B}$$

$$V = v(n_A+n_B)$$

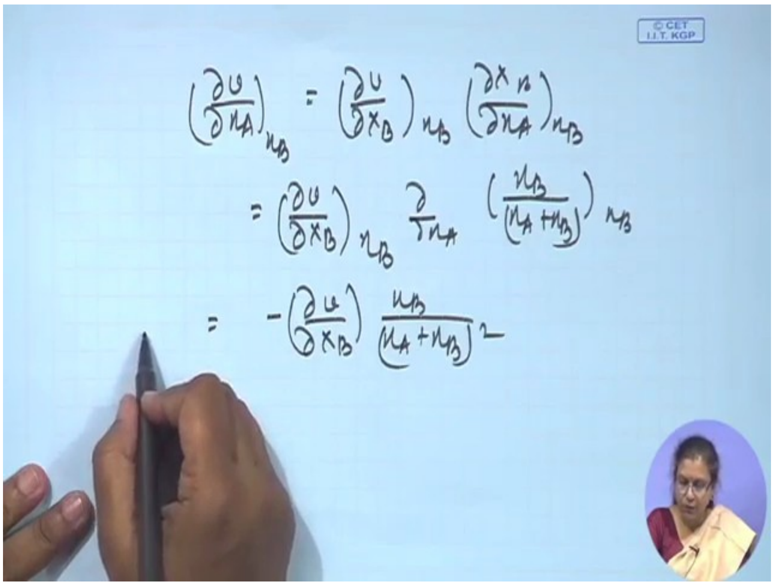
$$\bar{v}_A = \left(\frac{\partial V}{\partial n_A}\right)_{T,P,n_B} = \frac{\partial}{\partial n_A}\left[v(n_A+n_B)\right]_{T,P,n_B}$$

$$= v + n_A\left(\frac{\partial v}{\partial n_A}\right)_{T,P,n_B} + n_B\left(\frac{\partial v}{\partial n_A}\right)_{T,P,n_B}$$

$$= v + (n_A+n_B)\left(\frac{\partial v}{\partial n_A}\right)_{T,P,n_B}$$

This is at constant nB and T, P of course it remains

constant. (Refer Slide Time: 8:14)



$$\left(\frac{\partial v}{\partial n_A}\right)_{n_B} = \left(\frac{\partial v}{\partial x_B}\right)_{n_B}\left(\frac{\partial x_B}{\partial n_A}\right)_{n_B}$$

$$= \left(\frac{\partial v}{\partial x_B}\right)_{n_B}\frac{\partial}{\partial n_A}\left(\frac{n_B}{(n_A+n_B)}\right)_{n_B}$$

$$= -\left(\frac{\partial v}{\partial x_B}\right)\frac{n_B}{(n_A+n_B)^2}$$

So therefore can we not write it down from chain rule as Del v delxB at constant nB delxB delnA again at constant nB this is possible, what is this tell me? Is this not equal to Del v Del xB at constant nB into del del nA of xB is nothing but nB by n plus nB and what does this give you? Is this is not equal to minus of Del v Del xB into nB by nA plus nB whole square, simply differentiation that is what I am doing nothing else.

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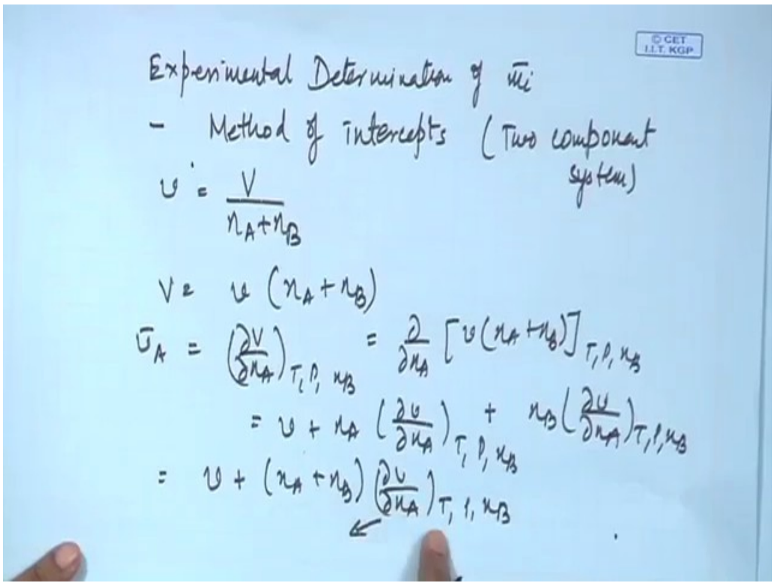

Experimental Determination of $\bar{m}_i$

- Method of Intercepts (Two component system)

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$$V = v(n_A+n_B)$$

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$$= v + (n_A+n_B)\left(\frac{\partial v}{\partial n_A}\right)_{T,P,n_B}$$

So from here what is this equal to? From where did we start? Now this particular equation, suppose I substitute it here so therefore what do I get then? Then I get this is vA bar the equation vA bar was equal to v.

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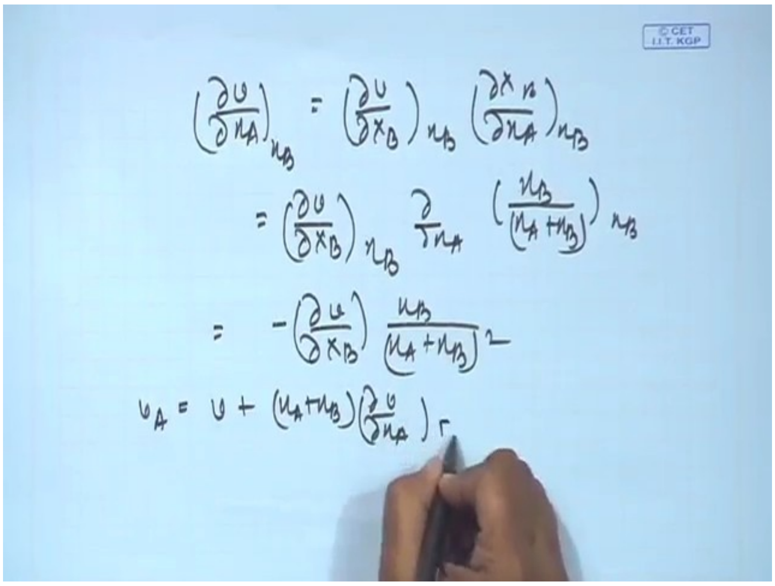

$$\left(\frac{\partial v}{\partial n_A}\right)_{n_B} = \left(\frac{\partial v}{\partial x_B}\right)_{n_B}\left(\frac{\partial x_B}{\partial n_A}\right)_{n_B}$$

$$= \left(\frac{\partial v}{\partial x_B}\right)_{n_B}\frac{\partial}{\partial n_A}\left(\frac{n_B}{(n_A+n_B)}\right)_{n_B}$$

$$= -\left(\frac{\partial v}{\partial x_B}\right)\frac{n_B}{(n_A+n_B)^2}$$

$$v_A = v + (n_A+n_B)\left(\frac{\partial v}{\partial n_A}\right)_T$$

If I just write down the equation this is v plus nA plus nB into del v del nA T, P nB, right? So if I substitute this particular path from here then what do I get? In this particular case I get vA bar this is equal to v minus xB because nA plus nB whole square and this cancels out del v del xB I get this. So therefore vA bar is this.

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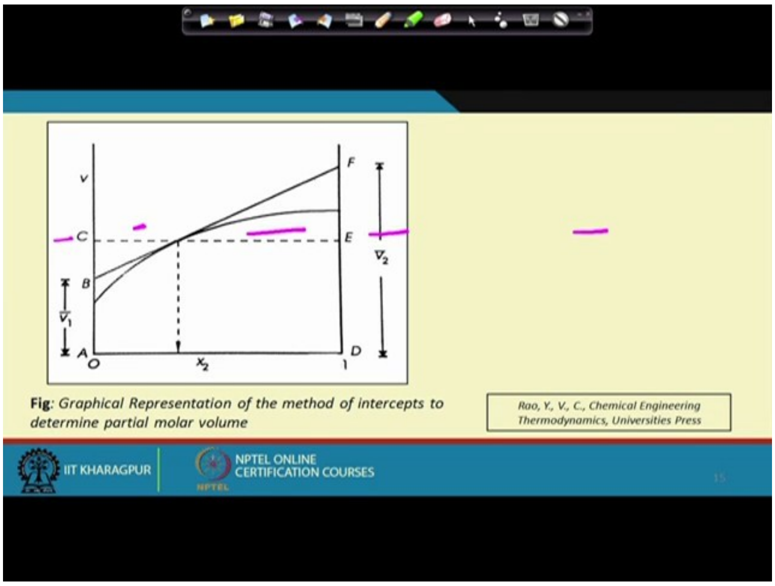

Fig: *Graphical Representation of the method of intercepts to determine partial molar volume*

Rao, Y., V., C., Chemical Engineering Thermodynamics, Universities Press

So suppose so suppose I have plotted in this particular case what have I done? In this particular case I have plotted the volume of the component the molar volume of the component as a function of its composition, right? So from there what do I have?

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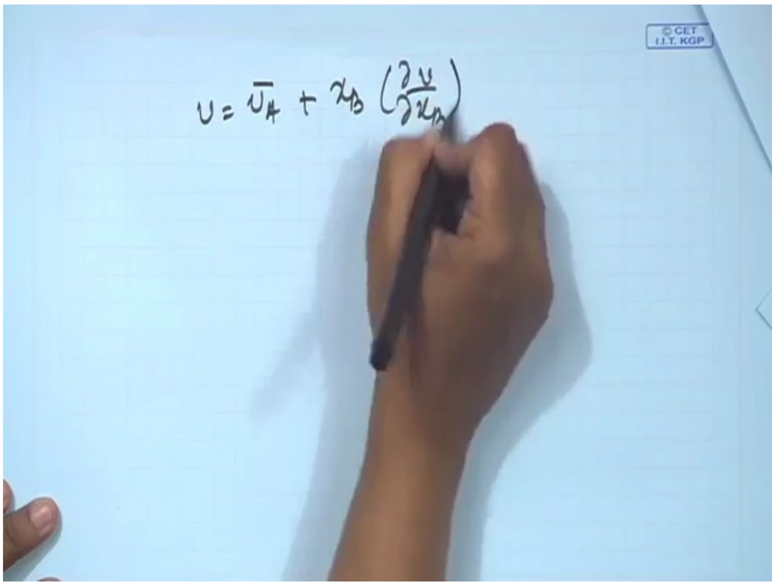

$$v = \bar{v}_A + x_B \left(\frac{\partial v}{\partial x_B}\right)$$

I can very well write down this particular equation as v equals to vA bar plus xB del v del xB I can write it down in the same way if I had started with component B and not component A then I would have landed in a equation as vB equals to v plus 1 minus xB del v del xB from where I know this v would have been equals to vB bar minus 1 minus xB del v del xB, it is alright v equals to, right? Now from this equation and this equation what do you find? We find that suppose we are plotting v versus xB.

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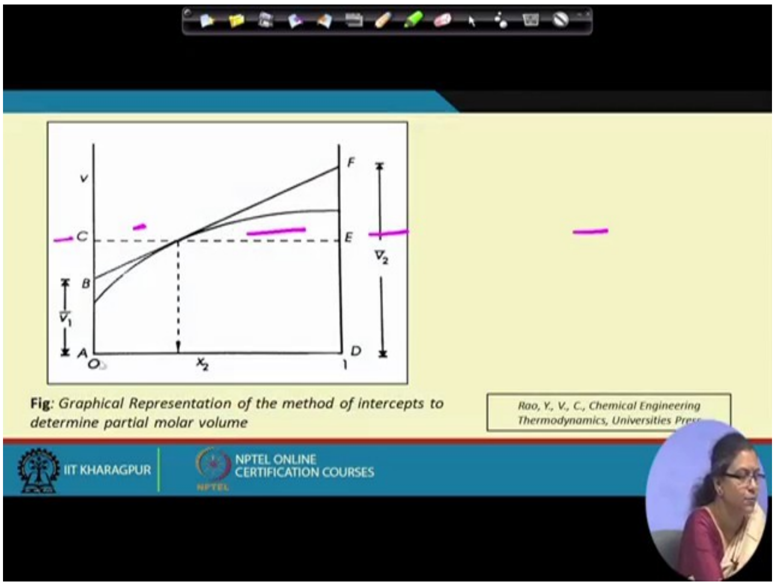

Fig: Graphical Representation of the method of intercepts to determine partial molar volume

Rao, Y., V., C., Chemical Engineering Thermodynamics, Universities Press

The thing which I have done in this particular graph we have plotted molar volume as a function of xB or x2 whatever it is, right? And we would like to find out the partial molar volume at say some particular say point say at x2 equals to 0.3 suppose I would like to find out. So this is the point at this particular point I would like to find out the partial molar volume, what do I do? I draw a tangent to the curve and from this equation what do I find?

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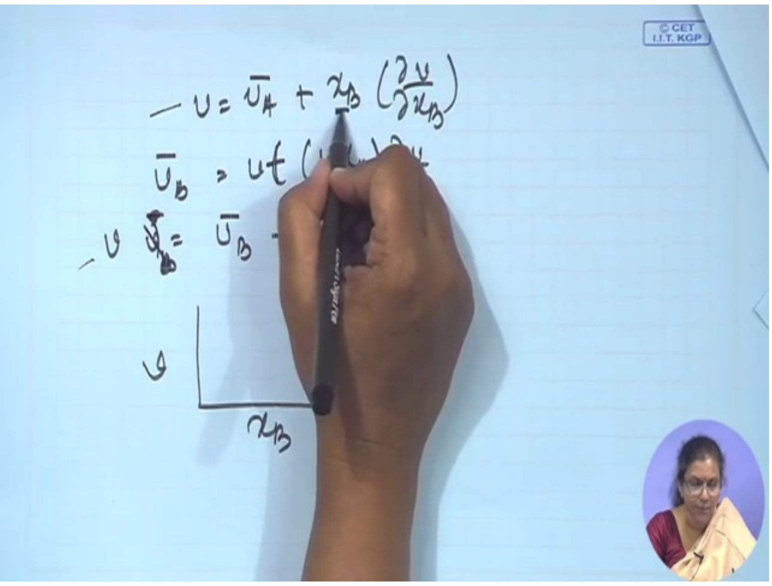

From this particular equation we will find that at xB equals to 0 what is v equals to? V equals to so therefore this reduces to the partial molar volume v equals to vA bar under what condition? When x yeah, v equals to vA bar for xB equals to 0 and v equals to vB bar at xB equals to 1, isn't it? Just check it up this is the thing that you are supposed to get.

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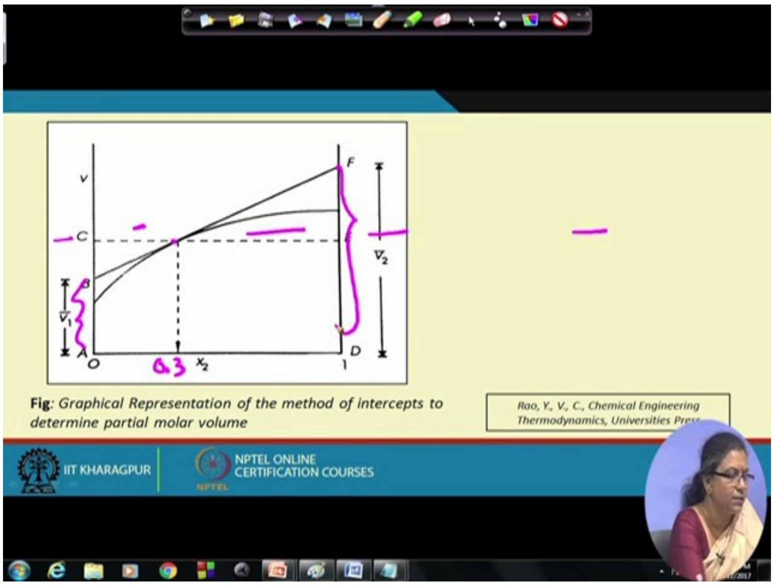

Fig: *Graphical Representation of the method of intercepts to determine partial molar volume*

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So therefore the thing which we do is we simply draw the tangent and then we find the intercepts on the two extreme axis and once you find the intercept we know that merely from the intercept at x2 equals to 0 that gives us the partial molar volume of component a or component 1 and the intercept at x2 equals to 1 that gives us the partial molar volume of component 2.

So therefore this is one particular way of finding out the, this experimental way of finding out partial molar volume of any of the components and then again I would like to remind suppose you are finding just the partial molar volume of any particular component the other component can be found out from Gibbs Duhem equation. So therefore what are things that we discussed? We first understood what are partial molar properties, we discussed the characteristics of the partial molar properties and we also found out how by the method of intercepts really from experimental data partial molar properties can be evaluated. Now before I end there is one particular partial molar property which is particularly important.

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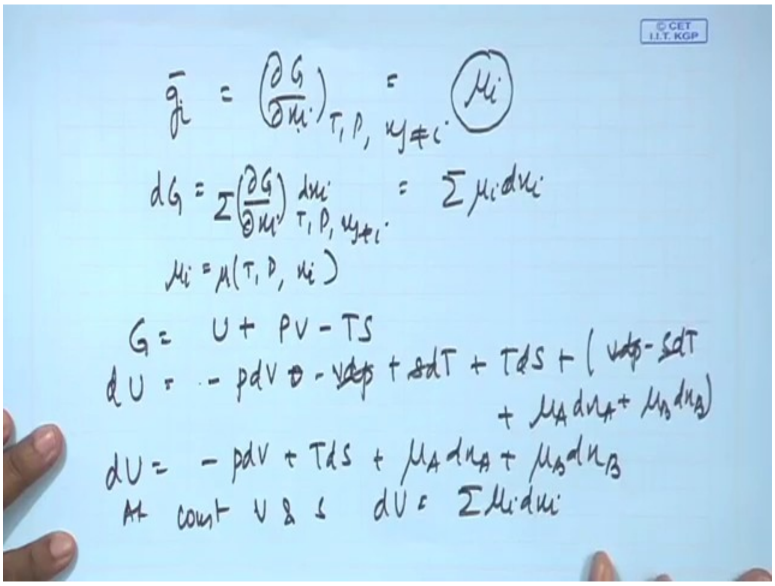

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$$\bar{g}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \boxed{\mu_i}$$

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

$$\mu_i = \mu(T, P, n_i)$$

$$G = U + PV - TS$$

$$dU = -pdV - \cancel{Vdp} + \cancel{SdT} + TdS + (\cancel{Vdp} - \cancel{SdT} + \mu_A dn_A + \mu_B dn_B)$$

$$dU = -pdV + TdS + \mu_A dn_A + \mu_B dn_B$$

At const V & S $\quad dU = \sum \mu_i dn_i$

We continued our discussion with the partial molar volume just because it is easy for us to understand and to imagine that particular quantity but the partial molar property which is going to be of importance to us is the partial molar Gibbs free energy gi bar, what is this equals to? This is equal to del G delni TP nj not equal to i and we have already defined this is nothing but equals to mu i and again just the way that we had discussed earlier in the same particular way we can very well be defined that dG equals to we can define it in this particular way this is nothing but at constant temperature and pressure, so this will be Sigma ni TP nj not equal to i, right into your dni.

So therefore here we can write it down as Sigma mu dni this can be written down where again mu this is a function of TP for binary mixtures it is a function of n1 n2 otherwise it is a function of ni if we have to deal with in this particular way again we find out that this particular term this does not only show how your Gibbs free energy varies with mole numbers. If we can write this equation in this particular form and then we differentiate dU equals to if we elaborate this particular differentiation and say I will just do it for you minus Pdv minus vdp plus sdT just differentiating it plus again that dG comes.

So therefore for dG we have vdp minus sdT plus if it is binary mixture we have just 2 terms muB, agreed? Now if we cancel out the terms this term this term this term this term if all of these they cancel out then in that case what do we get? We get dU equals to minus pdv plus Tds plus mu A dna plus mu B just the way we have done for pure component systems. So therefore at constant V and s what do we know? dU is nothing but equals to Sigma mu i dni, fine.

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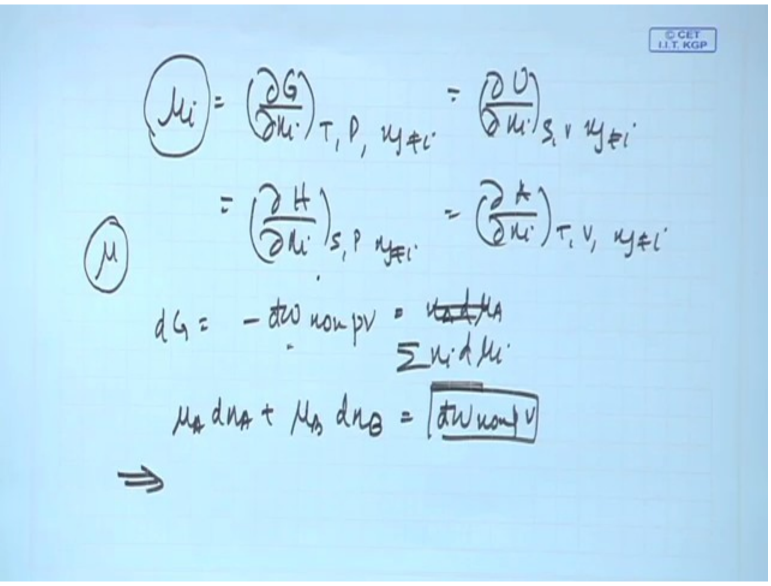

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \left(\frac{\partial U}{\partial n_i}\right)_{S,V\,n_{j\neq i}}$$

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

μ

$$dG = -dw_{non\,pv} = \cancel{v\,d}\mu_A$$

$$\sum n_i\,d\mu_i$$

$$\mu_A\,dn_A + \mu_B\,dn_B = \boxed{dw_{non\,pv}}$$

$\Rightarrow$

So there again in the similar way if you continue what do we find? We find mu i therefore it is delG del ni at constant T, P nj not equals to i this is equals to del u del ni at constant s, v nj not equals to i. This is equal to delH del ni just the way but we have just added this particular term and in terms of Helmholtz free energy it is T, V nj not equals to i. So from there we find that this particular term it is not only the partial molar Gibbs free energy but it also shows, how other thermal parts other thermodynamic properties they vary with change in composition under different interactions between the system and the surroundings.

So therefore mu i occupies a unique position just because of that we do not apply any sort of bar or anything on it we just keep it as mu i for component i in solution for a pure mixture we simply denote it by mu this is sufficient for you to remember. The other thing which is of importance in this particular case is that we very well-know that dG equals to minus dw non-PV this also we had defined under some particular conditions. So therefore what does this imply? This implies this is equals to nA dmuA or in other words if I write it in general it is ni dmu i.

So from this what do we deduce? From this we can deduce that suppose we can also bring about some particular change in the partial molar properties which gives us a change in the or rather suppose in an electrochemical cell we can perform reactions at 2 different sides due to which the mole fraction or the composition of the mixture can change and from there we can derive some amount of non-PV work which will be a function of the chemical potential.

So therefore chemical potential there in that case we find therefore that it has got some very special significance as compared to the chemical potential of, so we can just write it down that d mu A dnA plus mu B dnB just repeating what I have said this is equal to dw non-PV. So therefore from here it implies that additional non-PV work can be done just by changing the composition of the system and this is what is practiced in an electrochemical cell where chemical reaction is arranged to take place at 2 distinct sites at the 2 electrodes and electrical work that the cell performs can be related to its change in composition or to the changing of the chemical potential of the reactors, right?

So therefore this was all about partial molar properties we have defined a large number of partial molar properties and from there what have I told you? We have come to know that from these partial molar properties they have some particular relationships they obey all they have all the characteristics of total properties and molar properties we have found out that experimental determination the only thing only question which I keep before you which we will be discussing in the next class is, whatever properties we have defined we have defined that they have an additive characteristics all other properties.

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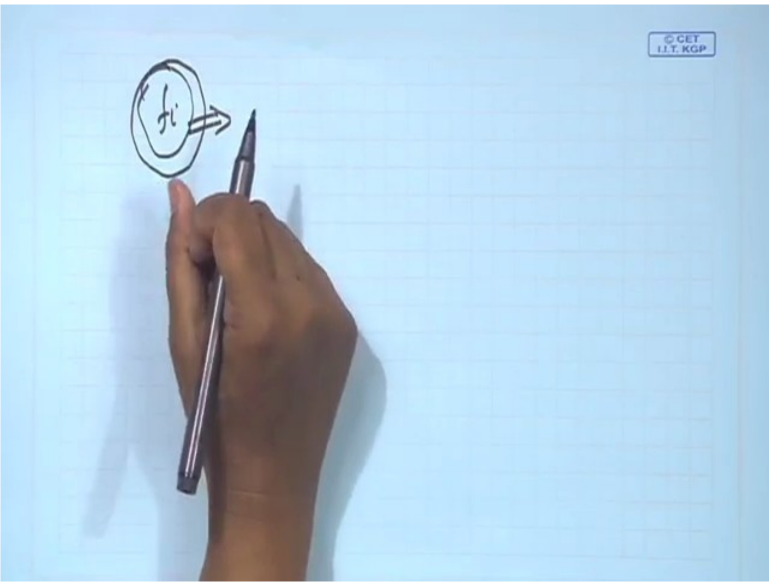

Does partial molar fugacity have identical properties or does this have some unique characteristics of its own? Think about it we are going to deal with partial molar fugacity in the next class. How it is unique as compared to other partial molar properties and this is of special concern to us because we started discussing partial molar properties just because we wanted to find out the fugacity of component i in a solution and from there the entire problem started. So therefore it is very important to understand the partial molar fugacity of component i in solution we will be dealing with this in the next class, thank you very much.