Thermodynamics of Fluid Phase Equilibria
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Lecture – 24
Partial Molar Properties from experimental data

Welcome back. In this lecture we are going to discuss how to calculate partial molar properties from experimental data.

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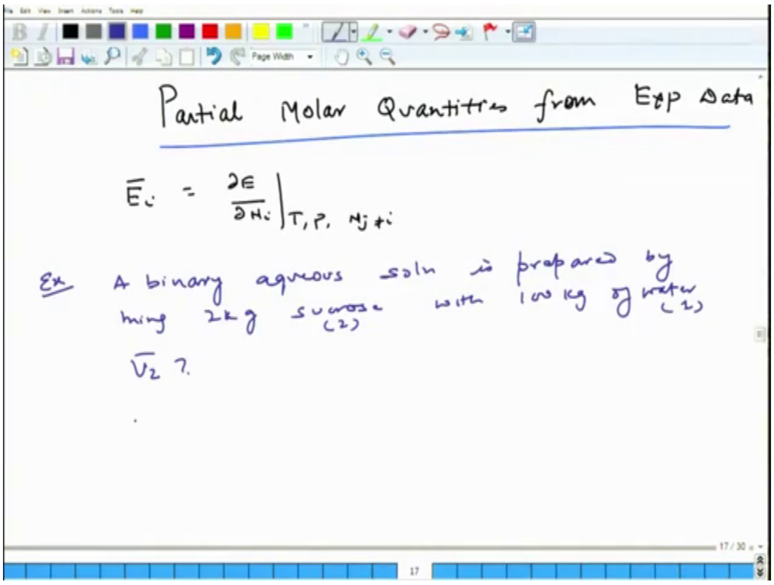

Partial Molar Quantities from Exp Data

$$\bar{E}_i = \frac{\partial E}{\partial N_i}\bigg|_{T,P,N_{j \neq i}}$$

Ex A binary aqueous soln is prepared by mixing 2 kg sucrose (2) with 100 kg of water (1)

$\bar{V}_2$?

So, let me first again start with the definition of partial molar quantities ok. So, this is the definition. Now, in case the data's are available particularly for E for a small change in E upon addition of N, small addition of N then of course, we can approximate it ok. We can represent this as simply delta E by del N i ok.

So, if the data available is straightforward particularly when we add small amount of component in a in a given mixture ok. So, let me just do one example and then we try to take a case where this partial molar quantities for complete composition we would like to value it. So, this is a case where we have a binary aqueous solution of water and a sucrose.

So, let us assume that you have want to prepare a binary eco solution by mixing 2 kgs of sucrose in 100 kg of water ok. So, 2 kg is relatively small compared to the amount of water present and you have been asked to find out the volumetric change or the partial molar volume of 2 ok; that means, what is 2 which in this case we are going to say one this is one component 1 and this is 2 ok.

So, what is partial molar volume of 2 sucrose in this condition. Let us, let me just write down some of the properties of sucrose and water. So, let us say that this solution mixture at 20 degree Celsius in 1 bar ok.

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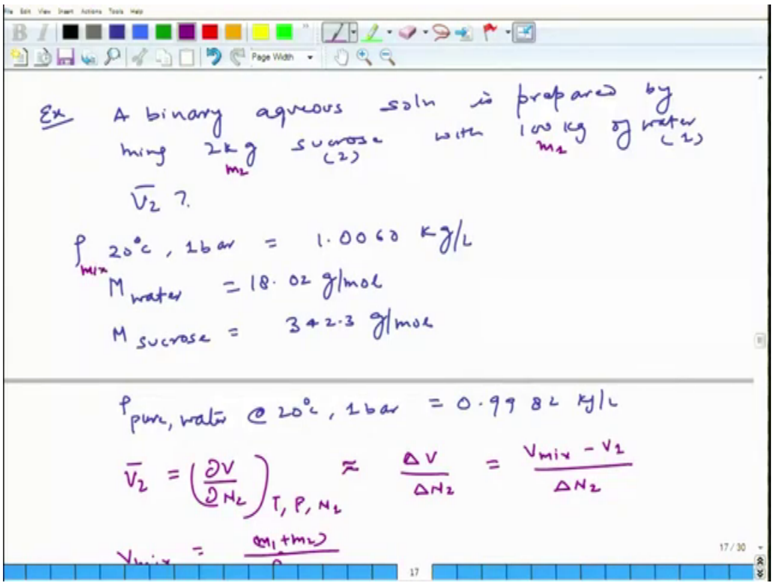

Ex A binary aqueous soln is prepared by mixing 2 kg (m_2) sucrose (2) with 100 kg (m_1) of water (1)

$\bar{V}_2$?

ρ_{mix} 20°c, 1 bar = 1.0060 kg/L

M_{water} = 18.02 g/mol

$M_{sucrose}$ = 342.3 g/mol

$\rho_{pure, water}$ @ 20°c, 1 bar = 0.9982 kg/L

$$\bar{V}_2 = \left(\frac{\partial V}{\partial N_2}\right)_{T, P, N_1} \approx \frac{\Delta V}{\Delta N_2} = \frac{V_{mix} - V_1}{\Delta N_2}$$

$$V_{mix} = \frac{(m_1 + m_2)}{\;}$$

So, the density at 20 degree Celsius in 1 bar is 1.0060 kg per liter ok. And the molecular weight for water is 18.02 gram per mole, molecular weight of sucrose is 342.3 gram per mole. So, these are the information given to us. In addition to this we have given that pure water at 20 degrees Celsius in 1 bar. So, this is the condition of the solution is 0.9982 kg per liter ok. So, how we are going to find out the partial molar volume of sucrose? That is a question.

Now, we do not have anything else. So, what we can see that the amount of sucrose we are adding to the solution is extremely small compared to the solution ok; that means, delta N 2 because one is water and 2 is sucrose is extremely small. So, in this condition if you look at again the definition of the partial molar volume this is del V by del N 2 at a constant temperature pressure and since it is a binary mixture at a constant N. So, the water is basically kept constant and we are changing N 2.

Now, considering very small amount of the change we can approximate this as the delta V by delta N 2 ok. Now, what is delta V here in this case? Is basically change in the volume of the mixture ok. So, upon addition of this small amount of sucrose. So, this is going to be V mixture minus the original or the volume contained by the water itself ok. So, V mix minus V 1 divided by delta N 2 or simply N 2 in this case the amount total I did.

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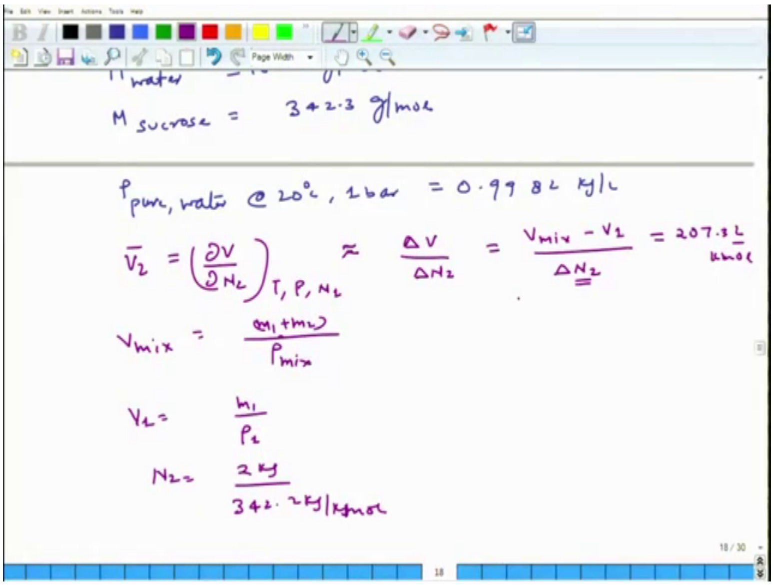

$M_{sucrose} = 342.3\ g/mol$

$\rho_{pure, water}$ @ 20°C, 1 bar $= 0.9982\ kg/L$

$$\bar{V}_2 = \left(\frac{\partial V}{\partial N_2}\right)_{T,P,N_1} \approx \frac{\Delta V}{\Delta N_2} = \frac{V_{mix} - V_1}{\underline{\underline{\Delta N_2}}} = 207.3\ \frac{L}{kmol}$$

$$V_{mix} = \frac{(m_1 + m_2)}{\rho_{mix}}$$

$$V_1 = \frac{m_1}{\rho_1}$$

$$N_2 = \frac{2\ kg}{342.2\ kg/kmol}$$

Now, what is V mix? So, V mix is a; how we are going to find out V mix; what is what are things which we are given to us? We have measured the density of the mixture and we are aware of the molecular weight of the components. So, we can make use of that. We know that volume is nothing, but mass divided by density ok. So, this is going to be m 1 plus m 2 divided by rho mix.

What about V 1? V 1 is rho 1 ok. So, m 1 is basically this mass is given here m 2 is this and rho mix is basically this is the system mix. So, and similarly we have been given m 1 and as well as basically the rho 1 of the water. So, considering this you can plug in here ok. Now, what you can do is you can you have to find out the number of moles of the second component. Now, some this is also easy for you because the number of moles what the mass is given to you 2 kg you can convert this based on the molecular weight.

Student: Yes.

You can convert these two into the number of moles which would be.

Student: (Refer Time: 07:02).

You know which will be 2 kg divided by 342.2 kg mole or kilo mole.

Student: Kg.

So because this is a gram per mole you can convert this to kg kilo mole and now, you can plug this information. If you plug in this information you get 207.3 liter per kilo mole. So, that is a value of one grid. Now, this is an approximation which you have made considering the fact that a very small amount of N 2 is added to the system; But what about if you are interested in getting the partial molar property for the complete composition?

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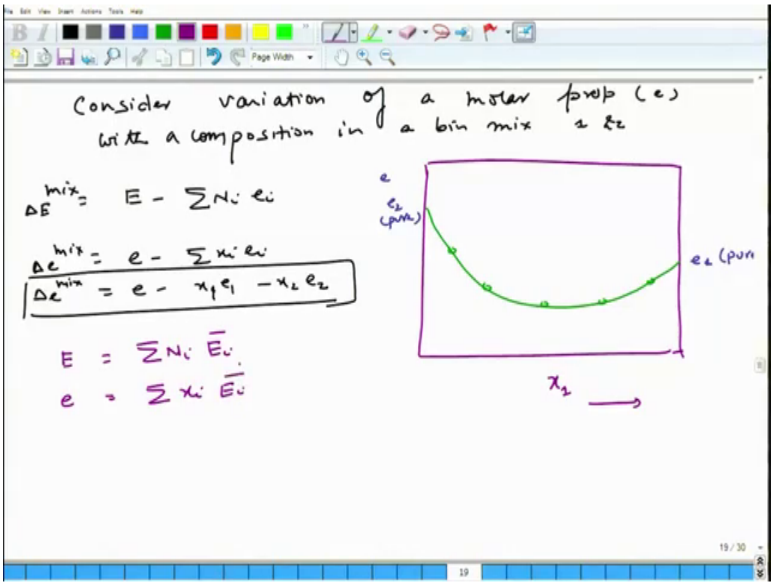

Consider variation of a molar prop (e) with a composition in a bin mix 1 & 2

$\Delta E^{mix} = E - \sum N_i e_i$

$\Delta e^{mix} = e - \sum x_i e_i$

$\boxed{\Delta e^{mix} = e - x_1 e_1 - x_2 e_2}$

$E = \sum N_i \bar{E}_i$

$e = \sum x_i \bar{E}_i$

So, let us now, take a take an example and analyze it. So, consider variation of a molar property with a composition in a binary mixture 1 and 2 ok.

Let us look at this property which let us say E. So, you have a property let us say molar property which is we are saying that say E ok, and you have some data let us say like this as a function of x 1 ok. And you can draw it, so let us assume that you have a, you have data which you have evaluated in the experiment and you can plot it against the composition ok. So, let us assume that this is the data which you have ok. Now, this data is you could draw this because you have data's along this curve ok.

So, this is nothing, but E ok. So, as of course obviously, you can see that when x 1 is one which means this is e 1 pure and the correspondingly this is e 2 pure now, but our interest is to find out the partial molar properties.

So, let me just start with the again the definition. So, the way we have written E mix is E minus summation N i e i that is y by definition which we have written E is a molar property of component i. We can divide this also by total number of moles and obtain something like in small E summation x i e i. So, in the case of the binary mixture this is x 1 e 1.

Student: Minus x 2.

Minus x 2 e 2. Now, so this is the definition by definition right ok. Now, I can also write E as summation N i E i like this and again I can write this E as if you divide by total number of moles this as x i E i.

Student: E i.

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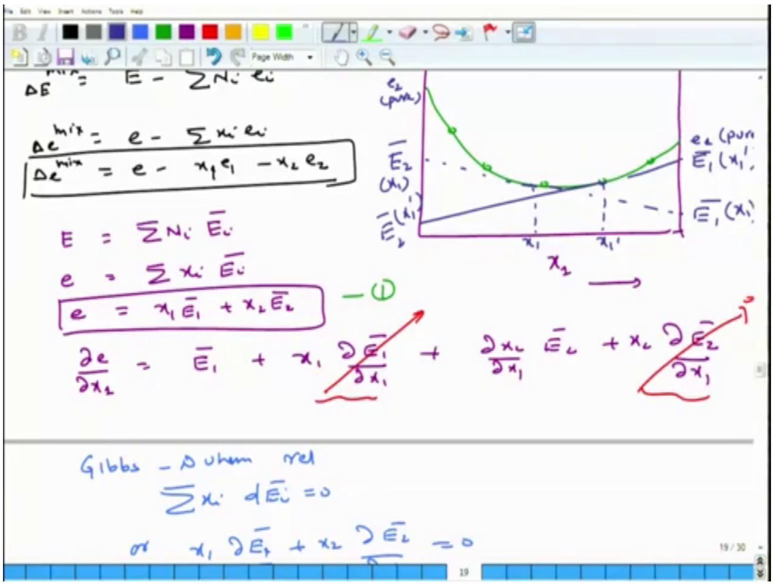

$$\Delta E^{mix} = E - \sum N_i e_i$$

$$\Delta e^{mix} = e - \sum x_i e_i$$

$$\boxed{\Delta e^{mix} = e - x_1 e_1 - x_2 e_2}$$

$$E = \sum N_i \bar{E}_i$$

$$e = \sum x_i \bar{E}_i$$

$$\boxed{e = x_1 \bar{E}_1 + x_2 \bar{E}_2} \quad — ①$$

$$\frac{\partial e}{\partial x_2} = \bar{E}_1 + x_1 \cancel{\frac{\partial \bar{E}_1}{\partial x_1}} + \frac{\partial x_2}{\partial x_1} \bar{E}_2 + x_2 \cancel{\frac{\partial \bar{E}_2}{\partial x_1}}$$

Gibbs - Duhem rel

$$\sum x_i \, d\bar{E}_i = 0$$

$$\text{or} \quad x_1 \partial \bar{E}_1 + x_2 \partial \bar{E}_2 = 0$$

So, we have now, this expression for binary mixture I can connect this as x 1 e 1 bar plus x 2 V 2 bar ok. So, this is for binary mixture right I can. Now, take a partial derivative of E with respect to x 1 let me try to do that E versus.

Student: E verse.

X 1. So, I got an expression of e 1 bar.

Student: (Refer Time: 11:06).

Plus x 1 this plus del x 2 by del x 1 plus x 2 ok. So, we have this expression. Now, what I am going to do is to simplify this. In order to simplify this when you look at this expression the automatic intuition you should take is make use of Gibbs-Duhem relations in order to simplify this expression.

So, what is it gives Duhem relation? Again we go back to the case Duhem relation we know that x i E i equal to 0 or for the binary mixture I can write this as when I take a differentiation with respect to x 1. When you look at this expression which is Duhem; that means, this add this together.

Student: Will be 0.

Will be 0 ok. So, I remove. So, what I have left with is del e by del x 1 is E 1 bar plus del x 2 by del x 1 E 2 bar ok. Now, this of course, is minus ok. So, I have this expression which I am going to again simply write it again just for the sake of cleanliness here.

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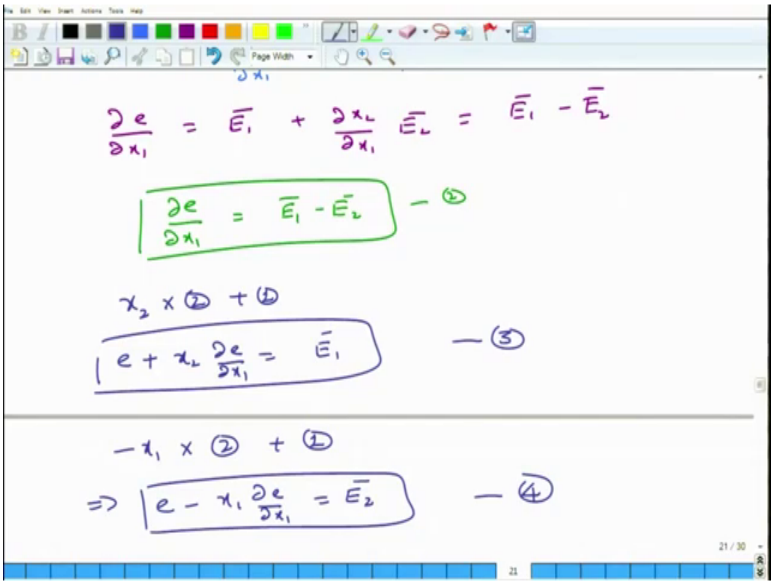

$$\frac{\partial e}{\partial x_1} = \bar{E}_1 + \frac{\partial x_2}{\partial x_1} \bar{E}_2 = \bar{E}_1 - \bar{E}_2$$

$$\boxed{\frac{\partial e}{\partial x_1} = \bar{E}_1 - \bar{E}_2} \quad - ②$$

$x_2 \times ② + ①$

$$\boxed{e + x_2 \frac{\partial e}{\partial x_1} = \bar{E}_1} \quad - ③$$

$-x_1 \times ② + ①$

$$\Rightarrow \boxed{e - x_1 \frac{\partial e}{\partial x_1} = \bar{E}_2} \quad - ④$$

So, this is going to be del e del x 1 is E 2 E 1 bar minus E 2. So, this is one expression I am interested in. Then I have another expression this one. So, this is let say 1 and this is let us say 2 ok.

Now, I am going to play with this, because I can actually make use of the right hand side look at it I can cancel some terms and I have now, one relation which is based on molar property another based on the partial derivative of the molar property basically ok. And what we have? We have the data of E versus x which we have plotted as a curve and we can make use of its slopes slope is first derivative of E ok.

So, if I use this 1, if I multiply x 2 multiply 2 by x 2 and then add one the first one what I am going to get is e plus because I am going to multiply x 2 here this is going to be x 2 del e by del x 1. And the right hand side since I have multiplied 2 x 2; that means, this part will x 2 here this will get cancelled out. So, what remains is basically nothing, but.

Student: e 1.

e 1. So, this is one expression we got ok. Now, there is another expression we can get by multiplying instead of x 2 if I multiply minus x 1 with two plus the first equation and what I get here is e minus x 1 del e by del x 1.

Student: Is equal to E 2.

Is equal to E 2. So, this is my second equation ok. Now, look at this second equation or the fourth equation rather. So, look at the first equation what you have E is nothing, but the value y minus mx is equal to c that is what this is the equation of line is not it. And what is the slope here? The slope is of course, the first derivative e.

So, if we compare with a typical equation of line then e 2 which is a partial molar property is nothing, but the intercept of this which essentially means if I have the value e and if I have the value of the slope at x 1 if then if I know of course, x 1 I can just take the you know subtract this two term and obtain my partial molar property, similarly, I can get it also for E 1.

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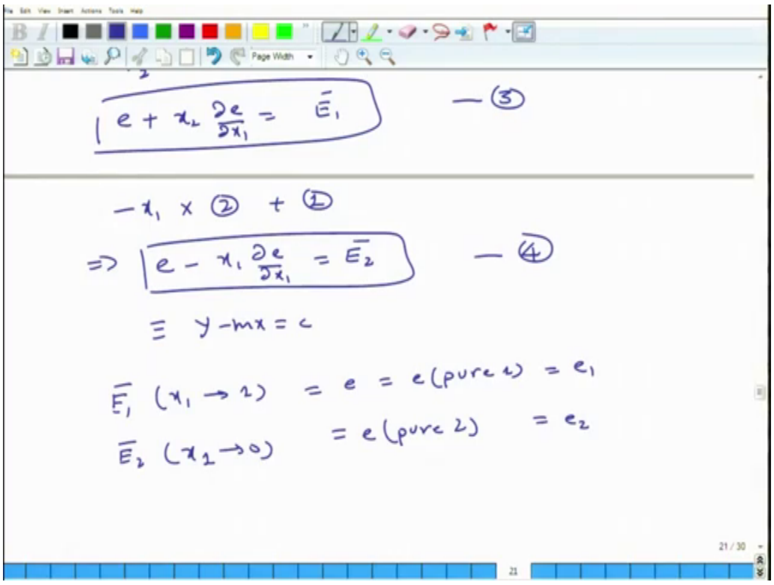

$$\boxed{e + x_2 \frac{\partial e}{\partial x_1} = \bar{E}_1} \quad — ③$$

$$-x_1 \times ② + ①$$

$$\Rightarrow \boxed{e - x_1 \frac{\partial e}{\partial x_1} = \bar{E}_2} \quad — ④$$

$$\equiv y - mx = c$$

$$\bar{E}_1 (x_1 \to 1) = e = e(\text{pure } 1) = e_1$$

$$\bar{E}_2 (x_1 \to 0) = e(\text{pure } 2) = e_2$$

Graphically it is much easier because it says that well E 2 is nothing, but a slope for equation which would be straightforward I mean based on the relation which we have developed here. So, if I this is the x 1 let us say assume which you are interested in I take a slope ok.

So, the left hand side the one which basically is the intercept would be E 2 bar similarly you can show that this is nothing, but E 1 bar. So, the graphically it is it is easy to evaluate if you have the data, but remember this E 1 is at x 1 and this E 2 is also at x 1 this is a track. So, so you keep changing the x 1 ok. So, for example, you interested in here so; that means, you can draw it tangent to that particular point. So, this will be your.

Student: (Refer Time: 16:48).

Yeah E 2 bar at x 1 dash this is E 1 bar at x 1 dash ok. So, the graphically you can evaluate like this now. So, let me just try to show this you know we will try to do some examples later ok, but let me just continue further from this and make some comments here. So, if I look at this equation and based on our analysis E 1 bar is nothing, but when you put x 1. So, if you take x 1 to 1 it means a pure 1. So, E 1 by in that case would be nothing, but e and this is nothing, but e because of course, this is also true from equation 3 and this is e would be your e of pure 1 similarly.

Student: (Refer Time: 17:48).

E for pure 2 ok. Now, now many times data may not be available or of exactly absolute molar property a many times it will be available as the delta a mix the change in the molar property of the mixture ok.

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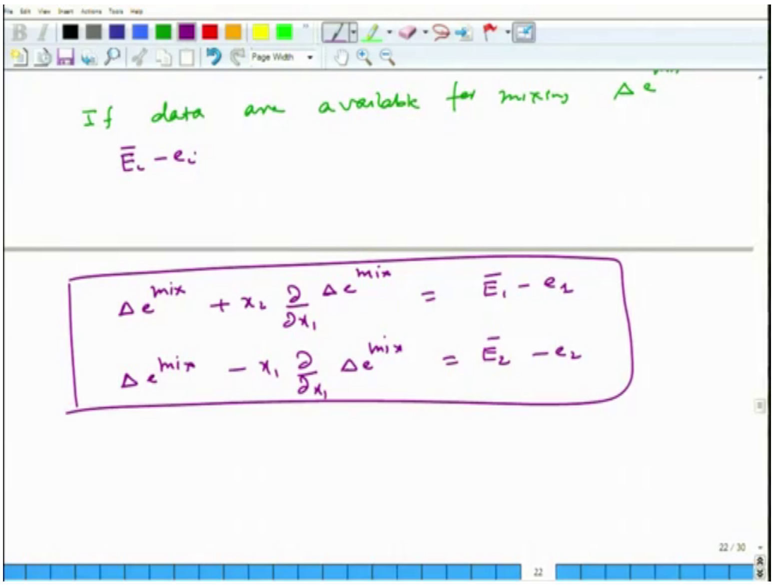
If data are available for mixing Δe

$\bar{E}_i - e_i$

$$\Delta e^{mix} + x_2 \frac{\partial}{\partial x_1} \Delta e^{mix} = \bar{E}_1 - e_1$$

$$\Delta e^{mix} - x_1 \frac{\partial}{\partial x_1} \Delta e^{mix} = \bar{E}_2 - e_2$$

So, if that is the case if data are available for mixing ; that means, this is available delta e mix is available then in that case what we are able to value it is E i minus e i we should be able to evaluate or get it from the experimental data ok.

So, you can use this you can use this expression what we have developed here and using this expression we can extend this for delta e mix. So, delta e mix by definition you know that we have to add if you subtract e here add minus summation and i, e i then this will become e mix on the left hand side plus x 2 d by dx 1. So, what I am doing is replacing basically a by e mix on the left hand side and instead of right hand side just E 1 bar it will become E 1 bar minus E 1 you can prove, that it is not difficult ok.

So, similarly here, so that is what I said when you have the data available for delta E mix then you should be able to calculate the difference between the partial molar property and pure molar property for components i basically ok. So, this is not the two relations we can get it if the data is delta m x ok.

Now, in order to appreciate this let us do an example. So, let me just write down the expression this is the case where you have a binary mixture, binary mixture of benzene which is of course, component which is component 1 with cyclo hexane which is component 2 ok.

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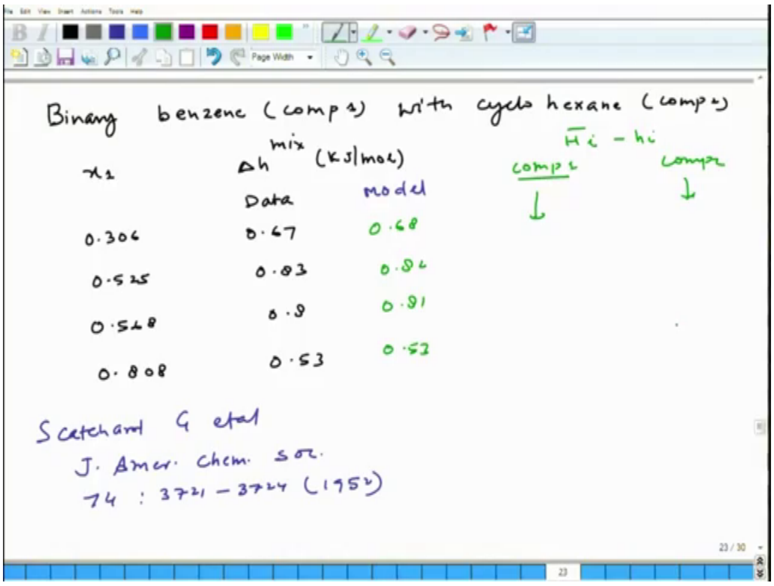

Binary benzene (comp 1) with cyclo hexane (comp 2)

x_1	Δh^{mix} (KJ/mol) Data	model
0.306	0.67	0.68
0.525	0.83	0.84
0.568	0.8	0.81
0.808	0.53	0.53

$\bar{H}_i - h_i$

comp 1 $\downarrow$

comp 2 $\downarrow$

Scatchard G et al

J. Amer. Chem. Soc.

74 : 3721 – 3724 (1952)

Now, we have been given data such as x 1 and the value which is given is delta h mix which is in kilo joules per mole ok. So, let me just write down first the data which is available. So, this is 0.306, 0.67, 0.525, 0.83, 0.568, 0.8 0.808 0.53 ok. So, this is the information available to us.

Now, the question is how do we get the partial property partial molar properties. Now, in this case since this is delta h what we are going to extract is basically h 1 bar minus h I, H i bar minus h i ok. Now, the data is in the discrete form. We need to actually smoothen this out by considering analytical form of the data in order to have an expression, so that we can draw it and get a the first derivative of this data that is most important. So, having analytical form is important.

Now, this particular example is taken from paper. So, how do we do that? Now, this is a trickier part like they were given this how to do that because you have only four points and if you know if you have done this first derivative you know that there is a issue with doing that.

So, now, but the way we should think about is what is the expression because which can fit very well ok. So, in order to apply we will be considering. So, in order to apply or make use of this data will be considering an analytical expression. So, let us first understand, the limiting condition of delta mix h mix.

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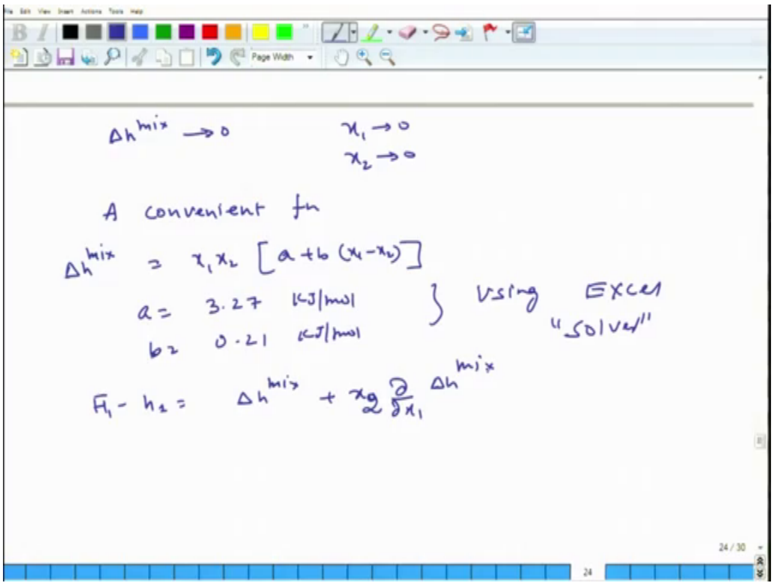

$\Delta h^{mix} \rightarrow 0 \qquad x_1 \rightarrow 0$

$\qquad\qquad\qquad\quad x_2 \rightarrow 0$

A convenient fn

$\Delta h^{mix} = x_1 x_2 \left[a + b(x_1 - x_2)\right]$

$a = 3.27$ kJ/mol

$b = 0.21$ kJ/mol

} Using Excel "Solver"

$\bar{h}_1 - h_2 = \Delta h^{mix} + x_2 \frac{\partial}{\partial x_1} \Delta h^{mix}$

In order to get an analytical solution you need to find as a expression which also satisfies the limiting conditions. So, what is the limiting condition? So, when x 1 goes to 0 what happens to delta h mix?

Student: It would be h 2 (Refer Time: 22:43).

Mix delta h mix 0. So, delta h mix also would tend to 0, when x 2 tends to 0 what would be the.

Student: h

Value of delta h mix.

Student: It is 0.

It is a 0. So, basically limiting condition is any of this composition if it goes to 0 it means that all composition is pure ok. So, now, we can come up with an expression considering this a convenient function is basically sum x 1, x 2 multiplication and sum term ok. So, x 1, x 2 has to be there because it has to be 0 if you put a live them, but then considering that this is the not a linear function. So, it will be a quadratic in nature in some form a polynomial function.

So, we will be adding a plus b difference of x 1 minus x 2, ok. So, this is just a convenient form which we are writing it there is a little bit of a experience goes into that in coming of this expression, but having this expression. Now, this constants are a and b have to be evaluated ok.

So, how do you find out this, constants? You can plug this equation and the data in some software for example, excel solver can solve a and b it can iterate such that or refine the values in a and such that this the data is fits very well ok. So, it turns out this expression actually fits very well the data with a is 3.27 kilo joules per mole b is 0.21 kilojoules per mole ok. So, this is using excel solver ok.

So, if you haven't done that you should try to make use of it you can just plug in this value all right this 8 this becomes your x and this becomes your y ok, and basically plug in this expression try to fit it put a and b as a variable which you would like to vary in solver and let the saw excel does its job we should get this expression.

Now, this since this model fits well. Now, I have this a discrete data in a continuous expression now, which is basically your analytical expression. Now, I can find out H 1 bar minus h 1 which is nothing, but delta h mix plus x 2 del i x 1. So, this is x 2 del by del x 1 delta h mix ok. So, this comes directly from our expressions which we have written here ok. So, here instead of e I am just putting h here and similarly I can write it for h 2 also.

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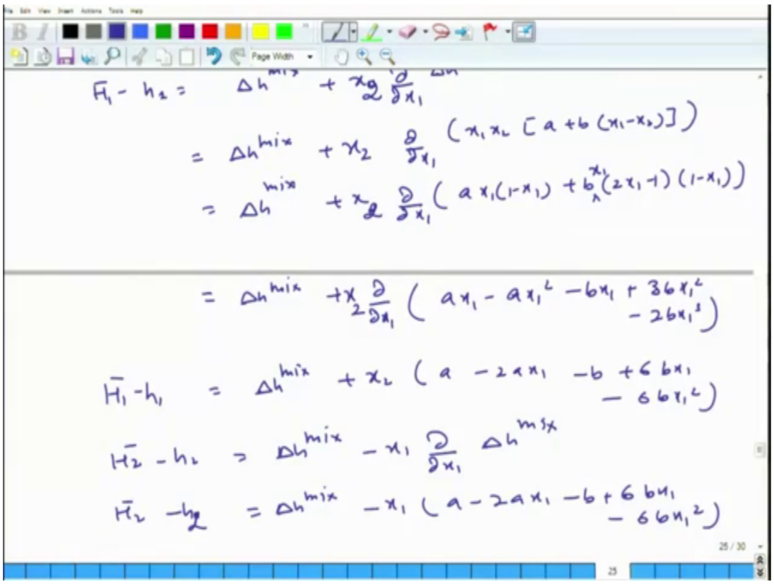

$$\bar{H}_1 - h_2 = \Delta h^{mix} + x_2 \frac{\partial}{\partial x_1} \Delta h^{mix}$$

$$= \Delta h^{mix} + x_2 \frac{\partial}{\partial x_1} \left(x_1 x_2 [a + b(x_1 - x_2)] \right)$$

$$= \Delta h^{mix} + x_2 \frac{\partial}{\partial x_1} \left(a x_1 (1 - x_1) + b \overset{x_1}{\wedge} (2x_1 - 1)(1 - x_1) \right)$$

$$= \Delta h^{mix} + x_2 \frac{\partial}{\partial x_1} \left(a x_1 - a x_1^2 - b x_1 + 3b x_1^2 - 2b x_1^3 \right)$$

$$\bar{H}_1 - h_1 = \Delta h^{mix} + x_2 \left(a - 2a x_1 - b + 6b x_1 - 6b x_1^2 \right)$$

$$\bar{H}_2 - h_2 = \Delta h^{mix} - x_1 \frac{\partial}{\partial x_1} \Delta h^{mix}$$

$$\bar{H}_2 - h_2 = \Delta h^{mix} - x_1 \left(a - 2a x_1 - b + 6b x_1 - 6b x_1^2 \right)$$

So, now, delta h mix is known I can take the partial derivative of x 1 with respect to a partial derivative of this expression delta h means with respect to x 1.

What I get? x 1 x 2 a plus b x 1 minus x 2 and this further can be simplified all right. So, now, further if I simplify this becomes a ax 1 minus ax 1 square minus bx 1 plus 3 b, 2bx 1 cube ok. I can take the derivatives.

Student: (Refer Time: 27:20).

X 1 is.

Student: (Refer Time: 27:24) b x 1 2 x 1 minus

B x.

Student: Second one.

This one b.

Student: (Refer Time: 27:34)

So, here what you saying x 1 is missing.

Student: Yes, sir we have x 1, x 2 (Refer Time: 27:47).

Right, this is one b x 1 minus x 2 which is 2 x 1 oh all right ok; yes indeed the x 1 is missing here all right. So, now, this expression if you take the derivative it yields are the following delta h mix plus x 2 a minus 2 ax 1 minus b plus 6 bx 1 minus 6 bx 1 square, ok.

Now, similarly you can also get the expression for delta h mix which will be like h x 1 a minus 2 a x 1 minus b plus 6 bx 1 minus 6 bx 1 square because this is same as this ok. So, you got basically the expression for H 1 bar minus h 1, H 2 bar minus a this one.

So now, you have an expression you know the values of x 1 you know exactly delta h mix ok. So, I can actually fill this the model which we have developed is basically an analytical model right. So, just to give you idea what was the fit after using the excel sheet I can actually plug in the values of the model for a given values here it was 0.68, 0.82, 0.81, 0.53 pretty good right.

Now, here I can using this model and these values using these values and this specific you could directly use this model try to use the data for delta h mix and you can plug in the a and b and x corresponding in order to get for come in order to get this difference for component 1 ok, you plug in here and for component 2 for a using this expression.

So, this is how we can solve the problem based on simple experimental data available for the partial molar properties if the molar properties information as a function of the compositions are given ok. So, now, what I am going to do is quickly make two points ok, before we end I would like to make another important point, is that most often we just do not use only the delta h mix or e mix or so forth, sometimes we also use excess information ok.

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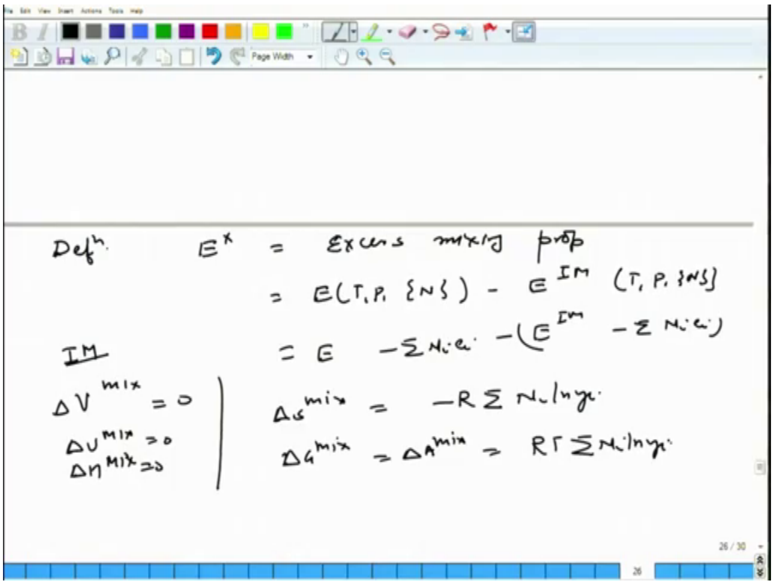

Defn. E^x = Excess mixing prop

$= E(T, P, \{N\}) - E^{IM}(T, P, \{N\})$

$= E - \sum N_i e_i - (E^{IM} - \sum N_i e_i)$

IM

$\Delta V^{mix} = 0$

$\Delta U^{mix} = 0$

$\Delta H^{mix} = 0$

$\Delta S^{mix} = -R \sum N_i \ln y_i$

$\Delta G^{mix} = \Delta A^{mix} = RT \sum N_i \ln y_i$

So, let me just define this excess mixing property which is basically excess mixing property ok. This is E T P minus E IM, IM is basically idle mixture ok, for the same ok.

So, in other word V Ex is all right. So, V Ex would be your. Now, what we can do is we can also also consider this as a delta of delta E. For example, let us say if I add this as E minus summation N i e i minus E IM summation N i e i then this would be corresponding to your delta V of idle mixture and this will be your corresponding to delta V mix ok. So, what is the delta V mix for idle mixture? Delta V makes is basically nothing, but 0.

Student: Ok.

Delta you mix 0 delta h mix is also 0 and we have also calculated earlier delta S mix is minus R summation N i, n y i. Delta G mix or delta A mix is RT summation N i, n and yi. So, this is something which we have calculated earlier.

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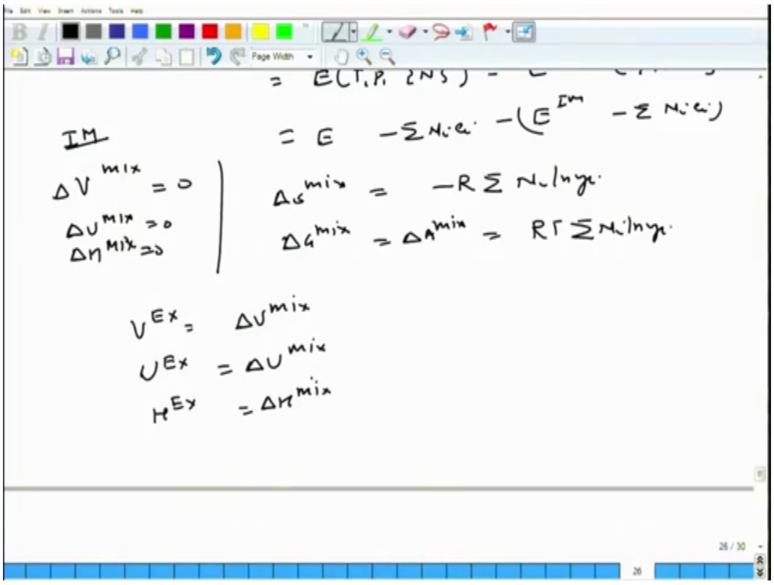

$= E(T,P,\{N\}) - \ldots$

IM

$= E - \sum N_i e_i - (E^{IM} - \sum N_i e_i)$

$\Delta V^{mix} = 0$

$\Delta U^{mix} = 0$

$\Delta H^{mix} = 0$

$\Delta S^{mix} = -R \sum N_i \ln y_i$

$\Delta G^{mix} = \Delta A^{mix} = RT \sum N_i \ln y_i$

$V^{Ex} = \Delta V^{mix}$

$U^{Ex} = \Delta U^{mix}$

$H^{Ex} = \Delta H^{mix}$

So, based on this information we actually can write V x is nothing, but delta V mix because the other part is going to be 0, U x is delta U mix and H Ex is delta H mix ok, all right.

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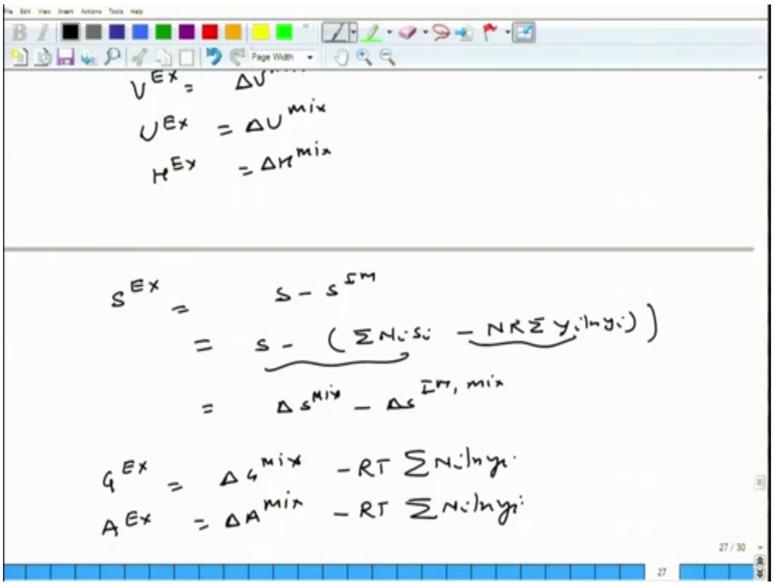

$V^{Ex} = \Delta V^{mix}$

$U^{Ex} = \Delta U^{mix}$

$H^{Ex} = \Delta H^{mix}$

$$S^{Ex} = S - S^{IM}$$

$$= \underbrace{S - (\sum N_i s_i} - \underbrace{NR \sum y_i} \ln y_i))$$

$$= \Delta S^{mix} - \Delta S^{IM,\,mix}$$

$G^{Ex} = \Delta G^{mix} - RT \sum N_i \ln y_i$

$A^{Ex} = \Delta A^{mix} - RT \sum N_i \ln y_i$

Now, we can also talk about S Ex ok. Now, this is nothing, but S minus S IM which I can write S as a or S IM I can write as nothing, but summation N i small si minus nr summation y i, n y i. So, I am just writing out the entropy of the ideal mixture ok and this is nothing, but your delta.

Student: S mix.

S mix ok, and this is nothing, but your minus of delta.

Student: Idle mixture.

Idle mixture mix something. So, we can we can write this kind of expression. Similarly I can write G Ex is basically delta G mix minus RT summation N i and then y i. A x as RT summation and I ok. So, this is something which I want to talk about as far as the excess property is concerned. So, last leg of today's lecture is to make a note of that the expression which we are writing for chemical potential do not hold particularly when we talk about idle gas mixtures it does not hold for the real systems ok.

So, I am just going to continue this and just talk about idle mixture that.

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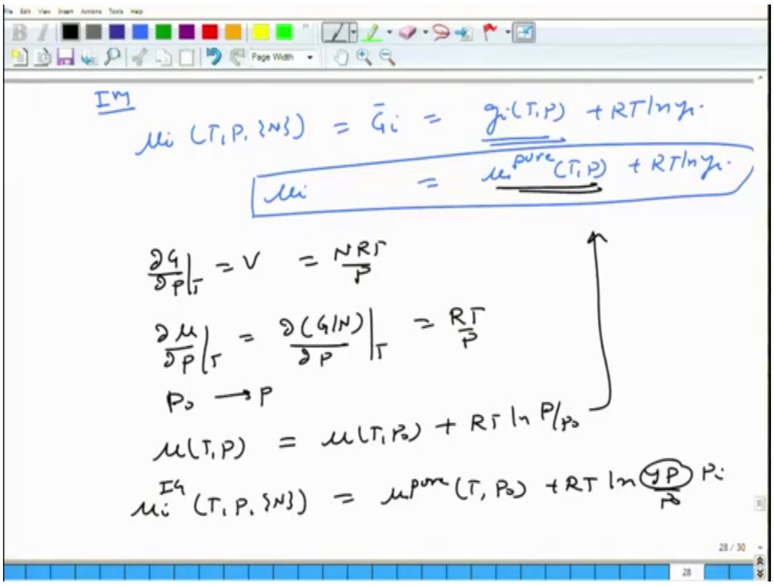

IM

$$\mu_i(T,P,\{N\}) = \bar{G}_i = \underline{g_i(T,P)} + RT\ln y_i$$

$$\boxed{\mu_i = \mu_i^{pure}(T,P) + RT\ln y_i}$$

$$\left.\frac{\partial G}{\partial P}\right|_T = V = \frac{NRT}{P}$$

$$\left.\frac{\partial \mu}{\partial P}\right|_T = \left.\frac{\partial (G/N)}{\partial P}\right|_T = \frac{RT}{P}$$

$$P_0 \longrightarrow P$$

$$\mu(T,P) = \mu(T,P_0) + RT\ln P/P_0$$

$$\mu_i^{IG}(T,P,\{N\}) = \mu^{pure}(T,P_0) + RT\ln \frac{\boxed{yP}}{P_0}\ P_i$$

If you recall we have written mu I which is T P and is nothing, but partial derivative of G and this is nothing, but small gi T P plus RT and then V I this is for idle mixture ok. And this is nothing, but mu I for pure T P plus RT and then y i and this is nothing, but mu i ok.

So, this we know this is what we have given are they talked about it. Now, we can try to get this expression with respect to some reference pressure ok. So, I can make use of del G by del P at T which is nothing, but by definition V for an ideal gas this is N RT by P.

So, on similarly I can also write del mu by del P T and this I can write G by N P by T and this is nothing, but RT by P.

If I integrate this expression P 0 to P, I get mu T P as mu T P 0 plus RT ln P by P 0 ok. So, we can and this is for a component let us a pure component we can plug in here what we get we get mu i for ideal gas mixture T P and is equal to mu i pure T P 0 plus RT ln y P by P 0 which is nothing, but partial pressure P i. So, this is the expression we got typically ok.

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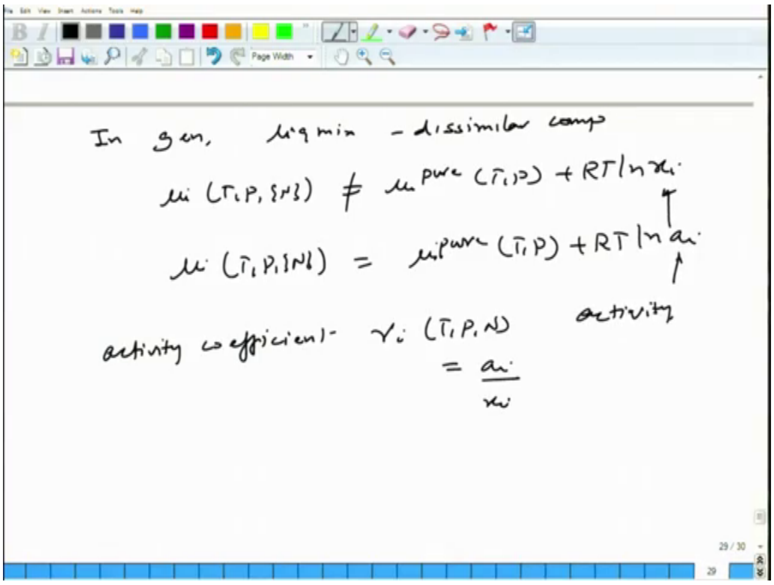

In gen, liq mix - dissimilar comp

$$\mu_i(T, P, \{N\}) \neq \mu_i^{pure}(T, P) + RT \ln x_i$$

$$\mu_i(T, P, \{N\}) = \mu_i^{pure}(T, P) + RT \ln a_i$$

activity

activity coefficient $\gamma_i(T, P, N) = \frac{a_i}{x_i}$

Now, in general this chemical potential with the way we have written that mu I is equal to mu I pure plus RT ln y this do not hold for liquids ok. So, for liquid ok, so in general, in general especially for liquid mixture having a dissimilar component mu i T P and is not equal to mu i pure T P plus RT ln.

Well instead of y i, since i is to be talking about liquid.

Student: (Refer Time: 37:20).

We can say plus ax i ok. Now, this leads to the definition of activity this leads to the definition of activity. So, the way we defined activity says that mu i T P N, is equal to mu i pure T P plus RT ln ai and that is what we defined this is an activity and of course, for an idle condition idle mixture ai is nothing, but x i.

Student: Sigma x i.

In this case of course, we are talking about x i because the liquid. So, yeah, if it is same it means basically an ideal solution ok. So, remember is x and y is our nomenclature it just means composition.

Student: (Refer Time: 38:02).

So, we defined activity coefficient to make these differences clear T P and which is nothing, but ai divided by x i. So, for an idle mixture gamma i is basically nothing, but 1 ok.

So, I think I will stop here because this is the moment we will take I mean we will take this concept further in our analysis of solutions and, but this is just to introduce that what we have done till a couple of lectures was all about ideal gas mixtures, idle solution mixtures. And here of course, there is a lot of assumptions ok. For ideal for real conditions we have a deviation from the ideal conditions and that is why we have introduced this kind of nomenclature.

So, in the next lecture we will start up the volumetric property on and this part of as phase the activity is concerned we will take up in a later part of the course ok. So, I will see you next lecture then.