

Thermodynamics (Classical) for Biological Students

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Module No. # 04

Module Name Thermodynamics of Solutions

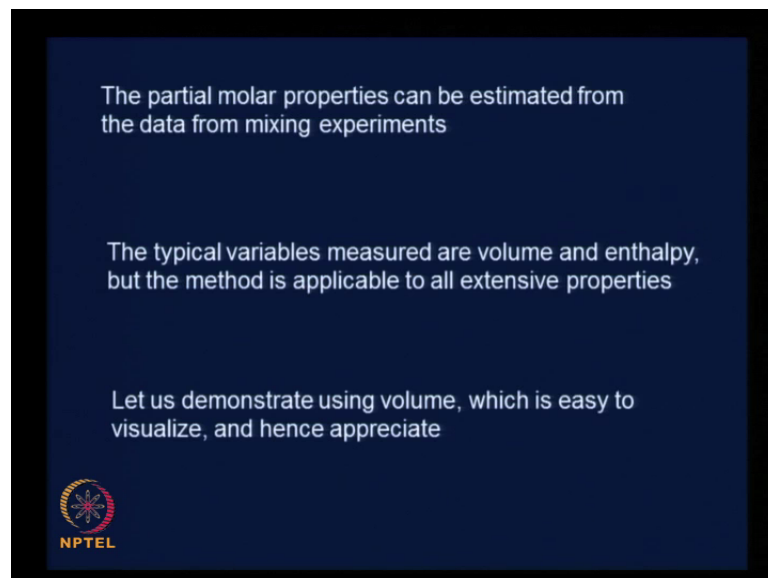
Lecture No. # 21

Partial Molar Property 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, whatever. ... Then you initially measure the property of the pure component. And 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. And 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 kind of extrapolate that to all other extensive properties.

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Usually, there is a change in volume when mixing of two components occurs

i.e. the final volume of the mixture is different from the sum of the volumes of the pure components before mixing

Let V_1 and V_2 : molar volumes of two pure components, 1 and 2

Let \bar{V}_1^T and \bar{V}_2^T be their partial molar volumes in a solution containing n_1 moles of component 1 and n_2 moles of comp. 2

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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. And 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 n_1 moles of component 1 and n_2 moles of component 2.


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The difference in volume upon mixing is

$$\Delta V^T = (n_1 \bar{V}_1^T + n_2 \bar{V}_2^T) - (n_1 V_1 + n_2 V_2)$$
$$= n_1 (\bar{V}_1^T - V_1) + n_2 (\bar{V}_2^T - V_2) \quad \text{Eq. 4.19}$$

Dividing Eq.4.19 throughout by $(n_1 + n_2)$, the volume change per mole of the solution can be written as

$$\Delta V = (1 - x_2)(\bar{V}_1^T - V_1) + x_2(\bar{V}_2^T - V_2) \quad \text{Eq. 4.20}$$

 x_2 is the mole fraction of component 2 in the binary solution

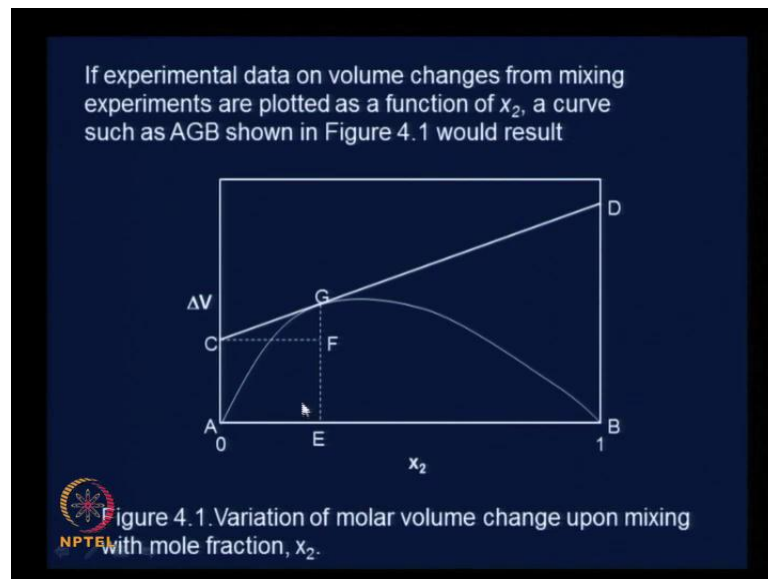
The difference in volume upon mixing is quite easy to see. Let us represent that as ΔV^T , the total difference in volume upon mixing. This is the volume after mixing minus the volume before mixing. The volume after mixing, we said, can be obtained by the weighted sum of the individual volumes, and that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

Therefore, the volume after mixing is $n_1 \bar{V}_1^T + n_2 \bar{V}_2^T$ 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 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. If we recombine the terms by taking n_1 common out, n_1 into $\bar{V}_1^T - V_1$ as here plus n_2 into $\bar{V}_2^T - V_2$. 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, ΔV^T becomes just ΔV ; this is the molar volume of the change. This is nothing but you know n_1 by $n_1 + n_2$ becomes x_1 . Since it is a binary solution, $x_1 + x_2$ will be 1, and therefore, x_1 can be written as $1 - x_2$. Therefore, $(1 - x_2)(\bar{V}_1^T - V_1) + x_2(\bar{V}_2^T - V_2)$. 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 ΔV , 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 V_1 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.

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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 ΔV versus 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, say E on the X-axis, can be obtained through differentiation of Eq.4.18

Note that the constancy of pressure and temperature is considered, and hence we use partial differentials

By using the chain rule on Eq. 4.20 when differentiated wrt x_2 :

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


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, you know, if we differentiate equation 4.18 ...

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Here, let us not go too far behind. It is quite easy to see. This you have a curve you have ΔV 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 $\frac{d\Delta V}{dx_2}$ at the point E – you know, here ... somewhere here ... we are doing this differentiation as the point E. And we are doing the differentiation of this equation. So, $\frac{d\Delta V}{dx_2}$ at the point E. Please keep this in mind when you are differentiating. It is nothing but $(1 - x_2) \frac{d\bar{V}_1^T}{dx_2} - (\bar{V}_1^T - V_1) + x_2 \frac{d\bar{V}_2^T}{dx_2} + (\bar{V}_2^T - V_2)$ – taking $(1 - x_2)$ into this.

Therefore first function into derivative the second function, ... which will turn out to be $(1 - x_2) \frac{d\bar{V}_1^T}{dx_2} - (\bar{V}_1^T - V_1) + x_2 \frac{d\bar{V}_2^T}{dx_2} + (\bar{V}_2^T - V_2)$

x_2 and x_1 will turn out to be 1. Therefore, that is the first term plus the second term is $x_2 d\bar{V}_2^T$ plus $x_1 d\bar{V}_1^T$ minus \bar{V}_2 both taken at the point E.

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Since $x_1 = 1 - x_2$ in a binary system

Using Eq. 4.18: $\sum x_i d\bar{M}_i^T = 0$

we can set the following in the previous Eq.

$$(1 - x_2) \frac{\partial \bar{V}_1^T}{\partial x_2} + x_2 \frac{\partial \bar{V}_2^T}{\partial x_2} = 0 \quad \text{Eq. 4.21}$$

Thus

$$\left(\frac{\partial \Delta V}{\partial x_2} \right)_E = [-(\bar{V}_1^T - V_1)]_E + [(\bar{V}_2^T - V_2)]_E \quad \text{Eq. 4.22}$$


Since x_1 equals $1 - x_2$ 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 $x_i d\bar{M}_i^T = 0$. So, 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.

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If, we apply the summation of $x_i d\bar{M}_i^T = 0$. What is this? This is nothing but ... in our current binary case ... $x_1 d\bar{M}_1^T$ plus $x_2 d\bar{M}_2^T = 0$. Or $1 - x_2 - x_1$ can be replaced as $1 - x_2 - 1 + x_2$... $d\bar{V}_1^T$ plus $x_2 d\bar{V}_2^T$ minus \bar{V}_1 plus $x_2 d\bar{V}_2^T$ minus \bar{V}_2 ; this equals 0.

And where does this happen? It happens in the previous equation here. You know, ... the combination of this and this can be set to 0. And therefore, $\left(\frac{\partial \Delta V}{\partial x_2} \right)_E$ this happens to be these two terms ... there is a minus here ... So, let us write this first $\bar{V}_2^T - V_2$, say at E, minus of $\bar{V}_1^T - V_1$ at E – that is what this

one says.

Therefore ΔV_E ... we have taken the minus here first, does not matter ... minus of \bar{V}_1^T minus V_1 at E plus \bar{V}_2^T minus V_2 at E. It is 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? You know, the figure 4.1 that I had shown the AGV curve ΔV versus 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.

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

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We can eliminate $(\bar{V}_2^T - V_2)$ at point E, between Eqs. 4.20 and 4.22 as follows

From Eq. 4.20, we get at point E

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

Thus,

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

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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 $\bar{V}_2^T - V_2$ at point E between equations 4.20 and 4.22. What is 4.20?

4.22 is this: we have a $\bar{V}_2^T - V_2$ at E. And 4.20 (No audio from 42:42 to 42:49) was this: x_2 into $\bar{V}_2^T - V_2$. This one exists here. Therefore, let us use these expressions to write $\bar{V}_2^T - V_2$ in terms of the other variables here. If we do that (No audio from 43:02 to 43:13), we will get ... please do this and check ... ΔV_E equals $(1 - x_2)_E$ into ... $\bar{V}_1^T - V_1$ at the point E, plus x_2 at

the point E into $V_2^T - V_2$ at the point E.

Therefore $V_2^T - V_2$ 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 ΔV_E minus, take this to the other side, $1 - x_2$ at E $V_1^T - V_1$ at E. And there is an x_2 in a factor here; therefore, divided by x_2 E.

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From Eq. 4.22 at point E, we get

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

Since the LHSs of the above two equations are equal, equating the RHSs of those equations gives

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

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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 (No audio from 44:18 to 44:24) $V_2^T - V_2$ at E equals $\frac{\Delta V_E - (1 - x_2)_E (V_1^T - V_1)_E}{x_2}$ of ΔV at E plus $V_1^T - V_1$ at E. Since the left hand sides are equal between the previous equation and this equation, we can equate the right hand sides. Therefore, ... $\frac{\Delta V_E - (1 - x_2)_E (V_1^T - V_1)_E}{x_2}$ of ΔV at E plus $V_1^T - V_1$ at E equals the right hand side on the previous equation, ΔV_E minus, $1 - x_2$ E, into $V_1^T - V_1$ at E divided by 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 $V_1^T - V_1$.

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Cross-multiplying:

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

Transposition, yields:

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


If I we do the algebra you would get this as a first step; cross multiply by $x_{2,E} - x_{2,E}$ into $x_{2,E} \Delta V_E + x_{2,E} (\bar{V}_1^T - V_1)_E = \Delta V_E - (1 - x_{2,E}) (\bar{V}_1^T - V_1)_E$.

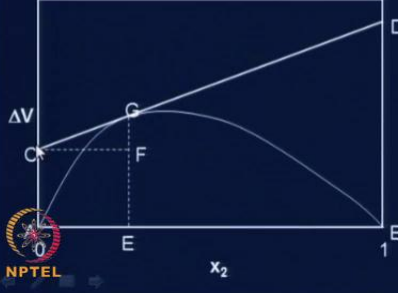
And transposition: getting $(\bar{V}_1^T - V_1)$ terms together, we could group them as $(\bar{V}_1^T - V_1)_E - (1 - x_{2,E}) (\bar{V}_1^T - V_1)_E - x_{2,E} \left(\frac{\partial \Delta V}{\partial x_2} \right)_E = \Delta V_E - x_{2,E} \left(\frac{\partial \Delta V}{\partial x_2} \right)_E$.

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Therefore,

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

Geometrically, on the graph, these represent



$$= EG - AE \frac{GF}{CF}$$

$$= EG - GF = AC$$


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

of ΔV at the point E. What does this represent on the graph, was the earlier question. What does this represent? You know, 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 ΔV_E . What is ΔV_E ? ... the value of ΔV at the point E, which happens to be the distance GE. Therefore, this can be replaced by this distance GE. x_2^2 is nothing but AE or CF, you know, this distance. And ΔV 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. And therefore, EG minus AE x_2^2 , 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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The intercept of the slope with the $x_2 = 0$ line gives $[(\bar{V}_1^T - V_1)]_E$

Thus, from the intercept value, and V_1 , the partial molar volume, \bar{V}_1^T , can be estimated

A similar geometric interpretation gives $[(\bar{V}_2^T - V_2)]_E = BD$, the intercept of the slope with $x_2 = 1$ line
try it out now

Hence the other partial molar volume at point E can also be estimated

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Therefore, the intercept of the slope with the x_2 equals 0 line, which is the y axis, gives us V_1^T minus V_1 at the point E. V_1 of course, is the molar volume of the pure component that is easily known. And once you know the intercept, you could get V_1^T . 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 V_2 T hash minus V_2 E equals 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.