

Thermodynamics (Classical) for Biological Systems

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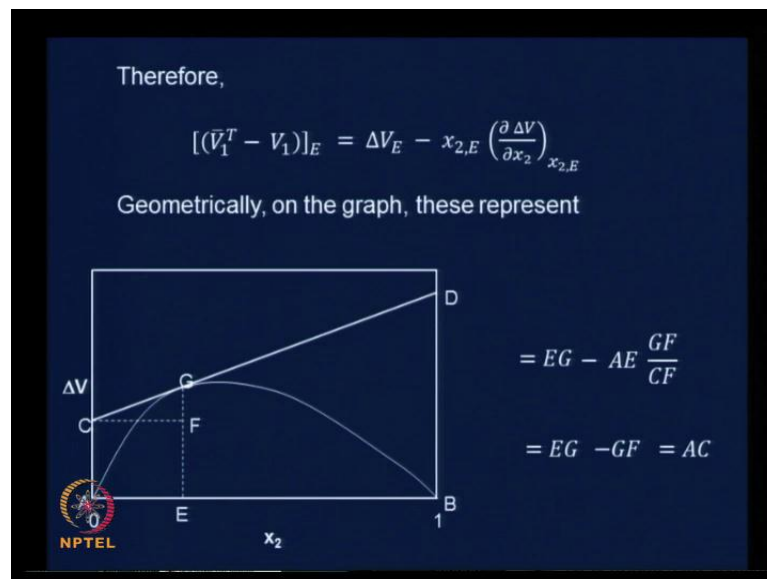
Module No. #04

Thermodynamics of solutions

Lecture No. #22

Partial Molar Property Estimation (Continued) Excess Properties

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Welcome!

In the last class, we saw method to estimate the partial molar volume from the data obtained from mixing experiments. In other words, the experiment is essentially mix a certain number of moles of one component and a certain number of moles of the second component, together. We know their initial molar volumes, and if we measure the final

molar volume, we can figure out the difference between the molar volume of the solution, and the molar volumes of these individual components. And with the change in molar volume plotted on the y axis as a function of the mole fraction of the second component, we said that we could estimate the partial molar properties.

For example, if this AGB is the curve that gives the variation of the volume change upon mixing as a function of the mole fraction x_2 , then, if you are interested in finding the partial molar volume say at a mole fraction of E, then all we need to do is, to the curve AGB at the point E, we draw a tangent. And where the tangent meets the y axis, this intercept would give us \bar{V}_1 .


The basis for that was brought down to this equation, which could be geometrically interpreted, or these have meanings as lengths on this graph. For example, ΔV_E , the volume change in mixing at the mole fraction given by the point E is nothing but this length GE, because that is the point that corresponds to the curve at the mole fraction which is given by the point E. So, GE is that distance, x_2 could be AE or CF, they are the same lengths. So, AE times GF by CF, which is essentially the slope of the tangent to the curve at the point G as given by $\frac{\Delta V}{\Delta x_2}$ at the point E. So, this is the slope, and we all know that AE equals CF. Therefore, these two can be canceled. Therefore, it becomes EG which is this length minus GF which is this length. This is actually FE which is the same length as CA, which is the intercept on the y axis of the tangent to the point G.

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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 \blacktriangleright
try it out now




Therefore, that was the way to find out the partial molar volume \bar{V}_1^T . I have been using hash dash and bar; please take them as being used interchangeably. They all mean the same at least in this local context here. So, \bar{V}_1^T ... and this was given as an exercise to you. I had asked you to work out a similar geometric interpretation to find out the partial molar volume, \bar{V}_2^T . And the formulation would yield that the difference here, \bar{V}_2^T minus V_2 , add a point E would be equivalent to the intercept on the other axis. And therefore, we could find \bar{V}_2^T from there. So that hopefully you went about completing that exercise.

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Example 4.1

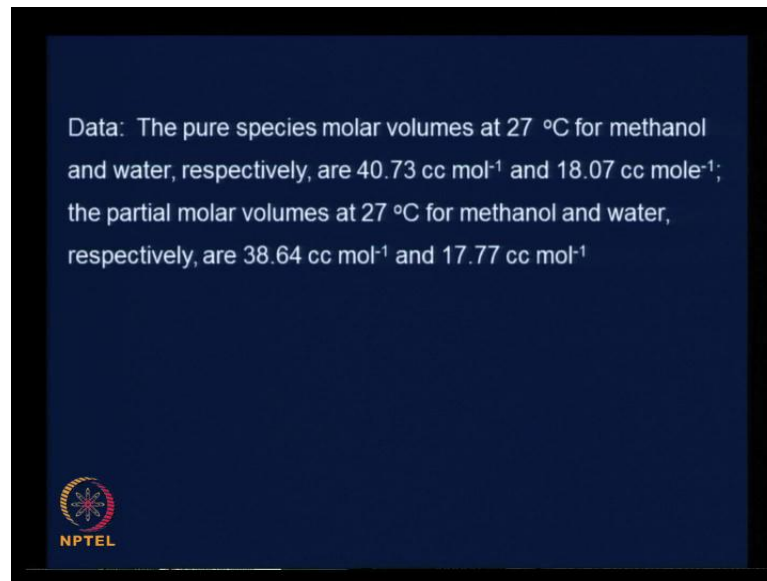
Biofuels have the potential to meet a significant fraction of our energy needs in the near future. Lipids from algae or plants are an important source of biofuels, especially bio-diesel. In one of the steps to extract lipids from cells, the methanol-water system is used. During studies on optimization of the extraction procedure, a PhD student needed a 30% (mole%) methanol in water system. To prepare 2 L of the needed solution, what are the needed volumes of pure methanol and pure water? The lab is maintained at a comfortable 27 °C.




Today, let us start out by working a problem to estimate the partial molar quantities. It is a problem of a current significance, example 4.1. The biofuels have the potential to meet a significant fraction of our energy needs in the near future. Lipids from algae or plants are an important source of biofuels, especially bio-diesel or it could yield many different biofuels. In one of the steps to extract lipids from cells, the methanol water system is used to extract lipids. During studies on optimization of the extraction procedure ... In fact this is something that we did in our lab ... so, I had kind of picked it up here.

During the studies on optimization of the extraction procedure, a PhD student needed 30 ... mole percent methanol in water system. The student who actually did that, or the person who actually did that in our lab was a project associate. In this case, anyway, PhD student needed 30 percent given as mole percent methanol in water system. To prepare 2 liters of the needed solution what are the needed volumes of pure methanol and pure water? The lab is maintained at a comfortable 27 degree C. This is a very standard thing that comes about in day to day requirements while working with these kinds of things.

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Data: The pure species molar volumes at 27 °C for methanol and water, respectively, are 40.73 cc mol⁻¹ and 18.07 cc mole⁻¹; the partial molar volumes at 27 °C for methanol and water, respectively, are 38.64 cc mol⁻¹ and 17.77 cc mol⁻¹


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And, let me also give you some data, before going forward. The data is that the pure species molar volumes at 27 degrees C for methanol and water are given, that is 40.73 centimeter cubed per mole for methanol and 18.07 centimeter cubed per mole. And I think we said we will remember this value, 18.07 cc per mole for water. The partial molar volumes are also given ... at 27 degree C. For methanol it is 38.64 centimeter cubed per mole, and the partial molar volume is 17.77 centimeter cubed per mole. Note this difference here: 18.07 for the pure component, whereas in this particular case it happens to be 17.77 – a significant difference here.

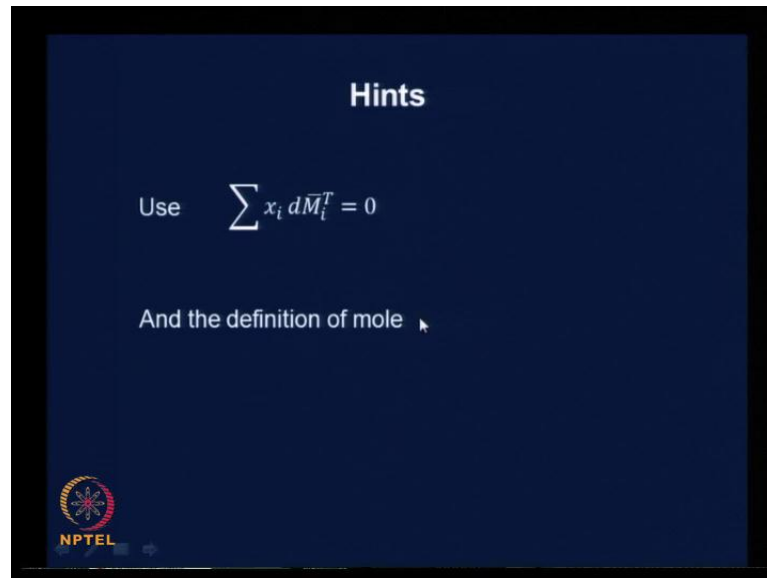
What I would like you to do is think about how would you go about solving this? Why do not you think about it? And then I will give you a couple of hints and some more time to work it out. Since, this would require essentially definitions and use of some fundamental concepts which you have been learning from the school stage, take about 15 minutes and try to come up with the solution on your own. It is a very doable. And anyway, I will give you the hints after 15 minutes. Go ahead please.

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Let me give you the hints that I mentioned earlier, now; some of you would have worked

this out for sure. ... I hope that many of you were able to do this.

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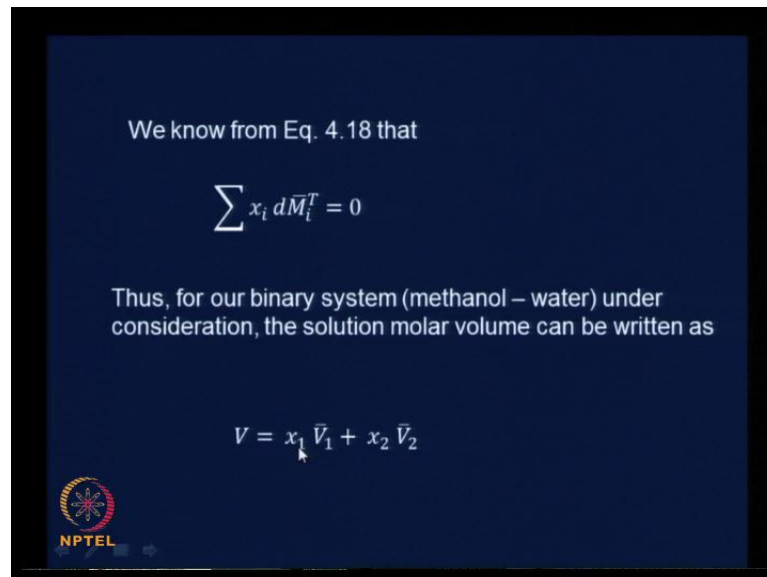
But, in any case, some hints in case you have not been able to do it. Use the basic definition. You know, summation of x_i the mole fraction times the d of the partial molar quantity $d\bar{M}_i^T$ equals 0; that is the first hint. The second hint, this something related to a concept, which is very simple, but which I found many students to have difficulty with even at an advanced stage. That is a definition of a mole; it is a very simple concept. Please pay attention to that. I will tell you more about it when we come back. Since it involves something that I find many students have some difficulty with, I will let you know figure it out on your own and give you some time to do it. Take another 15 minutes to come up with the solution. If you have already have the solution, you can just fast forward to the point, where the solution begins. Go ahead please. Otherwise, spend about 15 minutes more ... you have a lot of time to feel comfortable and work out the solution. 15 minutes.

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Now, let us look at the solution from the hints that we have given. Let us use sum over $x_i d\bar{M}_i^T$ equals 0, and the definition of a mole. The mole as we all know is defined

as the mass by the molecular mass of a substance. That is one mole of a substance. Or if you divide the mass of the substance you have by the molecular mass, you will get the number of moles ... as simple as that.

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We know from Eq. 4.18 that

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

Thus, for our binary system (methanol – water) under consideration, the solution molar volume can be written as

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

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Now, let us look at the solution itself, we know from equation 4.18, which is just given to you that, sum over $x_i d\bar{M}_i^T$ equals 0. This was given as the hint. ... Therefore, for our binary system in this case, the methanol and water system, the solution molar volume can be written by expanding this. The molar volume of the solution is nothing but $x_1 \bar{V}_1$ plus $x_2 \bar{V}_2$. I have just dropped the T's here, only for convenience, nothing else. You can take, 1 to be methanol 2 to be water or the other way. Let us see what I have taken here.


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Substituting the values, we get

$$V = (0.3) 38.64 + (0.7) 17.77 = 24.03 \text{ cc mol}^{-1}$$

The needed total volume is 2 L = 2000 cc.

Thus, the total number of moles needed:

$$n = \frac{2000}{24.03} = 83.23 \text{ mol}$$


You substitute the values ... we have taken 1 as methanol and 2 as water ... and the molar volume of the solution is 30 percent methanol. Therefore 0.3 is the mole fraction of methanol. 0.3 into the partial molar volume of methanol, 38.64, plus 0.7 (that is the mole fraction of water) times the partial molar volume of water – that is 17.77. You do the calculations it will turn out to be 24.3 centimeter cubed per mole. So, this is something that we need to calculate for whatever we need to do. We need to essentially find out how many how much of these two solutions we need to mix to get 2 liters of the total solution.

The total volume needed is 2 liters, which is two thousand centimeter cubed. We have these in terms of centimeter cubed. And therefore, let us also convert this into centimeter cubed; it is 2,000 centimeter cubed. And the total number of moles that is required... this is n you know, this is the total volume divided by the molar volume. In other words if one mole you know occupies 24.03 centimeter cubed per mole, how much would ... how many moles would be required to occupy 2,000 centimeter cubed? That is the unitary method that we are using here. Therefore, the number of moles is 2000 divided by 24.03, 83.23 moles is what it turns out to be. So, this is the total number of moles of the solution that we need.

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Thus, the number of moles of methanol, for the 30 mole% solution is

$$n_{\text{methanol}} = 0.3 \times 83.23 = 24.97 \text{ moles}$$

and

$$n_{\text{water}} = 0.7 \times 83.23 = 58.26 \text{ moles}$$

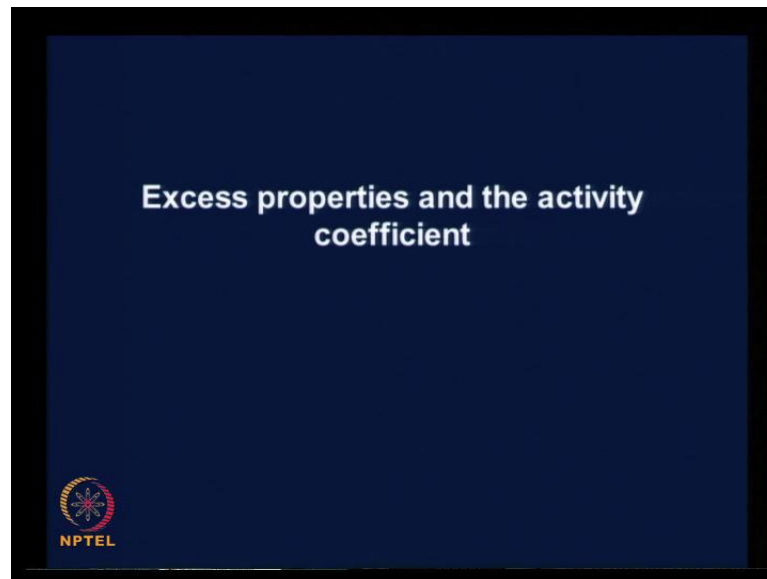
Thus the needed volumes of pure methanol and pure water are:

$$V_{\text{methanol}} = 24.97 \times 40.73 = 1017.03 \text{ cc}$$
$$V_{\text{water}} = 58.26 \times 18.07 = 1052.76 \text{ cc}$$


Therefore, the number of moles of methanol for the solution, ... it is 30 percent solution. So, number of moles of ethanol is nothing but 30 percent of 83.23 or in other words 0.3 times 83.23. It turns out to be 24.97 moles. And the number of moles of water is automatically 83.23 minus 24.97, or it is 70 percent or 0.7 times 83.23, that is 58.26 moles. Therefore the needed volumes of pure methanol and pure water – this is what we needed to find to make up the 2 liters of the required solution. 30 percent methanol solution is nothing but 24.97 times 40.73. We got this 40.73 ... this is the molar volume that was given to us in the beginning.

Let us go back and just check it out here. The molar volume of methanol was 40.73 centimeter cubed per mole. And the molar volume of water was 18.07 centimeter cubed per mole. So, the number of moles into the molar volume will give the volume of the pure component. That is what we are doing here. So, number of moles, which is what we found out, times 40.73, molar volume, turns out to be 1017.03 centimeter cubed. And volume of water is 58.26, number of moles of water, times the molar volume of water, 18.07, 1052.76 centimeter cubed. So, that brings us to whatever we need from the problem.

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The next thing that we are going to look at, is something called excess properties. And what we will also do is, see a little later after we look at excess properties, how to correlate the activity coefficient to the excess properties? Or in other words, we will come up with a method to estimate the activity coefficient from the so called excess properties.

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We saw in Chapter 3 that for pure substances, the difference between the actual value and the ideal value of a thermodynamic property is called the residual of that property

In other words, for any extensive thermodynamic property, M , (U , S , H , A , G or V) the relevant residual property is

$$M^R \equiv M - M^{ig} \quad \text{Eq. 3.25}$$

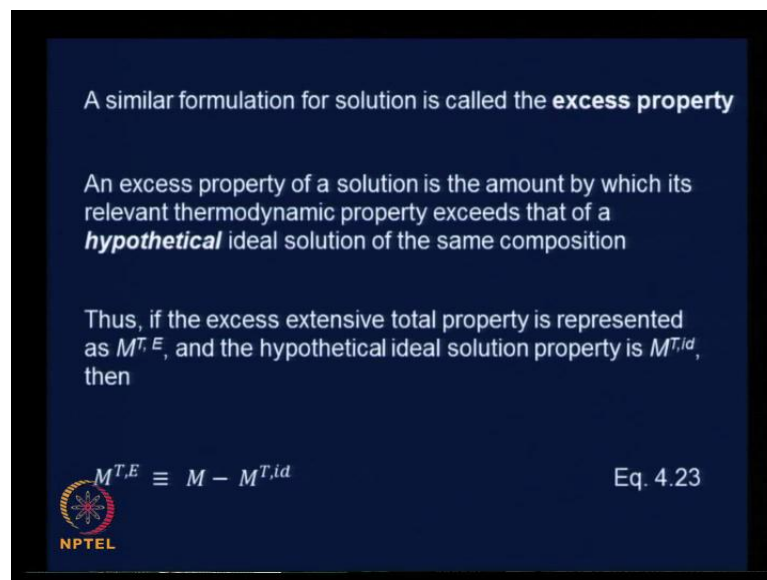
We also saw that the residual properties were useful in evaluating the thermodynamic properties

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But, first let us look at what excess properties are? To understand excess properties, let us review residual properties. To give out the secret, what residual properties were, for pure substances, Excess properties are, for solutions. It is as simple as that. Here we saw that in module 3 that the difference between the actual value and the ideal value of the thermodynamic property. Any extensive thermodynamic property is called the residual of that property. Remember that M^R equals M minus M ideal gas.

So, in other words, for any extensive thermodynamic property, M , it could be internal energy, entropy, enthalpy, Helmholtz free energy, Gibbs free energy or volume for that matter, the residual property was as mentioned. This was equation 3.25 that we saw earlier and we had used the residual properties extensively to estimate the various thermodynamic properties. And that is a utility of these residual properties. It is a very simple definition, but, it comes in handy, because the data is easily available in terms of residual properties.

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A similar formulation for solution is called the **excess property**

An excess property of a solution is the amount by which its relevant thermodynamic property exceeds that of a **hypothetical** ideal solution of the same composition

Thus, if the excess extensive total property is represented as $M^{T,E}$, and the hypothetical ideal solution property is $M^{T,id}$, then

$$M^{T,E} \equiv M - M^{T,id} \quad \text{Eq. 4.23}$$

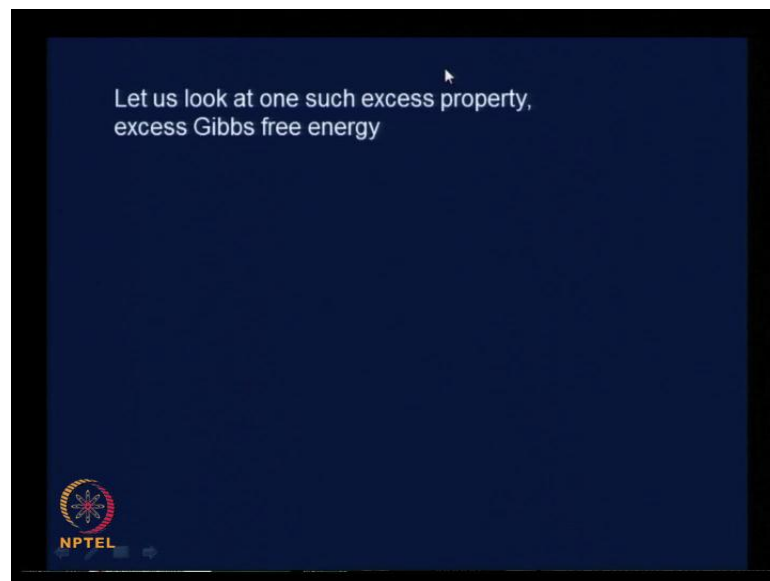
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A similar formulation for solution, for solutions ... you know ... that was for the pure substance. ...this is for the solutions or mixtures, is called excess property. And excess property of a solution as you would have guessed is the amount by which the relevant thermodynamic property exceeds that of a hypothetical ideal solution of the same

composition. You need to keep this in mind. We are we taking the difference between actual and ideal. The ideal is hypothetical, it does not really exist. It is, what it would be, if it is ideal.

Thus, ... the excess extensive total property is represented as $M T E$. I am going to use the superscript E to denote excess properties, the same way that we had used the superscript R to denote the residual properties for pure substances. So, $M T E$ and the hypothetical ideal solution property is $M T id$you know id for ideal. Then the excess property $M T E$ is defined as the difference between M the actual property and the ideal property, $M T id$. Let us call this equation 4.23.

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And, what we are going to look at in detail is one such excess property, namely the excess Gibbs free energy. I think we should start looking at that in the next class, because if I start this now, in the amount of time that is available to us which is about less than a minute, we will not be able to do justice. Therefore, when we start up the next class, we will look at excess properties, which are nothing but the difference ... to repeat, the difference between the actual property, and the hypothetical ideal property. And we are going to look at the excess Gibbs free energy.