Thermodynamics for Biological Systems:
Classical and Statistical Aspects
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Lecture – 30
Partial Molar Properties Estimation From Mixing Experiments

Welcome!

In the last class, we saw a quantity called the partial molar property. We said that it is a conceptual quantity, which we had defined, so that we could estimate the total property as just a weighted sum made with the mole fractions of this conceptual property.

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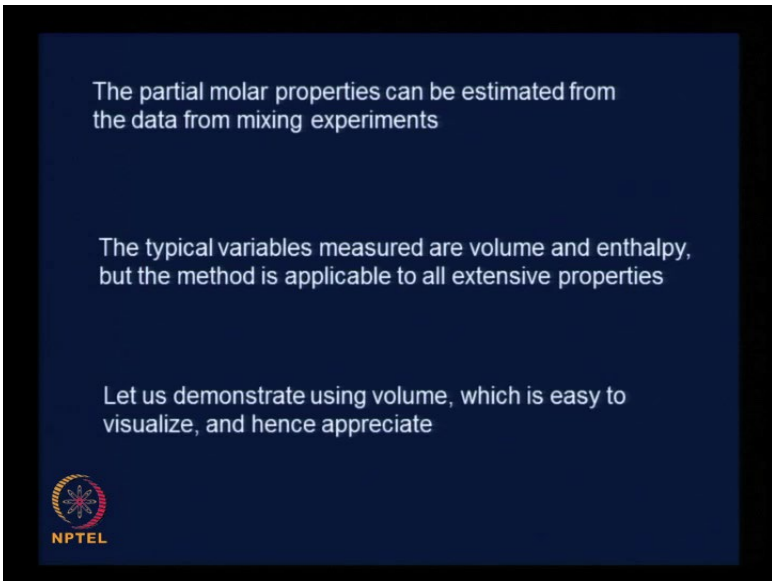

Now, in this class let us look at one of the ways of estimating partial molar properties from experimental data. The data that we need is from mixing experiments. You know you mix 1 and 2 and 3, … Then you initially measure the property of the pure component. Then you measure the property of the mixture very carefully of course, and this is the kind of data that we need to estimate the partial molar properties.

The typical variables that are measured are volume and enthalpy, but the method is applicable to any extensive property. Since volume has an intuitive feel to it – we know that volume mean something, it is the amount of space that it occupies – we will use that to demonstrate the partial molar property. Enthalpy might be a little more difficult to imagine. Therefore, we will use volume, and then you can extrapolate that to all other extensive properties.

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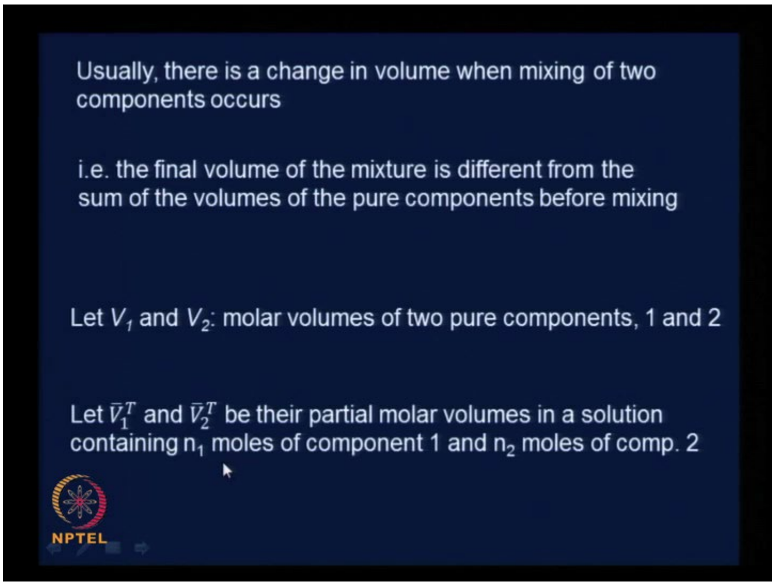

Usually, there is a change in volume, when mixing of two components occurs. That is the reason why we are doing this. We will limit ourselves to a binary system. The final volume of the mixture is going to be different from the sum of the volumes of the pure components before mixing. Let us say that in this binary system, V_1 and V_2 are the molar volumes of the two pure components 1 and 2. And let us say that $\bar{V}_1^T$ and $\bar{V}_2^T$ be the partial molar properties in a solution containing n1 moles of component 1 and n2 moles of component 2.

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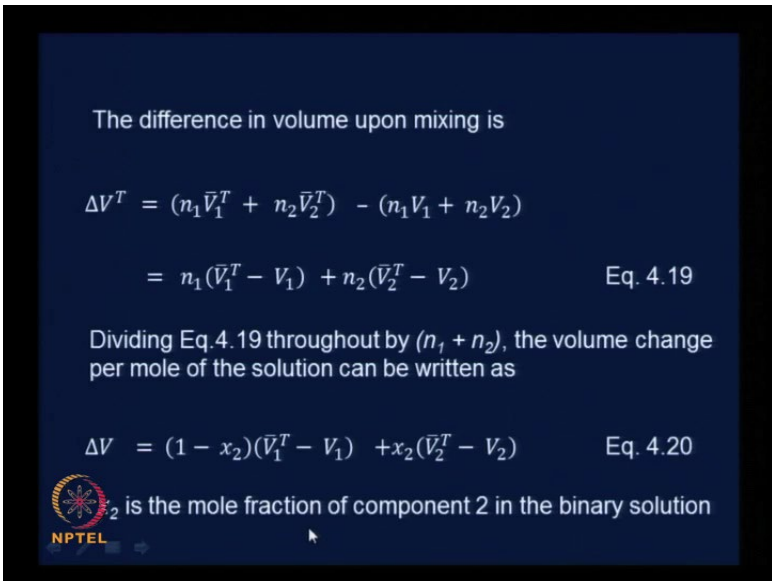

The difference in volume upon mixing is quite easy to see. Let us represent that as ΔV^T, the total difference in volume upon mixing. This is the volume after mixing minus the volume before mixing. The volume after mixing, we said, can be obtained by the weighted sum of the individual volumes, and that is where we brought the partial molar quantities.

Therefore, the volume after mixing is n 1 V 1 T hash plus n 2 V 2 T hash minus the volume before mixing is for each pure component; n 1 moles of the pure component 1; therefore, n 1 times the molar volume of 1 V 1 gives you the volume of 1. And n 2 times V 2 gives you the molar volume of the second component. Therefore; this minus this is quite obviously, the difference in volume upon mixing.

$$\Delta V^T = \left(n_1\bar{V}_1^T + n_2\bar{V}_2^T\right) - \left(n_1V_1 + n_2V_2\right)$$

If we recombine the terms by taking n 1 common out,

$$\Delta V^T = n_1\left(\bar{V}_1^T - V_1\right) + n_2\left(\bar{V}_2^T - V_2\right)$$

We will call this equation 4.19.

If we divide equation 4.19 throughout by *(n_1 + n_2)*, the volume change per mole of the solution can be written down. … Therefore, delta V^T becomes just delta V; this is the molar volume of the change. This is nothing but n 1 by n 1 plus n 2 becomes x 1. Since it is a binary solution, x 1 plus x 2 1 will be 1, and therefore, x 1 can be written as 1 minus x 2. Therefore,

$$\Delta V = (1 - x_2)(\bar{V}_1^T - V_1) + x_2(\bar{V}_2^T - V_2)$$

Let us call this equation 4.20. x_2 of course, was the mole fraction of component 2 in the binary solution – that was quite clear.

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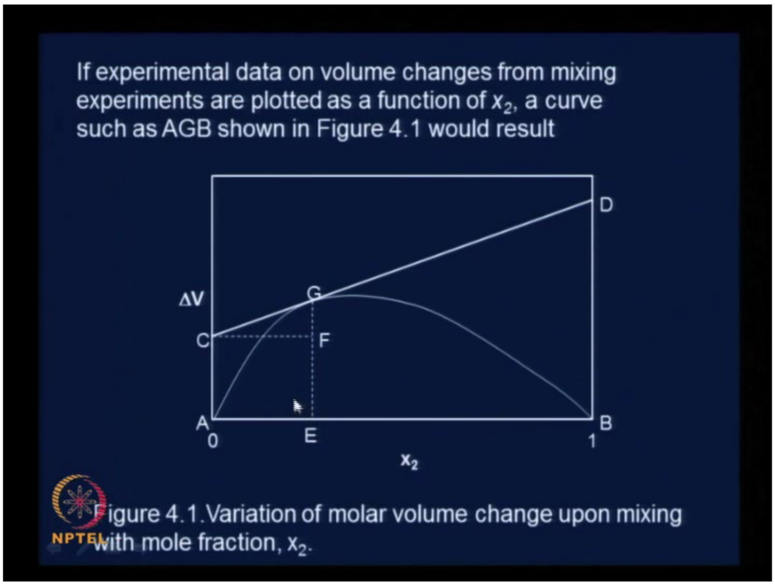

If we plot the experimental data on volume changes from mixing experiments as a function of x 2 – you know, the volume change in the Y axis and the mole fraction of the X axis – we will get a curve something like this. This is delta V, the molar volume change upon mixing, as a function of the mole fraction of the component 2 varies between 0 and 1; we get a curve AGB. This is the variation in the volume upon mixing.

Take a look at this figure. CGD is the slope of this curve AGB. At the point G it is quite evident here. … Also these are distances, which are indicated by dotted lines GF, FE, CF, CA, and so on. What I would like you to do is juggle your brains around a little bit and try to figure out how we can use this figure to get at the partial molar property. That is say V1 hash …. Why don't you think about it, do it. Take about 15 to 20 minutes to do it. There is no hurry. But, this is the basis here I would like you to think about: it comes from the definition of the slope. You know, which is essentially … the derivative here, derivative at this point, and then relating it to the distances here. So, take about 15 to 20 minutes to come up with that. Then I will give you solution step by step. Go ahead please.

Let me start working this out for you and give you some hints and help you get to the solution. As we had seen, this is nothing but delta V verses x 2; this is the curve AGB that we will get – the variation and molar volume change upon mixing as a function of x 2.

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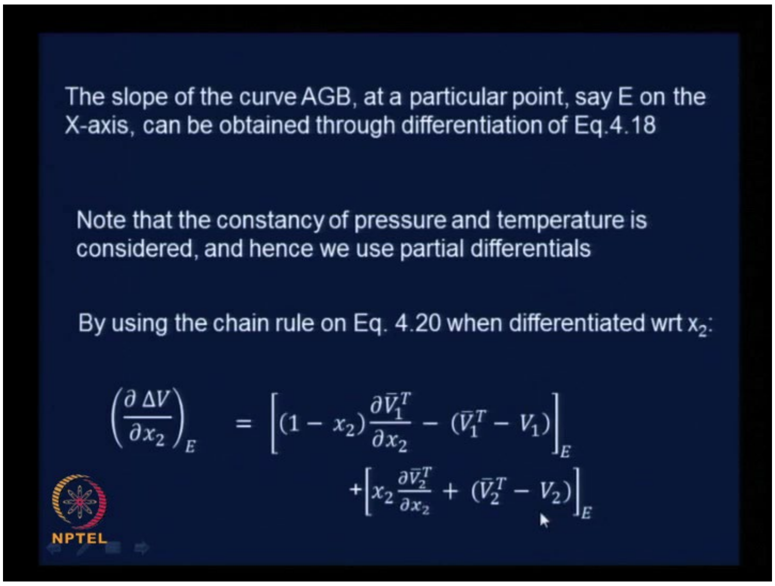

The slope of the curve AGB at a particular point E on the x axis – you know this particular point E – at this point what would be the slope here is nothing but the derivative if we differentiate equation 4.18

Here, let us not go too far behind. It is quite easy to see. This you have a curve you have delta V as a function of x 2, which you got from here itself. You can start with this itself, 4.20 itself, and if you differentiate that assuming constancy of pressure and temperature... If we use equation 4.20 differentiated by the chain rule dou delta V dou x 2 at the point E – we are doing this differentiation as the point E. We are doing the differentiation of this equation. So, dou delta V dou x 2 at the point E. Please keep this in mind when you are differentiating. It is nothing but 1 minus x 2 again by chain rules 1 minus x 2 dou V 1 T hash dou x 2 minus V 1 T hash minus V 1 – taking 1 minus x 2 into this.

Therefore first function into derivative the second function, … which will turn out to be V 1 T hash d x 2 minus the second function into the derivative of the first function d dou x 2 dou x 2 will turn out to be 1. Therefore, that is the first term plus the second term is x 2 dou V 2 T hash dou x 2 plus V 2 T hash minus V 2 both taken at the point E.

$$\left(\frac{\partial\, \Delta V}{\partial x_2}\right)_E = \left[(1 - x_2)\frac{\partial \bar{V}_1^T}{\partial x_2} - \left(\bar{V}_1^T - V_1\right)\right]_E + \left[x_2 \frac{\partial \bar{V}_2^T}{\partial x_2} + \left(\bar{V}_2^T - V_2\right)\right]_E$$

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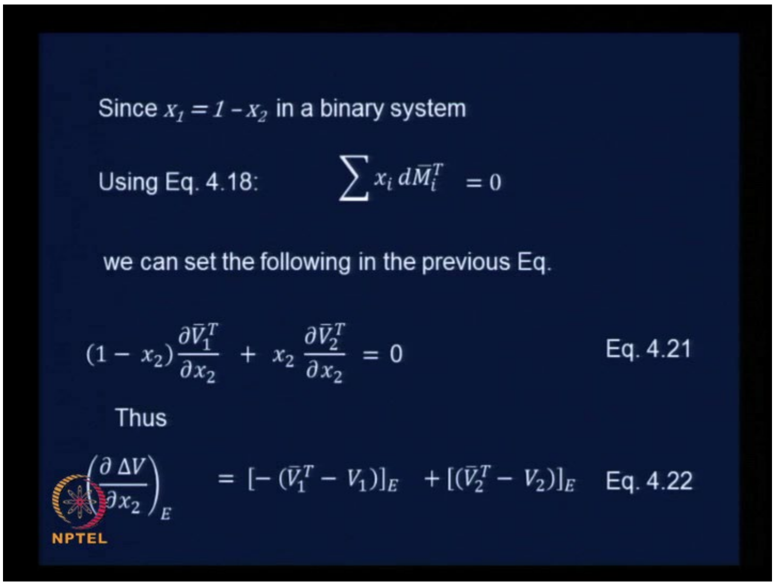

$x_1 = 1 - x_2$ in the binary system. We have already seen from equation 1.8,

$$\sum x_i \, d\bar{M}_i^T = 0$$

therefore, what do you get? Using this, how can you simplify whatever derivative that we had written previously – here, this is the derivative we have here, and this is the hint that I am giving you for the next step: summation of x i d M i T hash equals 0. How can you simplify the previous equation? Go ahead, take the next 5 minutes, 5 to 10 minutes if you want, and do it. Go ahead please.

If, we apply the summation of x i d M i T equals 0. What is this? This is nothing but … in our current binary case … x 1 d M 1 T hash plus x 2 d M 2 T hash equals 0. Or 1 minus x 2 – x 1 can be replaced as 1 minus x 2 – 1 minus x 2 … dou d 1 T hash dou x 2 plus x 2 dou V 2 T hash dou x 2; this equals 0.

$$(1 - x_2)\frac{\partial \bar{V}_1^T}{\partial x_2} + x_2 \frac{\partial \bar{V}_2^T}{\partial x_2} = 0$$

Therefore,

$$\left(\frac{\partial \Delta V}{\partial x_2}\right)_E = \left[-\left(\bar{V}_1^T - V_1\right)\right]_E + \left[\left(\bar{V}_2^T - V_2\right)\right]_E$$

Equation 4.22. Now, can you take another 5 minutes to see how you can interpret these in terms of the distances given in the figure? Figure 4.1 that I had shown the AGV curve delta V verses x 2 … See how these quantities can be related to the distances given in the figure. Take another 5 minutes. This is a geometric interpretation of that and that gives us the basis for estimating the partial molar properties.

You would have probably figured out what these mean in terms of the distances.

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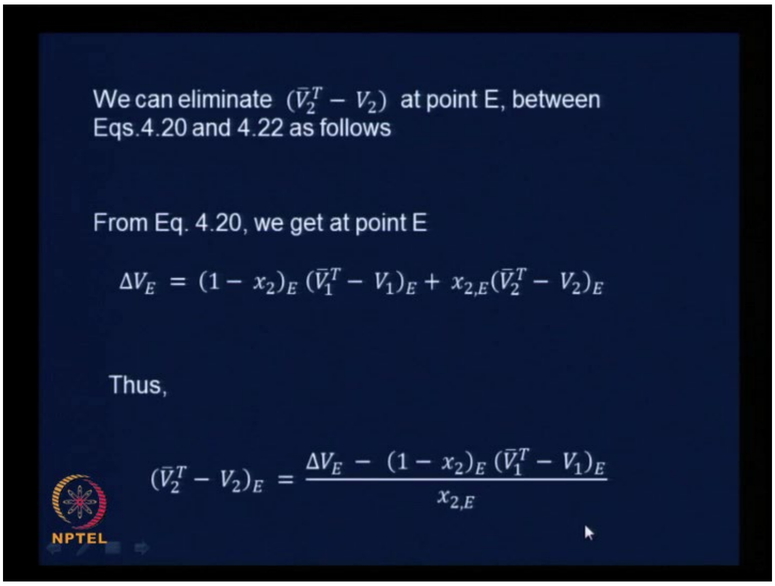

Now, let me tell you what it is. Just check whether you got it right. Before we do that, … let us eliminate V 2 T bar minus V 2 at point E between equations 4.20 and 4.22.

$$\Delta V_E = \left(1 - x_2\right)_E \left(\bar{V}_1^T - V_1\right)_E + x_{2,E}\left(\bar{V}_2^T - V_2\right)_E$$

We have a V 2 T bar minus V 2 at E. And 4.20 was this: x 2 into V 2 T bar minus V 2. This one exists here. Therefore, let us use these expressions to write V 2 T bar minus V 2 in terms of the other variables here. If we do that we will get … please do this and check … delta V E equals 1 minus x 2 at E into … V 1 T hash minus V 1 at the point E, plus x 2 at the point E into V 2 T hash minus V 2 at the point E.

Therefore V 2 T hash minus V 2 at the point of E, which we are trying to eliminate … we had used equation 4.20 to eliminate this … we could write this in terms of the other variables by transposing delta V E minus, take this to the other side, 1 minus x 2 at E V 1 T hash minus V 1 at E. And there is an x 2 in a factor here; therefore, divided by x 2 E.

$$\left(\bar{V}_2^T - V_2\right)_E = \frac{\Delta V_E - (1 - x_2)_E \left(\bar{V}_1^T - V_1\right)_E}{x_{2,E}}$$

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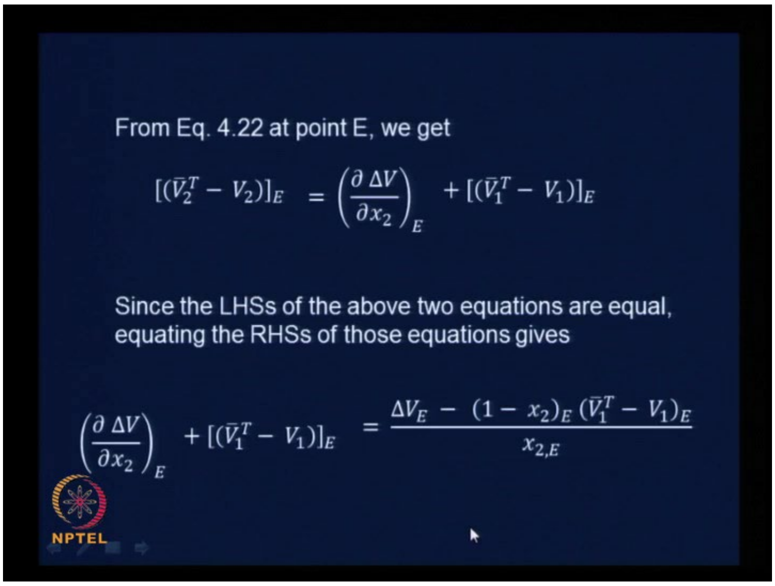

And from equation 4.22 at the point E, … the equation 4.22 was this and this and this, by transposing, we can write this in terms of a derivative. And this particular quantity V 2 T hash minus V 2 at E equals dou dou x 2 of delta V at E plus V 1 T hash minus V 1 at E.

$$\left[\left(\bar{V}_2^T - V_2\right)\right]_E = \left(\frac{\partial \Delta V}{\partial x_2}\right)_E + \left[\left(\bar{V}_1^T - V_1\right)\right]_E$$

Since the left hand sides are equal between the previous equation and this equation, we can equate the right hand sides. Therefore, … dou dou x 2 of delta V at E plus V 1 T hash minus V 1 at E equals the right hand side on the previous equation, delta V E minus, 1 minus x 2 E, into V 1 T hash minus V 1 at E divided by x 2 E.

$$\left(\frac{\partial \Delta V}{\partial x_2}\right)_E + \left[\left(\bar{V}_1^T - V_1\right)\right]_E = \frac{\Delta V_E - (1 - x_2)_E \left(\bar{V}_1^T - V_1\right)_E}{x_{2,E}}$$

Therefore, if we transpose this equation – you know cross multiply, and you know how to do this – you can cross multiply and get … essentially, we are looking at getting some way of finding out V 1 T hash.

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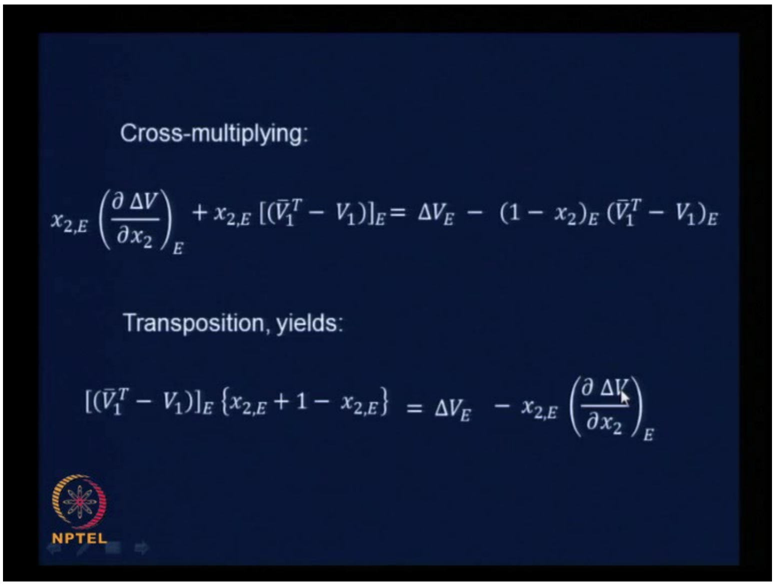

If I we do the algebra you would get this as a first step; cross multiply by x 2 E –

$$x_{2,E}\left(\frac{\partial\,\Delta V}{\partial x_2}\right)_E + x_{2,E}\left[\left(\bar{V}_1^T - V_1\right)\right]_E = \Delta V_E - \left(1 - x_2\right)_E\left(\bar{V}_1^T - V_1\right)_E$$

And transposition: getting V 1 T hash minus V 1 terms together, we could group them as V 1 T hash minus V 1 at E – common take out – times x 2 E plus 1 minus x 2 E equals delta V E minus of x 2 into dou dou x 2 of delta V at the point E.

$$\left[\left(\bar{V}_1^T - V_1\right)\right]_E\left\{x_{2,E} + 1 - x_{2,E}\right\} = \Delta V_E - x_{2,E}\left(\frac{\partial\,\Delta V}{\partial x_2}\right)_E$$

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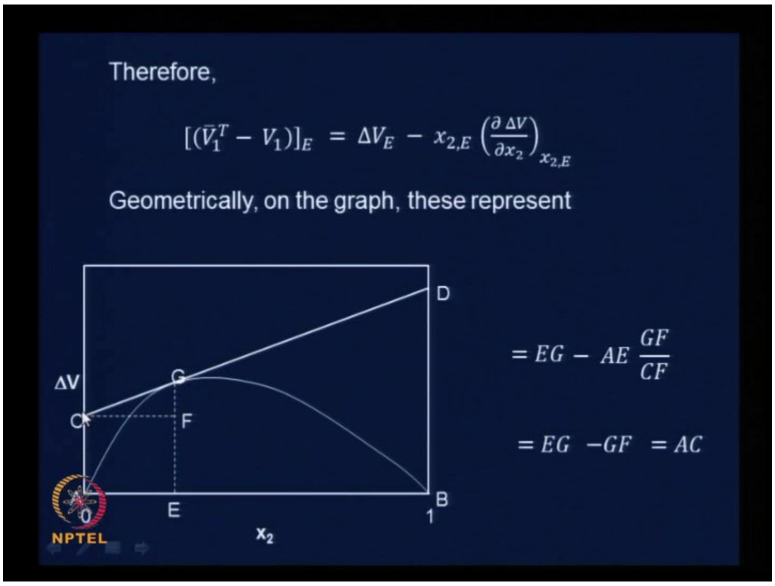

Therefore,

$$[(\bar{V}_1^T - V_1)]_E = \Delta V_E - x_{2,\,E}\left(\frac{\partial \Delta V}{\partial x_2}\right)_{x_{2,\,E}}$$

What does this represent on the graph, was the earlier question. The derivative is the slope of the line or the tangent of the angle made at a particular point in this graph.

Now, we are trying to get delta V E. What is delta V E? … the value of delta V at the point E, which happens to be the distance GE. Therefore, this can be replaced by this distance GE. x 2 E is nothing but AE or CF, you know, this distance. And dou delta V dou x 2 at the point E is nothing but the slope of the tangent. That is the definition of the derivative itself, from your calculus class, which is nothing but the tan of the angle that this line makes with the horizontal line here. What is tan? Opposite side, by adjacent side, GF by CF. Therefore, EG minus AE x2, times GF by CF. That is what this is.

This is the geometrical interpretation of this particular quantity, which can of course, be written as EG minus GF. Why? Because AE and CF are the same quantities. Therefore, you can cancel AE and CF here. Therefore, EG minus GF, which is nothing but AC, which is nothing but the intercept of the tangent made at the point G on the y axis.

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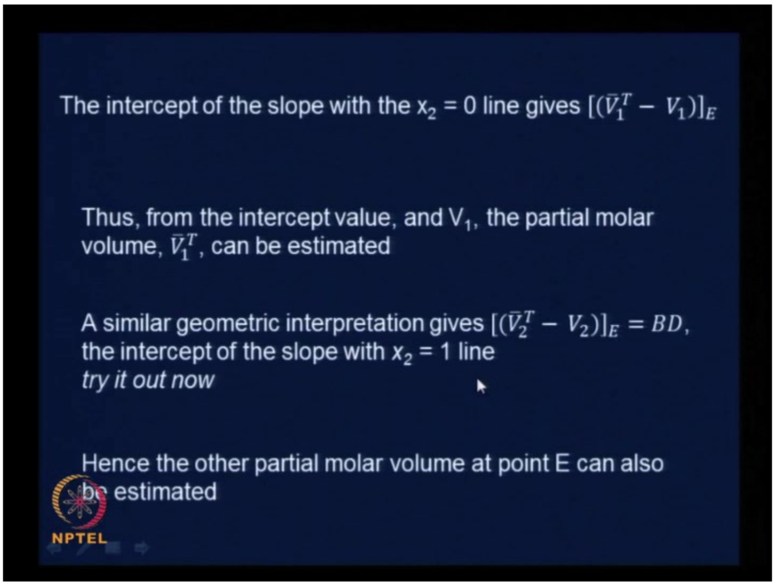

Therefore, the intercept of the slope with the x 2 equals 0 line, which is the y axis, gives us

$$[(\bar{V}_1^T - V_1)]_E$$

V 1 of course, is the molar volume of the pure component that is easily known. Once you know the intercept, you could get V 1 T hash. That is what is given here: from the intercept value and V 1, the partial molar volume, V 1 T hash, can be estimated.

Now, a similar geometric interpretation gives $\left[\left(\bar{V}_2^T - V_2\right)\right]_E = BD$, the other intercept. What I would like you to do is to convince yourself that it is indeed the other intercept. Convince yourself by going through the same procedure again. I would like to leave that as home work for you, and when we begin the next class, we will take things further.