Thermodynamics of Fluid Phase Equilibria
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Lecture – 23
Partial Molar Properties

Welcome back in this lecture. We are going to solve some problems related to our partial molar properties.

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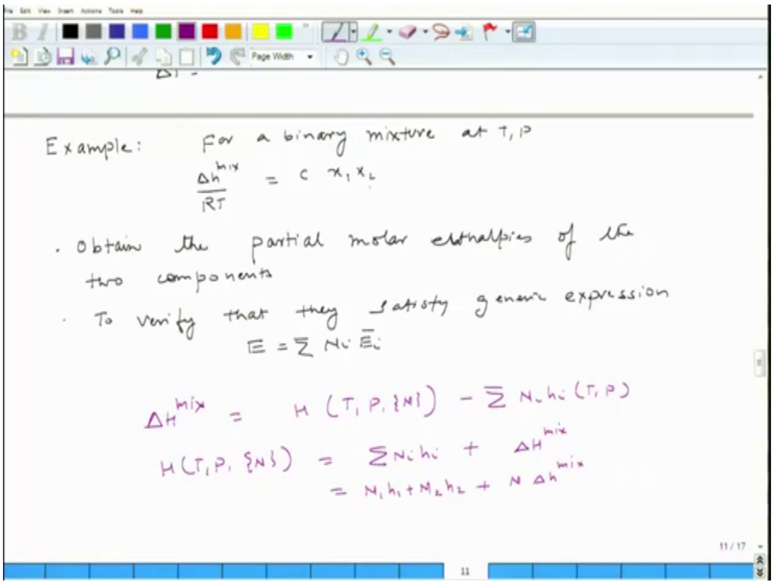

So, let me just start with the first example here. So, for a binary mixture at temperature T and P , we have been given the change in enthalpy of the mixture in this form ok, where C is a constant. Now what is being asked is to obtain the partial molar enthalpies of the two components ok, that is the question 1. And the second part is to verify that they satisfy the generic expression E as summation N i E i bar ok.

So, we have two now. So, E basically in this case is nothing, but H ok. So, we have this expression of delta H mix, from there we must find out the partial molar enthalpy and show that this exists, and this holds this particular expression holds ok. So, let me first start with the definition of delta H mix, let us do this exercise um. So, we can write delta H mix as H T P N minus summation N i h i for the (Refer Time: 02:40) ok.

So, with the same temperature and pressure where which we have now, you can rearrange this expression we can write that as H [no 1 plus N 2 h 2 and this I can write as total n multiplied by, since we are using superscript. So, I am going to write this in superscript all right. So, now, this expression we know delta H small delta h mix expression is given to us in this form C x 1 x 2 multiplied by RT.

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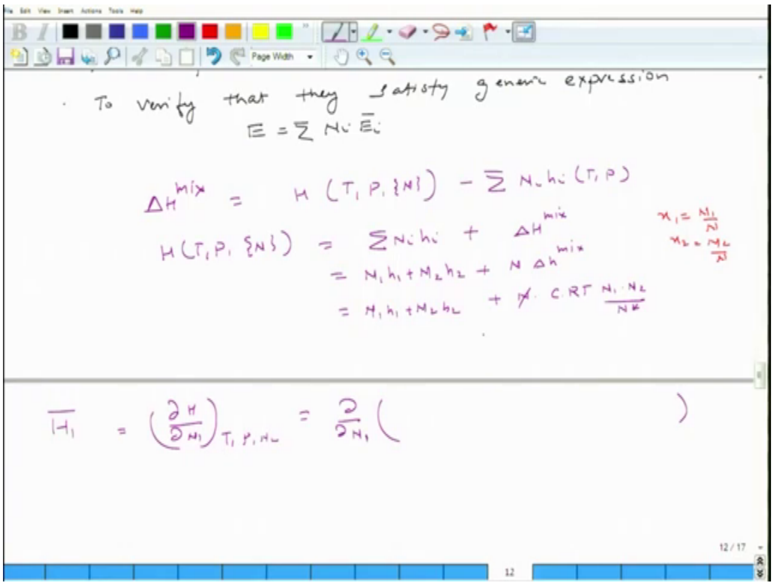

So, I am going to plug in this here x 1. So, CR T and then x 1 and x 2, and so what is x 1 all right. So, x 1 is N 1 by N ok, and similarly x 2 is N 2 by N right. So, we are going to make use of that and here we write simply N 1 N 2 by N square right. So, this get cancelled all right. So, now, we have an expression N 1 h 1 plus N 2 h 2 plus this part ok. So, from here we can now get del H by del N 1 keeping TP N 2 constant and this will be your h 1 bar ok. So, I take a partial derivative of with this expression with respect to N 1 and this is going to be h 1 this part plus since N 2 is constant.

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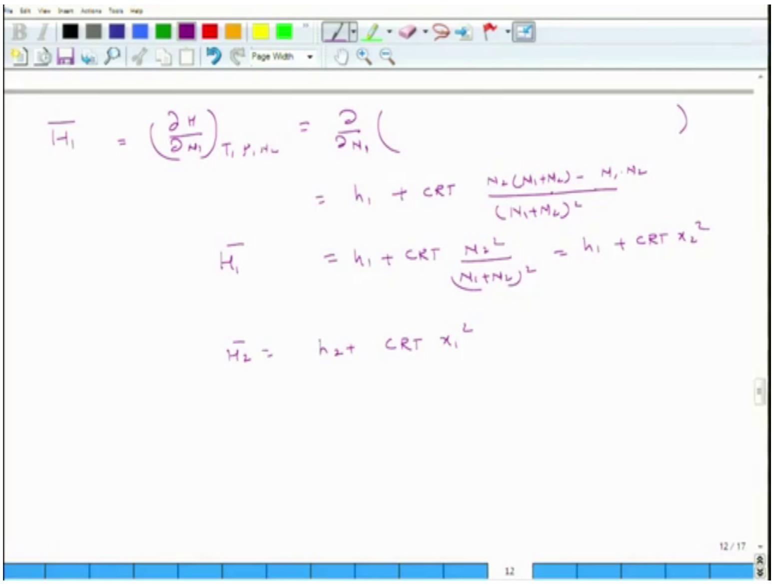

So, this is going to be 0 right, plus you have CRT ok. So, this N is nothing, but N 1 plus N 2 right. So, this becomes N 1 plus N 2 square. So, I will take the diff differentiation of this term first. So, that would be N 2 multiplied by N 1 plus N 2 minus. I will take a differentiation of this first, which would be just 1 multiplied by N 1 times N 2 ok. So, I have this expression now and then I can rewrite this. If you look at it, this, this is N 2 N 1 which will cancel out this. So, what we are going to get is N 2 square plus CR T N 2 square divided by N 1 plus N 2 square, and this is nothing, but h 1 plus C R T x 2 square ok.

Now, this is what we got H 1 bar. Now considering that the expression which we have, is symmetric ok, and this without deriving h 2 I can simply write H 2 bar as h 2 plus CR T x 1 square ok, we can derive it, but to cut down the time. I am just writing this expression based on the symmetric expression of delta H mix, this is what we have got the first part of the problem.

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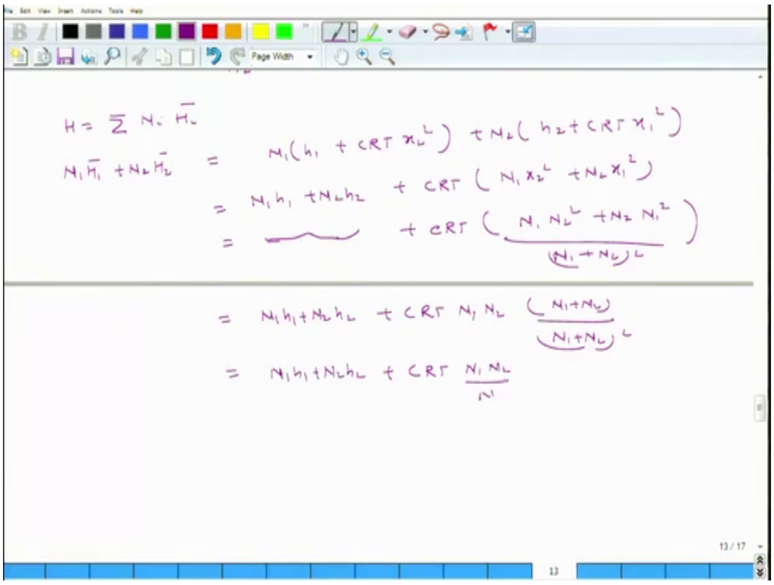

In order to prove the second part of the problem I simply write H is equal to N i H i bar. Now we have this expression. So, we can simply check N 1 H 1 bar plus N 2 H 2 bar first and see whether this is equal to H ok. I will just write down this expression, this is equivalent to N 1 h 1 plus CRT ok. This I can write like this N 2 h 2 plus CRT, this is going to be N 1 x 2 square plus N 2 x 1 square ok. So, this is same expression.

So, this would be same plus CRT, I can write x 2 as N 2 square divided by N 1 plus N 2 squares. So, in the denominator I get this, and then you have N 1 multiplied N 2 square plus N 2 multiplied by N 1 square ok. Now, here of course, N 1 and N 2 are common. So, I can take that out. So, this is going to be N 1 h 1 plus N 2 h 2 plus CRT N 1 N 2 N 1 plus N 2 divided by and N 1 plus N 2 square.

So, what we got expression is N 1 h 1 plus N 2 h 2 plus CRT N 1 N 2 divided N ok. So, this is the expression number and this is, this is exactly the expression what we have here ok. This is what we had H ok. So, this is exactly the expression what we had. So, we indeed had, could show that the partial molar properties of enthalpy satisfy the generic expression of E is equal to summation N i E i ok. Basically this exercise is helping us to understand how to make use of the partial molar property. Now, I am going to work on another example which will help us or which will allow us to make use of Gibbs Duhem expressions ok. And without that it would be difficult to solve the problem.

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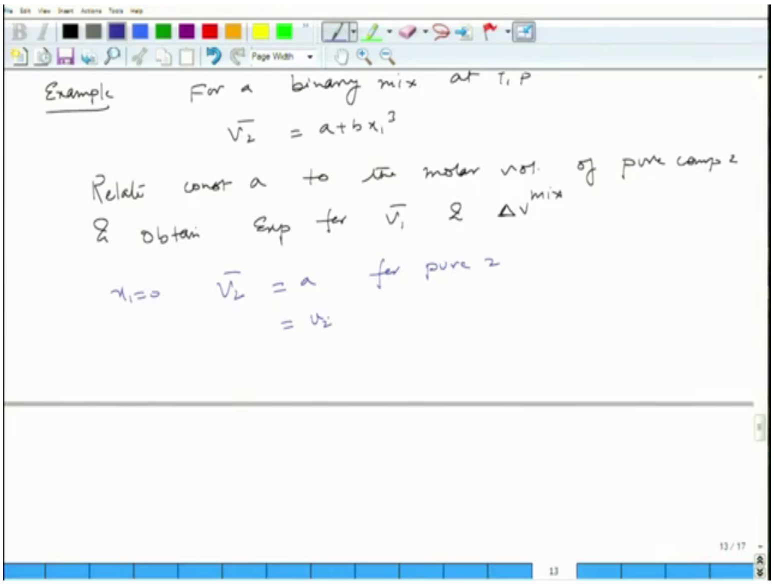

So, this is an example, again for a binary mixture ah, we have been given , at T and P. We have been given partial molar property of component 2 as a plus b b b x one cube ok, and the question is to relate constant a to the molar volume of pure component 2 and obtain expression for V 1 bar , and we need to also obtain delta V mix ok, volume of mixing.

So, this is a very simple question given to us and the only information we have is partial molar volume of component 2. So, how we are going to solve the problem? Now this is where we have to make use of Gibbs Duhem expression, its ok. So, let me start with the fact that when you put x 1 equal to 0 you have a pure component 2 right. So, V 2, from this expression is nothing, but a, but this is for pure component a nothing, but for pure component 2, and this is nothing, but V 2 ok.

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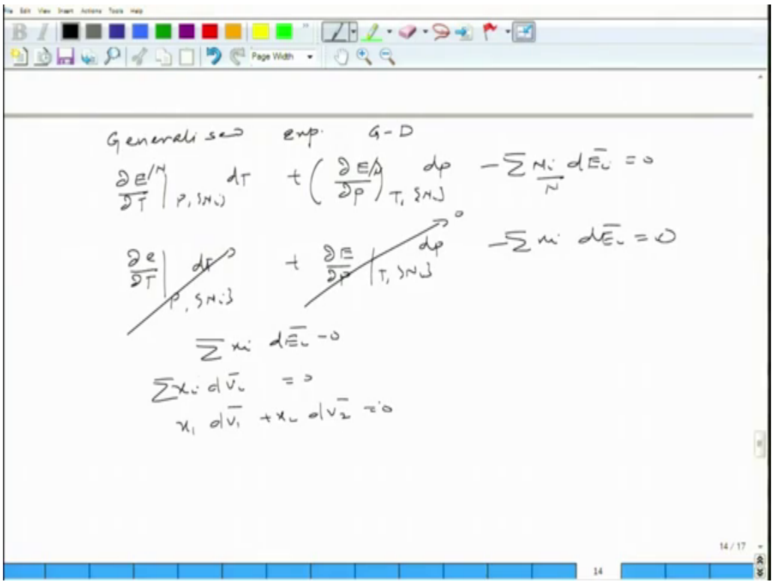

Now, what I am going to do is, basically make use of Gibbs Duhem expression. Remember the generalized expert Gibbs Duhem expression, generalized expression for Gibbs Duhem relation. So, for E any extensive property we know that del E by del T. Remember that we have done this exercise earlier and this was nothing, but Gibbs Duhem relation ok. We can divide by N total number of moles and keep. So, if you divide by N we will get something like this A by N ok.

So, we can write this as also as del E by del T d T plus del E by del P T P constant ok, minus summation x i d E i for a constant temperature and pressure, this is going to be 0 , and what we get is the expression summation x i d. So, for the case of volume, this will be your x i d V i bar ok. For binary mixture this is going to be d 1 ok. Now if you take a derivative with respect to x 1 then you can show that this is nothing, but in general, actually I can write it, but let me just write it for volume.

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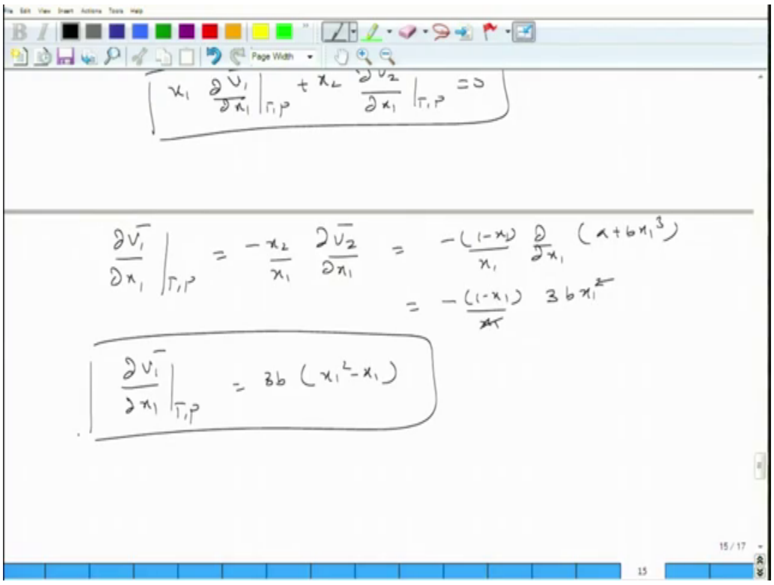

So, we have this general expression for the binary mixture, where we have connected this composition in its partial molar volume properties ok. So, we are going to make use of this expression. So, we can actually replace E by anything E by h u g and so forth. So, in this case, since our interest is volume we have replaced E by V. So, this is our expression. Now from here I can now start deriving this. So, this is; so let us say what is your d by d x 1 at T P ok. This is nothing, but if you look at the expression V 1 this one.

So, this is nothing, but minus x 2 by x 1 del V 2 by del x 1 ok. We know del x del V 2, del V 2 is a plus b x 1 cube. So, now, we can take the derivative, this is minus of this and this going to be b x 1 cube all right. I can rewrite this, take the differentiation here minus 1 minus x 1 x 1 and this is nothing, but 3 b x 1 square ok. So, x 1 get cancelled, and I have the expression. Now as 3 b x 1 square minus x 1 ok. So, this is the expression for this one ok.

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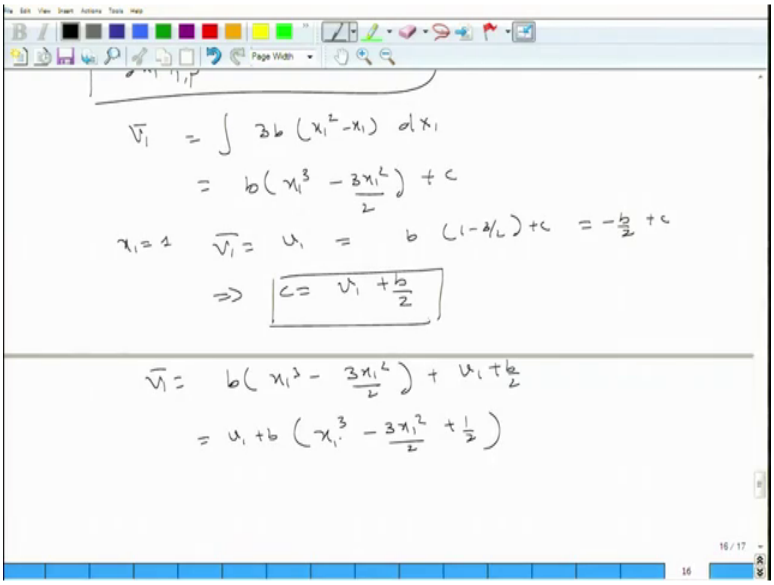

Now, I can integrate this ok, I can integrate this and I can get as 3 b x 1 square minus x 1 dx 1 and this is nothing, but b x 1 cube minus 3 x 1 square by 2 plus c some constant c ok. So, how do you obtain this constant of integration? We know that for x 1 equal to V 1 bar is going to be molar volume of component 1 ok. So, in that case if I plug in x 1 equal to 1 what you get? This is going to be b 1 minus 3 by 2 plus c , this is minus b by 2 plus c.

This essentially means c is nothing, but V 1 plus b by 2 ok, and remember that b, we have b is a part of the expression here. Once I have this constant c, I can get the expression of V 1 bar is b x 1 cube minus 3 x 1 square by 2 plus this value V 1 plus b by 2. I can rearrange and I can get this expression ok. So, this is x here ok.

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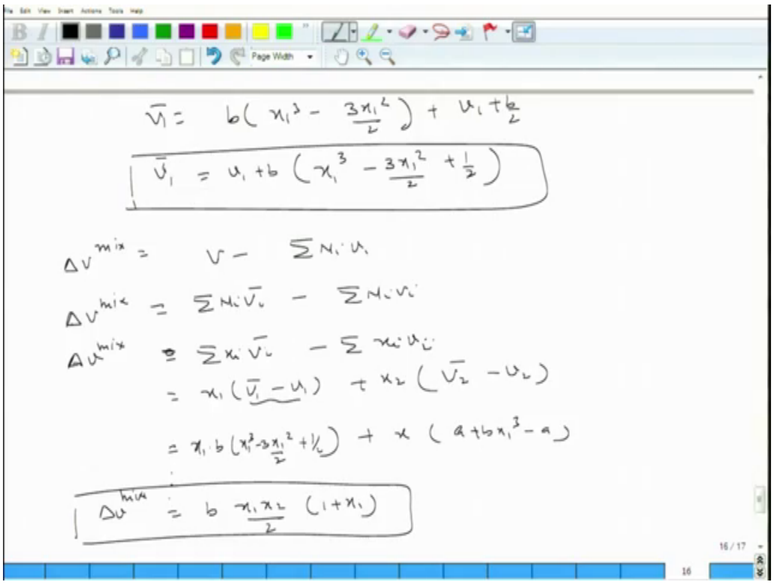

So, this is my partial molar volume expression. So, this is what we wanted to find right. The second part of the question was, to find out delta V mix and this is nothing, but V minus summation and i V i right. So, if I divide by right, if I divide by total moles I can get. So, first let me just write this V as simply N i V i bar which we know minus N i V i. Now what a, I am interested is, I am going, I am interested in dividing it by total ok, making this is a small mix, this is going to be x i V i bar and this is going to be x i V i ok.

Since this binary mixture I can get x 1 V 1 bar minus V 1 plus x 2 V 2 bar minus V 2. So, this I can rearrange, because this is only x 1. This would be x 1 V 1 plus x 2 V 2, this would be x i x 1 small V 1 plus x 2 small V 2 ok. Now this expression we have already V 1 minus this part is nothing, but b times this expression ok, and this term V 2 minus V 2 is nothing, but because we small v 2 is nothing, but a ok. So, this is nothing, but a plus b x 1 cube minus a and this is nothing, but x 1 times b x cube minus 3 x 1 square plus 2 plus half ok.

So, if you rearrange this expression. So, without going into details, you can obtain this as after a couple of steps as b times x 1 x 2 divided by 2 1 plus x 1 ok. So, this is how we have made use of, gives you expression in order to solve a simple problem, we obtained for a given partial molar volume for component 2, we have obtained that for component 1 as well as delta V mix, considering the constraints which ah, by which we can exploit these expressions and information ok. So, with this I will stop here. We will continue this exercise, but with the different examples particularly how to extract partial molar properties from experimental data ok.

So, see you next time.