Chemical Engineering Thermodynamics
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Lecture: 35
Partial molar properties and examples

Welcome back. We have been discussing about partial molar properties and so I will just do a quick recap of what we have learned in the last lecture.

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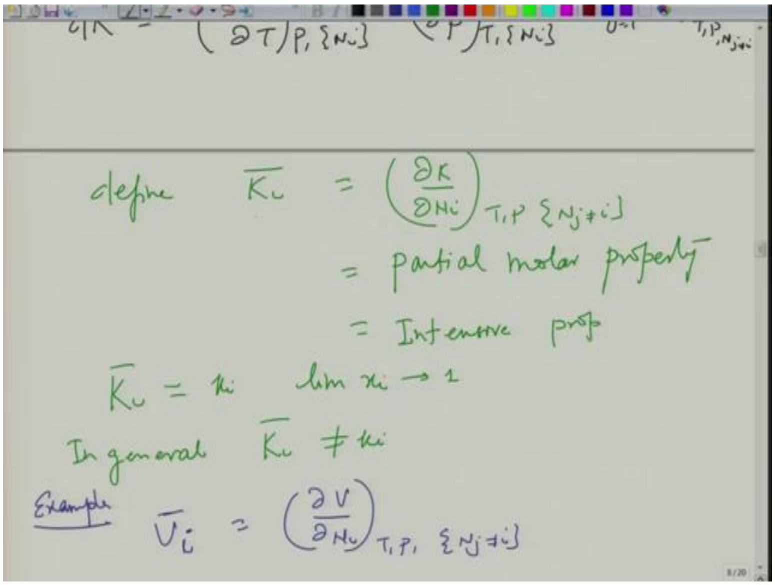

define $\overline{K_i} = \left(\frac{\partial K}{\partial N_i}\right)_{T,P\{N_{j\neq i}\}}$

= partial molar property

= Intensive prop

$\overline{K_i} = k_i$ lim $x_i \to 1$

In general $\overline{K_i} \neq k_i$

Example $\overline{V_i} = \left(\frac{\partial V}{\partial N_i}\right)_{T,P,\{N_{j\neq i}\}}$

We defined a term generic property partial molar property, which is a nothing but the partial derivative of K where K could be energy enthalpy, energy enthalpy another extensive property with respect to ni. Okay. So, this is nothing but a intensive property and we said well Ki bar is going to be Ki that is a molar property of a component i for the pure case when the Xi goes to 1.

$$We\ define,\ \ \overline{K_i} = \left(\frac{\partial K}{\partial N_i}\right)_{T,P,\{N_{j\neq i}\}} = partial\ molar\ property = Intensive\ property$$

$$\overline{K_i} = k_i \quad \lim x_i \to 1\ ; \quad In\ general, \qquad \overline{K_i} \neq k_i$$

$$Example\colon\ \overline{V_i} = \left(\frac{\partial V}{\partial N_i}\right)_{T,P,\{N_{j\neq i}\}}$$

$$\overline{H_i} = \left(\frac{\partial H}{\partial N_i}\right)_{T,P,\{N_{j\neq i}\}}$$

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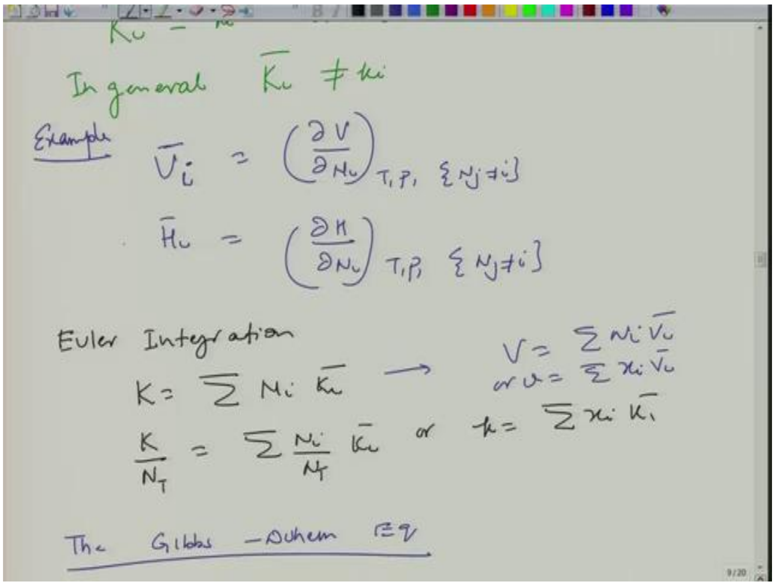

In general $\bar{K}_i \neq k_i$

Example

$$\bar{V}_i = \left(\frac{\partial V}{\partial N_i}\right)_{T,P,\{N_j \neq i\}}$$

$$\bar{H}_i = \left(\frac{\partial H}{\partial N_i}\right)_{T,P,\{N_j \neq i\}}$$

Euler Integration

$$K = \sum N_i \bar{K}_i \rightarrow \quad V = \sum N_i \bar{V}_i \quad \text{or } v = \sum x_i \bar{V}_i$$

$$\frac{K}{N_T} = \sum \frac{N_i}{N_T} \bar{K}_i \quad \text{or} \quad k = \sum x_i \bar{K}_i$$

The Gibbs-Duhem EQ

And the examples could be partial molar property for the volume case, partial molar enthalpy and so forth. Then we also talked about Euler integration that the K which we talked about in here is generic property. If you take a, if you use a similar approach as we have done in the past for the Gibbs free energy, we should be able to show that K is nothing but summation NiKi bar.

$$Euler\ Integration: \quad K = \sum N_i \overline{K_\iota} \rightarrow \quad V = \sum N_i \overline{V_\iota} \quad or, \qquad v = \sum x_i \overline{V_\iota}$$

$$\frac{K}{N_T} = \sum \left(\frac{N_i}{N_T} \overline{K_\iota}\right) \quad or, \qquad k = \sum x_i \overline{K_\iota}$$

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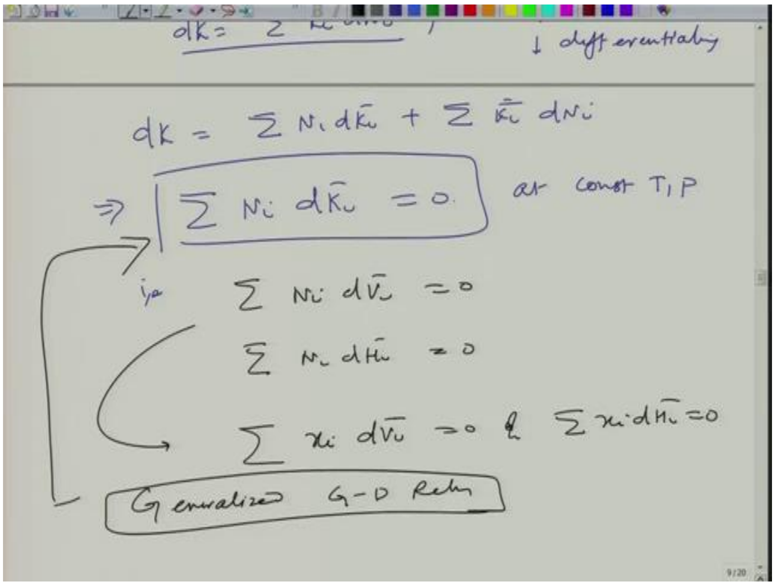


↓ differentiating

$$dK = \sum N_i d\bar{K}_i + \sum \bar{K}_i dN_i$$

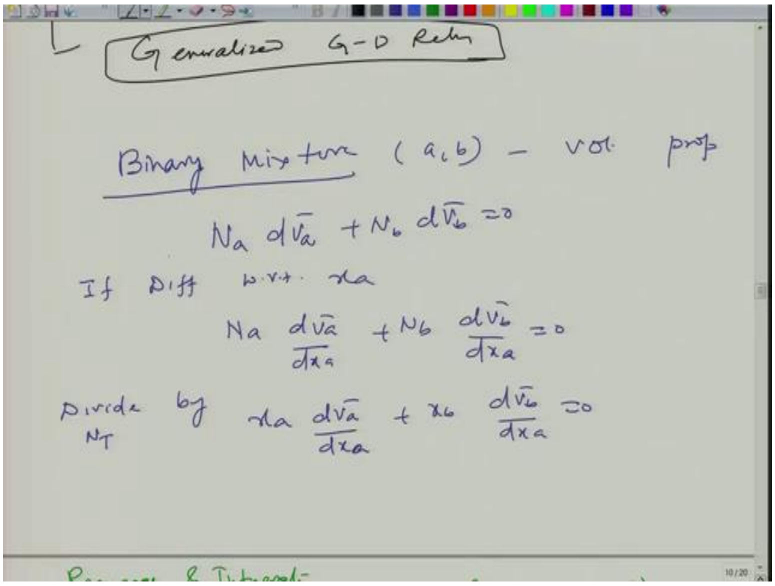
$$\Rightarrow \boxed{\sum N_i d\bar{K}_i = 0} \quad \text{at const } T, P$$

i.e. $\sum N_i d\bar{V}_i = 0$

$\sum N_i d\bar{H}_i = 0$

$\sum x_i d\bar{V}_i = 0$ & $\sum x_i d\bar{H}_i = 0$

Generalized G-D Reln



Generalized G-D Relns

Binary Mixture (a, b) – vol. prop

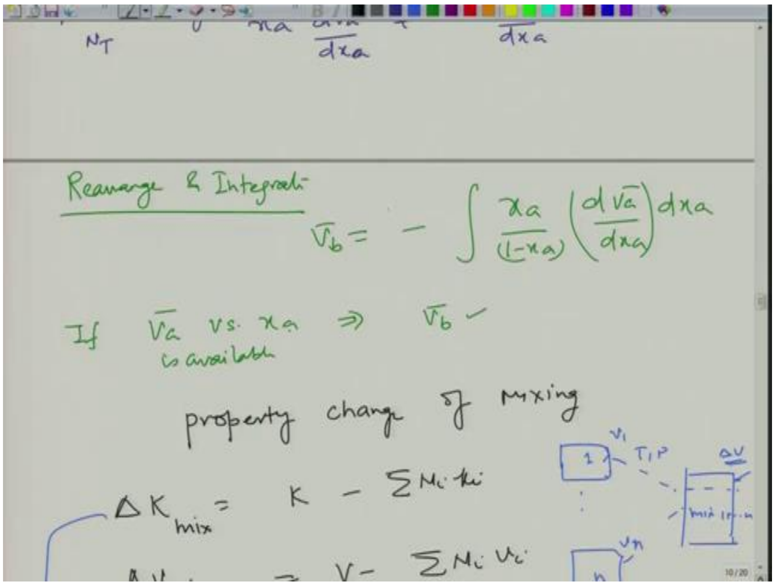
$$N_a\, d\bar{V}_a + N_b\, d\bar{V}_b = 0$$

If Diff w.r.t. x_a

$$N_a \frac{d\bar{V}_a}{dx_a} + N_b \frac{d\bar{V}_b}{dx_a} = 0$$

Divide by N_T

$$x_a \frac{d\bar{V}_a}{dx_a} + x_b \frac{d\bar{V}_b}{dx_a} = 0$$



Rearrange & Integrati

$$\bar{V}_b = -\int \frac{x_a}{(1-x_a)}\left(\frac{d\bar{V}_a}{dx_a}\right)dx_a$$

If $\bar{V}_a$ vs. x_a is available $\Rightarrow$ $\bar{V}_b$ ✓

property change of mixing

$$\Delta K_{mix} = K - \sum N_i k_i$$

$$= V - \sum N_i v_i$$

And using this, and using the concept of Euler integration one can show that Ni dKi is equal to 0 that is the Gibbs-Duhem relation at a constant temperature and pressure and this is something which we can use it, for example, for relating some variables as we have done that for binary mixtures to those which we know another word we can relate let us say the partial molar volume for component B to the derivative of the partial molar volume for component A as if an integral of that with respect to dx A, okay. If you have information of this then essentially you will be able to obtain Vb bar.

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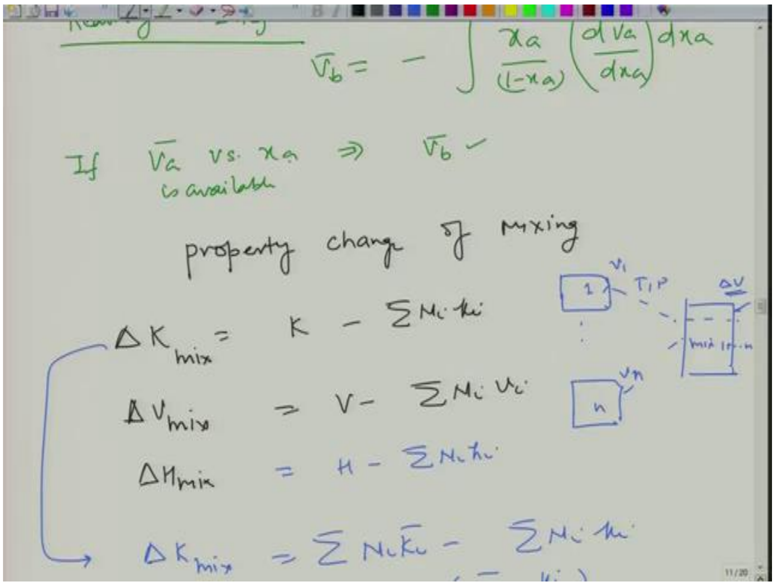


$$\bar{V}_b = -\int \frac{x_a}{(1-x_a)}\left(\frac{d\bar{V}_a}{dx_a}\right)dx_a$$

If $\bar{V}_a$ vs. x_a is available ⇒ $\bar{V}_b$ ✓

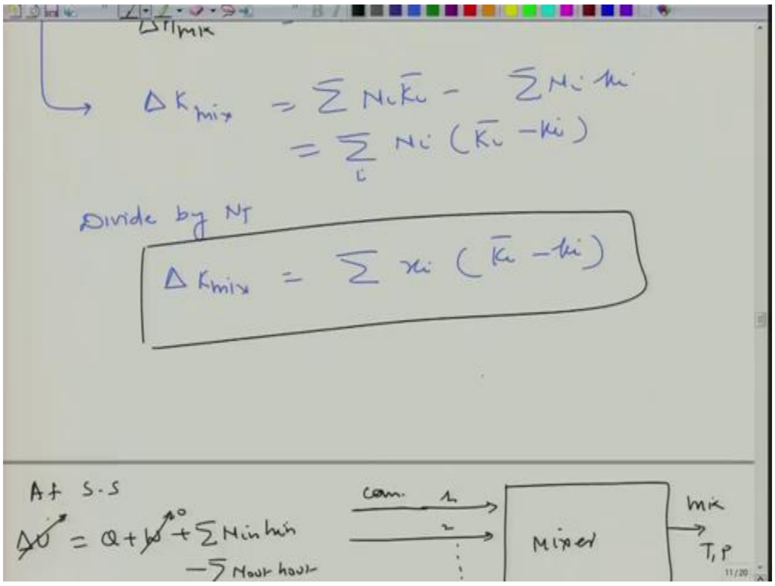
property change of mixing

$$\Delta K_{mix} = K - \sum N_i k_i$$

$$\Delta V_{mix} = V - \sum N_i v_i$$

$$\Delta H_{mix} = H - \sum N_i h_i$$

$$\Delta K_{mix} = \sum N_i \bar{K}_i - \sum N_i k_i$$



$$\Delta K_{mix} = \sum N_i \bar{K}_i - \sum N_i k_i$$
$$= \sum_i N_i (\bar{K}_i - k_i)$$

Divide by N_T

$$\boxed{\Delta K_{mix} = \sum x_i (\bar{K}_i - k_i)}$$

At S.S

$$\cancel{\Delta U} = Q + \cancel{W}^0 + \sum N_{in} h_{in} - \sum N_{out} h_{out}$$

Then we also talked about that property chain of mixing that means how much change in a given variable or accessible K. Okay when you mix few components and this is something which we can generalize this K minus summation of NiKi okay, and then these divided by N and we obtain that that delta K mix is nothing but summation Xi Ki bar small ki.

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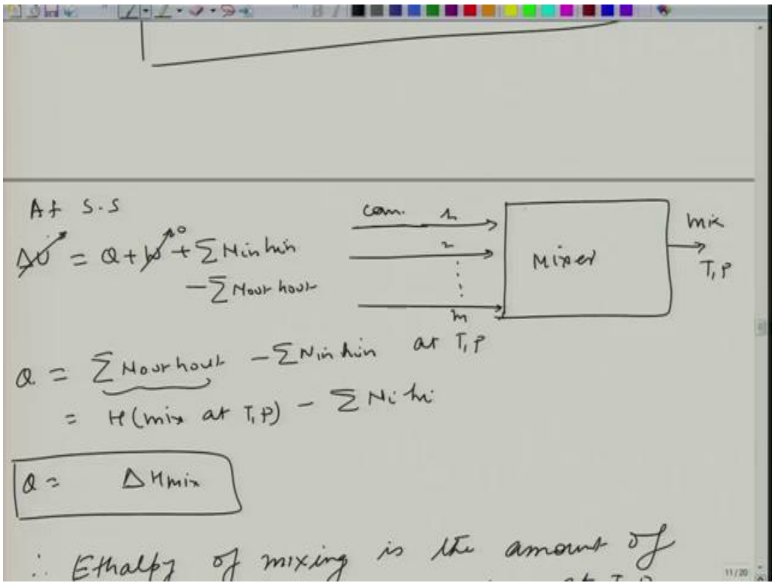


At S.S

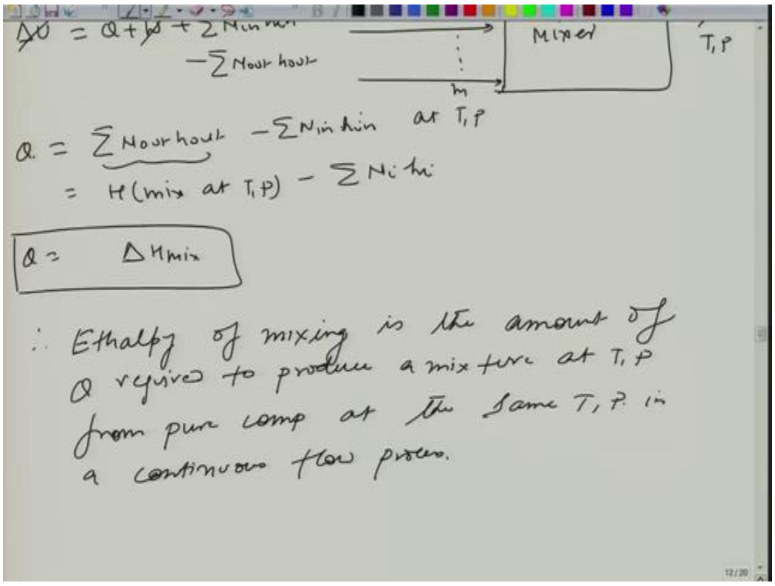
$$\cancel{\Delta U} = Q + \cancel{W}^{0} + \sum N_{in} h_{in} - \sum N_{out} h_{out}$$

$$Q = \underbrace{\sum N_{out} h_{out}} - \sum N_{in} h_{in} \quad \text{at } T, P$$

$$= H(\text{mix at } T, P) - \sum N_i h_i$$

$$\boxed{Q = \Delta H_{mix}}$$

∴ Ethalpy of mixing is the amount of



$$\cancel{\Delta U} = Q + \cancel{W} + \sum N_{in} h_{in}$$

$$- \sum N_{out} h_{out}$$

$$Q = \underbrace{\sum N_{out} h_{out}} - \sum N_{in} h_{in} \quad \text{at } T, P$$

$$= H(\text{mix at } T, P) - \sum N_i h_i$$

$$\boxed{Q = \Delta H_{mix}}$$

∴ Ethalpy of mixing is the amount of Q required to produce a mixture at T, P from pure comp at the same T, P in a continuous flow process.

Then we took a case of a mixture at a steady state where we said well, if you mix component 1 to m at a constant temperature and pressure, then the final mixture is at a temperature and pressure than delta h of this mixing is nothing but the Q here. So, enthalpy of mixing is the amount of Q required to produce a mixture temperature and pressure from pure component at the same temperature and pressure in a continuous flow process.

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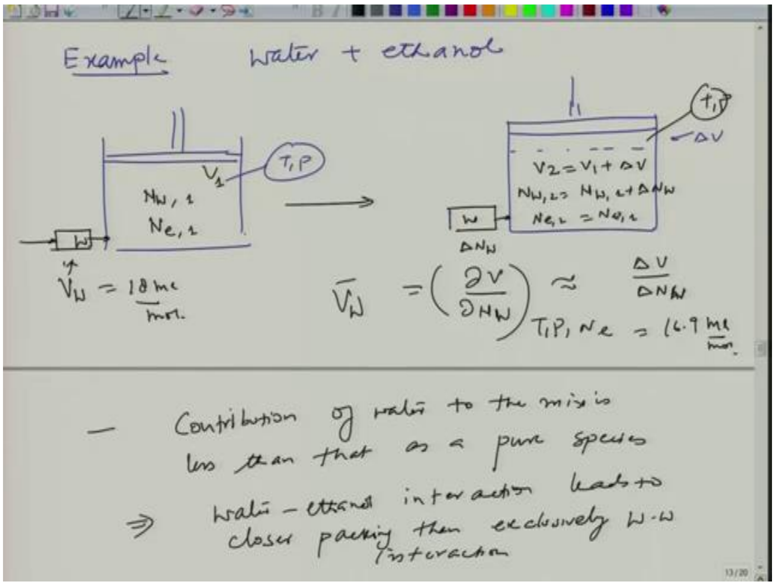

Example water + ethanol

$\bar{V}_W = 18 \frac{ml}{mol}$

$\bar{V}_W = \left(\frac{\partial V}{\partial N_W}\right)_{T,P,N_e} \approx \frac{\Delta V}{\Delta N_W} = 16.9 \frac{ml}{mol}$

- Contribution of water to the mix is less than that as a pure species

⇒ water – ethanol interaction leads to closer packing than exclusively W-W interaction

Now, so we will continue from here, I will take a case to get a feeling of partial molar property. We will start with the molar volume, partial molar volume okay, so let us consider the case of of water in ethanol, okay, and what we are more interested is to understand what happens to the contribution of the water when it is mixed, let us say you have container, which is maintained at constant temperature and pressure, okay, and there is a flow here which allows water to get in and this is a volume v and number of water water and this is for let us say ethanol, okay.

So, this is the case that initially this is a straight and this is a water flow and one can find out the volume, molar volume of water for such a case, for the pure case is nothing but we know that here is coming at 80 milliliter per mole okay. Now, we will take a case where basically so this is the initial state and now, we will take a case where we have added a small amount of mole to the to the volume, okay.

So, let me just again draw it here. Now, in this case, of course, there is a small change in the volume delta V and what has happened that you know, or we have added small amount of double small delta and has been added here. Again, remember this is this molar volume still remains the same and now the total volume is now changed to V1 plus delta V. So this was V 1 okay, and then delta NW2 to is NW1 plus delta NW and number of moles of ethanol still remains the same, okay.

$$V_2 = V_1 + \Delta V$$

$$N_{W,2} = N_{w,1} + \Delta N_W$$

So, what will be the V of partial molar volume for water in such a case okay, so let this will be your del V by del Nw; that is the definition at a constant temperature and pressure have Ne and this is this particular experiment which we just did entirely realize that that we have maintain the temperature here with T and P keeping the number of 4 moles of ethanol fixed and that is a small differential amount of water and the that means I can differentiate I can approximate this as okay.

So, if you do this exercise and experiment you would be able to find that this is nothing but 16.9 millilitre per mole, okay. So, what it tells you that the contribution, okay, of water to the mixture is less, right, then that of pure species, okay. So this is what it tells you that a small that contribution finally is less which also tells you that ethanol apparently interaction leads to closer packing.

$$V_W = 18\frac{mL}{mol} \qquad \overline{V_W} = \left(\frac{\partial V}{\partial N_w}\right)_{T,P,N_l} \approx \frac{\Delta V}{\Delta N_w} = 16.9\frac{mL}{mol}$$

Then exclusive, it tells you what water ethanol interaction leads to closer packing than exclusively water water interactions? So this is precisely due to the hydrogen bonding in this case, okay? So we talked about delta H here, right? If you look at it here with your talked about delta h, let us say now we again go back to this water ethanol case and find out from experiment using the same exercise which we have done because delta H is nothing but Q.

Now you can do, you can you can vary the composition of the water and ethanol in such a way that you should be able to measure the Q here as if you can measure the Q essentially you can find out the delta H make sure as a function of the composition of let us say ethanol in a given mixture and then you can plot it, okay.

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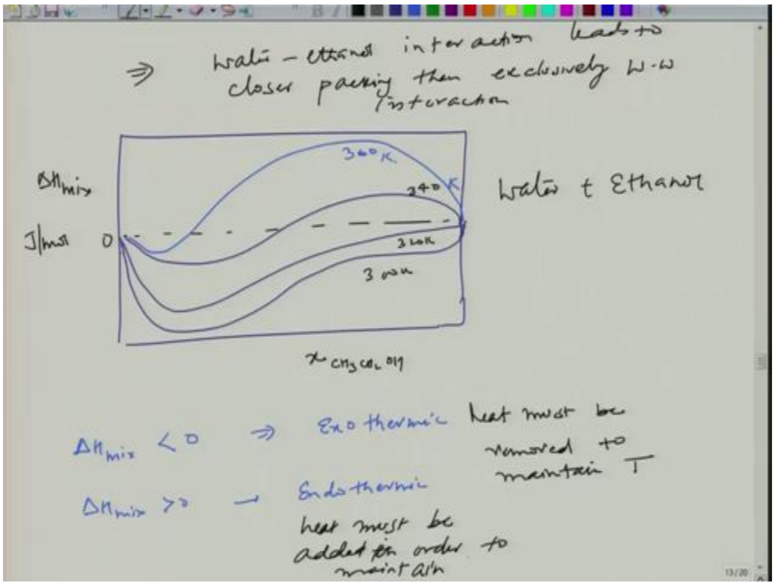
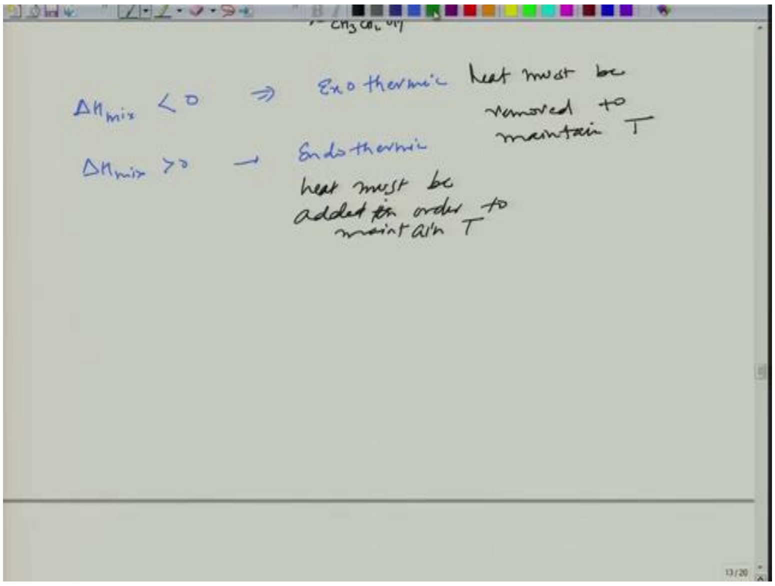


⇒ water – ethanol interaction leads to closer packing than exclusively w-w interaction

$\Delta H_{mix} < 0$ ⇒ Exothermic heat must be removed to maintain T

$\Delta H_{mix} > 0$ → Endothermic heat must be added in order to maintain



$\Delta H_{mix} < 0$ ⇒ Exothermic heat must be removed to maintain T

$\Delta H_{mix} > 0$ → Endothermic heat must be added in order to maintain T

So, let me show you one of the plot for different temperature. So, this is your 0 and this is your delta H mix and this is joules per mole and this is a composition X where we are saying this is essentially composition of X ethanol okay. So, again this is water, so this is a water ethanol. Now, so if I can measure the Q for different temperatures and compositions, you should be able to see the variation of behaviour of delta H mix with respect to temperature.

So, this is the case where we are getting something like this, okay. So this is, this is your 300, 320, 340 and then I can go up to get, so this is approximate to get the schematic representation here, okay. So this kind of behaviour where position variation can also means the sigh of the delta H is also observed in such kind of function. So what does this sigh represent here?

For the case of negative, there will be less than 0, we know that it is going to be exothermic, okay, which means that you need to remove the heat from the your chamber or container where this mixing is happening in order to maintain the temperature, okay, means heat must be removed to maintain temperature. Similarly, you can for the case of greater than 0, you have endothermic which means temperature must, sorry, which means heat must be added in order to maintain the temperature, okay.

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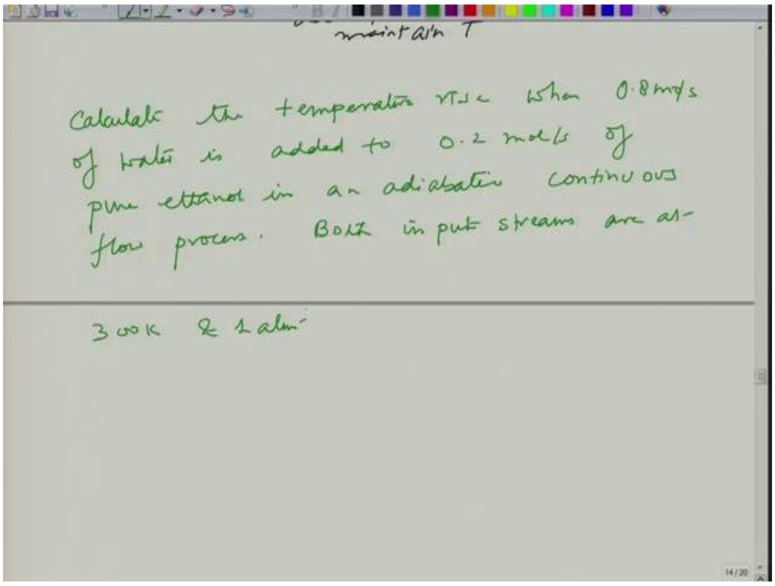

maintain T

Calculate the temperature rise when 0.8 mol/s of water is added to 0.2 mols of pure ethanol in an adiabatic continuous flow process. Both input streams are at 300 K & 1 atm.

So, let us do one example here, okay. So this is a question related to again water and ethanol, so just to calculate the temperature rise, okay, when 0.8 moles per second of water is added to 0.2 moles per second of pure ethanol in an adiabatic, so basically, the Q is 0 in such case, adiabatic continuous flow process, okay. So the other thing is that the input conditions are both the input streams or at 300 kelvin and 1 atmosphere, okay. So, how do you proceed for such a, such a case?

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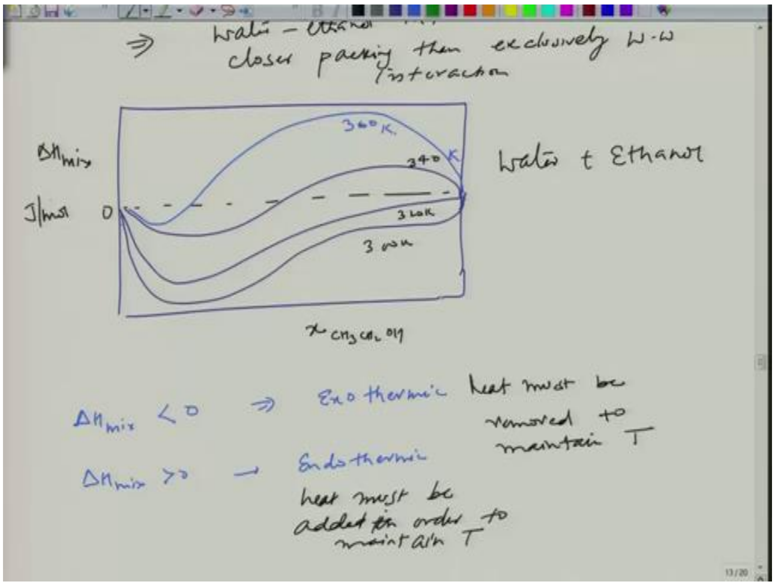

⇒ Water – ethanol … closer packing than exclusively W-W interaction

Water + Ethanol

$\Delta H_{mix} < 0$ ⇒ Exothermic heat must be removed to maintain T

$\Delta H_{mix} > 0$ → Endothermic heat must be added in order to maintain T

The diagram here, if you have this, such a diagram available to you, you know precisely what is delta H mix for X is equal to 0.2 mole fraction, okay. So, mole fraction is 0.2 for ethanol, so we can find out here. So, this should be somewhere some value is there are 300 kelvin which essentially here somewhere and this value turns out to be minus 750 joules per mole, okay.

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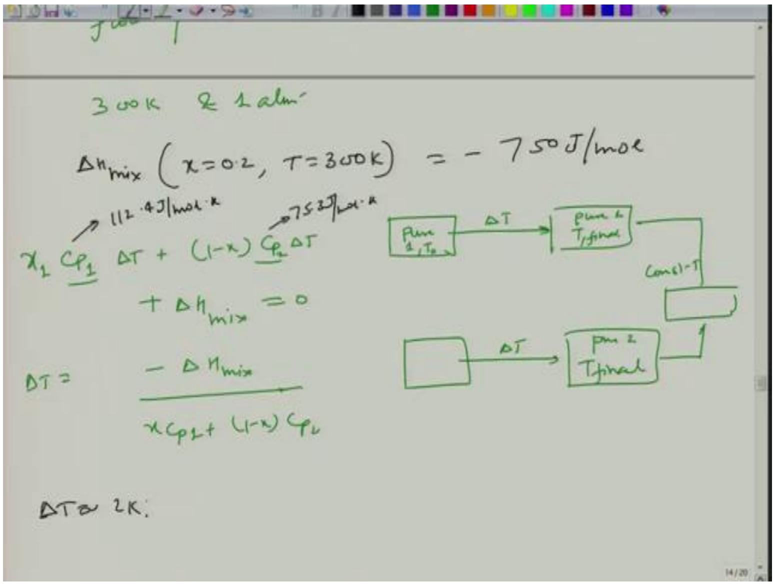

300 K & 1 atm

$\Delta H_{mix}(x = 0.2,\ T = 300 K) = -750\ J/mol$

$$x_1 \underbrace{C_{p_1}}_{} \Delta T + (1-x) \underbrace{C_{p_2}}_{} \Delta T + \Delta H_{mix} = 0$$

112.4 J/mol·K

75.3 J/mol·K

$$\Delta T = \frac{-\Delta H_{mix}}{x C_{p1} + (1-x) C_{p2}}$$

$\Delta T \approx 2K$

So, let us say this is given to us, so delta H mix, at X is equal to 0.2, T is equal to 300 kelvin is minus 7, of course, 1 atmosphere. Okay. This tells you this is exothermic, right? So this is an exothermic so temperature will rise because mixing is done in adiabatic continues fashion.

Now, in order to find out the temperature wise we need heat capacities, so we can think of this way that, you know, you so essentially the final temperature.

Let, me try to simplify this so we can assume that there are two components, right? So one is water and other one is ethanol, so we can take this that is a pure component, that is a 1 at temperature T0 which is 300 to a temperature pure 1 at T final and similarly, you can have the second component which you can also go to another one pure 2 T final and then mixing can occur at a constant temperature, so this mixing can occur at a constant temperature, right?

So, in that case essentially what we can find out is your delta T is that is the change from here, right? So, this is a change in the temperature from taking to 0 to final, so what I can do is I can actually consider based on the heat capacity because this is nothing but a sensible heat or energy which is taken from this point to this point. Now we have the information the mole fraction, so this will be C1, Cp 1 delta T plus 1 minus X Cp delta T.

And then this total energy plus whatever the energy related to mixing, this must be 0 because the because of the adiabatic conditions. So, with this you can find out delta T is nothing but minus delta H mix by X Cp 1 plus 1 minus X Cp 2, okay.

$$\Delta H_{mix}(x = 0.2, T = 300K) = -750\frac{J}{mol}$$

$$x_1 c_{P_1}\Delta T \ + (1-x)c_{P_2}\Delta T + \Delta H_{mix} = 0$$

$$\Delta T = -\frac{\Delta H_{mix}}{x c_{P_1} + (1-x)c_{P_2}}$$

Now, you can think of this as one approach, the other approach is, of course, you can mix it at a T is 0 okay, and then take the complete mixture to that, there also you would be doing the same exercise.

So this could be also at H delta H mix at T0 which is basically the 300. Now with this information and with this delta H mix information available for us, we rather use the second part where we as say that well we mixing it at T0 and taking it each of the component to the final statement or final temperature. So with this you should be able to add this part here and then you are, you get this information of Cp 1 and Cp 2 from the any estimable signs or from various different text book tables.

This information is given to us and the problem here which is 112.4 for ethanol and this is 75.3 joules per mole for the case of water. So, using this with we are using the information of delta X mix we should be able to find delta T. which turns out to be around 2 kelvin, okay, so that is a problem one which I wanted to solve.

Now let us move and so let us try to further explore this concept and a look into the partial molar enthalpy is from total enthalpy, in other word will do another problem to understand this concept and in this case what is given to us is not in a diagrammatic form delta H mix but in some expression, analytical forms of delta H mix is available to us and then subsequently we would like to find out what is the partial molar enthalpy in this case, okay.

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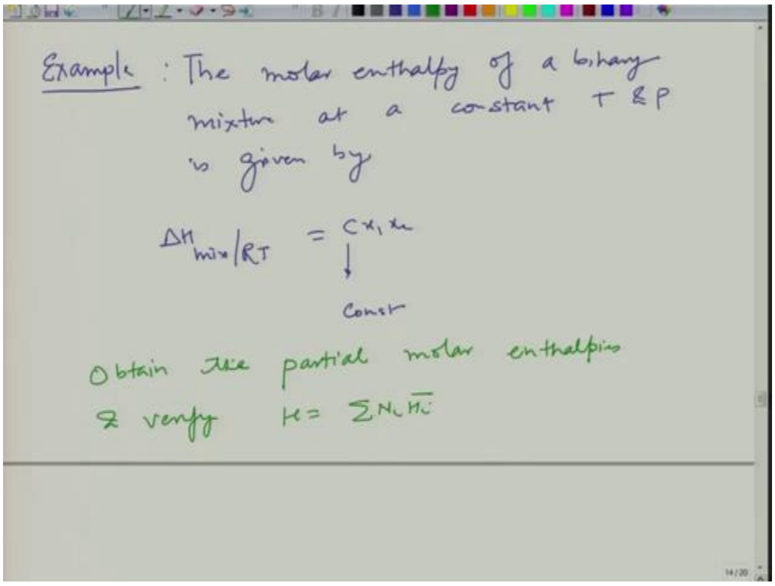
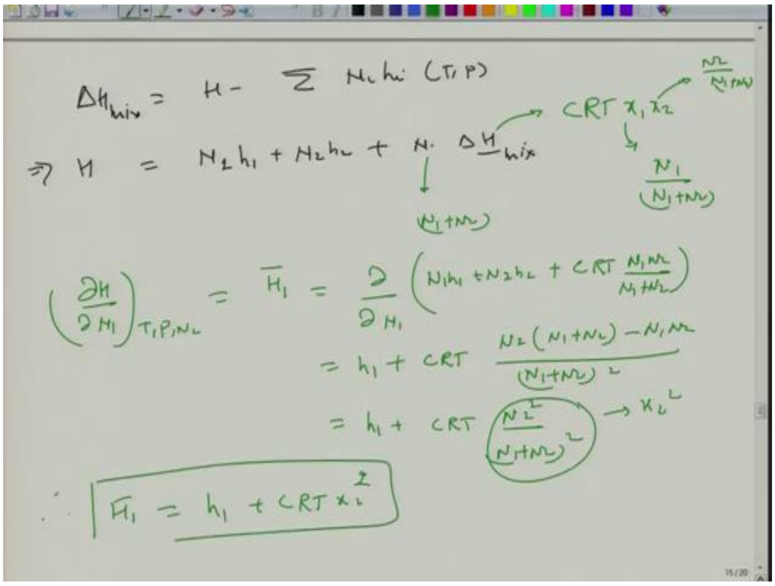


Example : The molar enthalpy of a binary mixture at a constant T & P is given by

$$\Delta H_{mix}/RT = \underset{\substack{\downarrow\\ \text{Const}}}{C}\, x_1 x_2$$

Obtain the partial molar enthalpies & verify $H = \sum N_i \overline{H_i}$



$$\Delta H_{mix} = H - \sum N_i h_i \,(T,P)$$

$$\Rightarrow H = N_1 h_1 + N_2 h_2 + \underset{(N_1+N_2)}{\underset{\downarrow}{N}} \cdot \Delta \underline{H}_{mix} \longrightarrow CRT\, x_1 x_2, \quad x_1 \to \frac{N_1}{(N_1+N_2)}, \quad x_2 \to \frac{N_2}{N_1+N_2}$$

$$\left(\frac{\partial H}{\partial N_1}\right)_{T,P,N_2} = \overline{H_1} = \frac{\partial}{\partial H_1}\left(N_1 h_1 + N_2 h_2 + CRT\,\frac{N_1 N_2}{N_1+N_2}\right)$$

$$= h_1 + CRT\,\frac{N_2(N_1+N_2) - N_1 N_2}{(N_1+N_2)^2}$$

$$= h_1 + CRT\,\frac{N_2^2}{(N_1+N_2)^2} \to x_2^2$$

$$\therefore \boxed{\overline{H_1} = h_1 + CRT\,x_2^2}$$

So again, this is example, okay, so let us say that the molar enthalpy of a binary mixture at a constant temperature and pressure is given by delta H mix C X1, X2, so this is the expression given to us where C is basically nothing but a constant, not a function of temperature pressure and composition, okay. Now, the question is that we need to find out the obtain the partial molar enthalpies of the two components, okay and verify the Euler theorem for homogeneous function, which is H is equal to summation of NiHi bar.

So this is nothing but Euler theorem for homogeneous function, okay, so this is a problem given to us. Let us start with the definition of a delta H mix first, because that is a expression given for us. Delta H mix here is nothing but H minus summation NiHi at the same temperature and pressure, okay. Now, I can find from here H is N1 because there are two components here N1H1 plus N2H2, H is nothing but the, small h is nothing but the pure molar enthalpy of the pure component plus delta H.

$$\Delta H_{mix} = H - \sum N_i h_i(T,P)$$

$$H = N_1 h_1 + N_2 h_2 + \Delta H_{mix}$$

$$\left(\frac{\partial H}{\partial N_1}\right)_{T,P,N_2} = \overline{H_1} = \frac{\partial}{\partial H_1}\left(N_1 h_1 + N_2 h_2 + CRT\ \frac{N_1 N_2}{N_1 + N_2}\right)$$

$$\overline{H_1} = h_1 + CRT\,\frac{N_2^2}{(N_1+N_2)^2}$$

$$\overline{H_1} = h_1 + CRT * x_2^2$$

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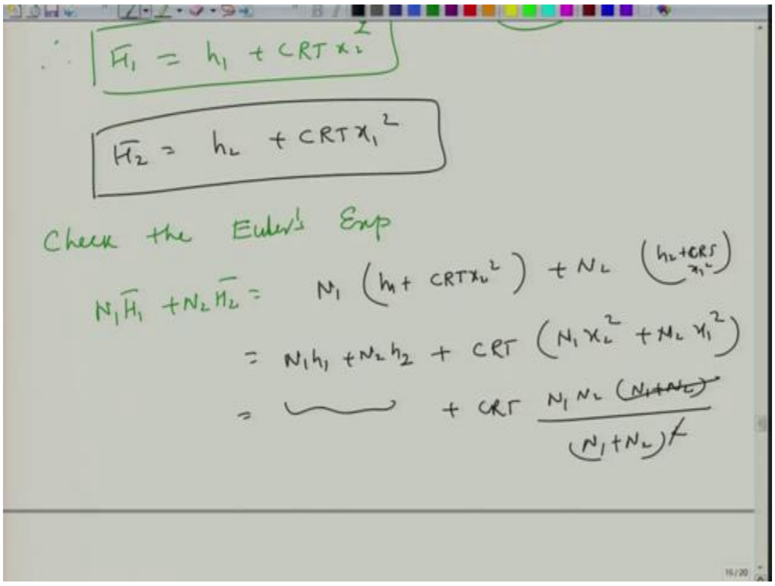

$$\therefore \boxed{\overline{H_1} = h_1 + CRT x_2^2}$$

$$\boxed{\overline{H_2} = h_2 + CRT x_1^2}$$

Check the Euler's Exp

$$N_1\overline{H_1} + N_2\overline{H_2} = N_1(h_1 + CRT x_2^2) + N_2(h_2 + CRT x_1^2)$$

$$= N_1h_1 + N_2h_2 + CRT(N_1x_2^2 + N_2x_1^2)$$

$$= \underbrace{\qquad} + CRT\frac{N_1N_2\cancel{(N_1+N_2)}}{(N_1+N_2)^{\cancel{2}}}$$

Similarly, you can show that

$$\overline{H_2} = h_2 + CRTx_1^2$$

. Now given this two we should be able to now show the Euler relation of this. So, if I plug in this what you get,

$$N_1\overline{H_1} + N_2\overline{H_2} = N_1(h_1 + CRTx_2^2) + N_2(h_2 + CRTx_1^2)$$

$$N_1\overline{H_1} + N_2\overline{H_2} = N_1h_1 + N_2h_2 + CRT(N_1x_2^2 + N_2x_1^2) = CRT\frac{N_1N_2(N_1 + N_2)}{(N_1 + N_2)^2}$$

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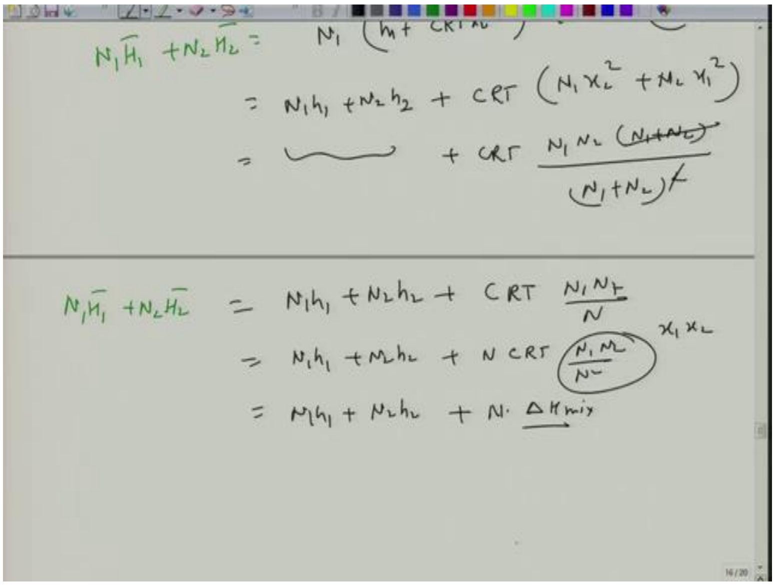


$N_1\overline{H_1} + N_2\overline{H_2} = N_1(h_1 + CRT x_2^2) \ldots$

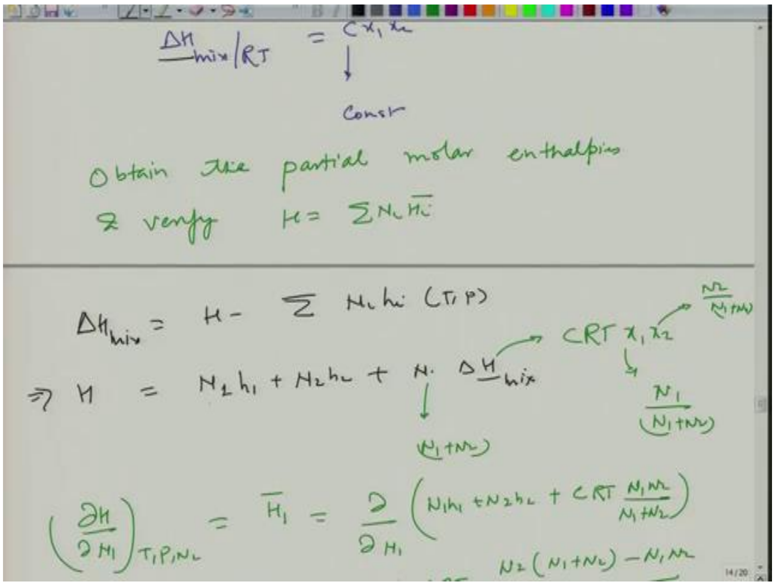
$= N_1h_1 + N_2h_2 + CRT(N_1x_2^2 + N_2x_1^2)$

$= \underbrace{\quad}\ + CRT\frac{N_1N_2\cancel{(N_1+N_2)}}{(N_1+N_2)^{\cancel{3}}}$

$N_1\overline{H_1} + N_2\overline{H_2} = N_1h_1 + N_2h_2 + CRT\frac{N_1N_2}{N}$

$= N_1h_1 + N_2h_2 + N\,CRT\boxed{\frac{N_1N_2}{N^2}}\ x_1x_2$

$= N_1h_1 + N_2h_2 + N\cdot\Delta H_{mix}$



$\Delta H_{mix}/RT = Cx_1x_2$

$\downarrow$ Const

Obtain the partial molar enthalpies & verify $H = \sum N_i\overline{H_i}$

$\Delta H_{mix} = H - \sum N_ih_i(T,P)$

$\Rightarrow H = N_1h_1 + N_2h_2 + \underset{(N_1+N_2)}{N}\cdot\Delta H_{mix}$

$\Delta H_{mix} \to CRT\,x_1x_2$, $x_2 \to \frac{N_2}{N_1+N_2}$, $x_1 \to \frac{N_1}{N_1+N_2}$

$\left(\frac{\partial H}{\partial N_1}\right)_{T,P,N_2} = \overline{H_1} = \frac{\partial}{\partial N_1}\left(N_1h_1 + N_2h_2 + CRT\frac{N_1N_2}{N_1+N_2}\right)$

$N_2(N_1+N_2) - N_1N_2$

$$N_1\overline{H_1} + N_2\overline{H_2} = N_1h_1 + N_2h_2 + CRT\frac{N_1N_2}{N}$$

$$N_1\overline{H_1} + N_2\overline{H_2} = N_1h_1 + N_2h_2 + N\ CRT\frac{N_1N_2}{N^2}$$

$$N_1\overline{H_1} + N_2\overline{H_2} = N_1h_1 + N_2h_2 + N\ \Delta H_{mix}$$

So, we obtained the same expression and that is what how we verified it as well, right? So, this is something which we have not done. Now, well let me take it another problem and I think perhaps that will further elaborate the use of these partial molar properties in terms of solving it through analytical means.

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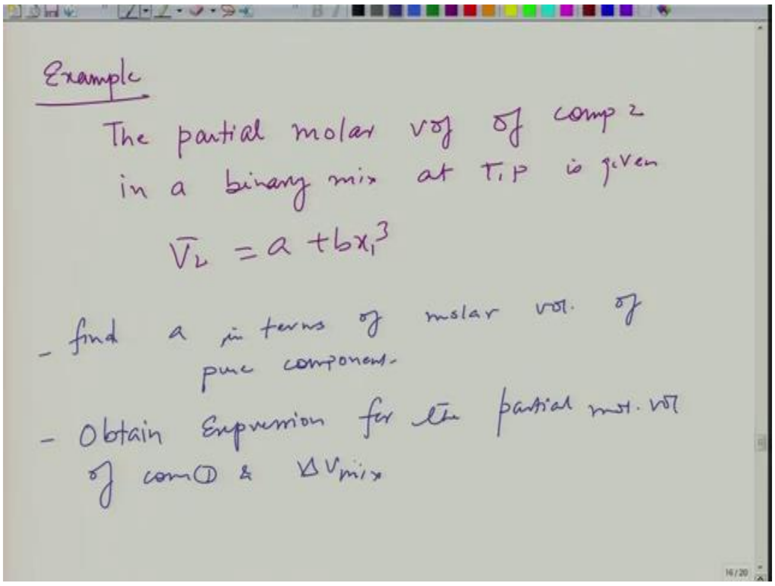
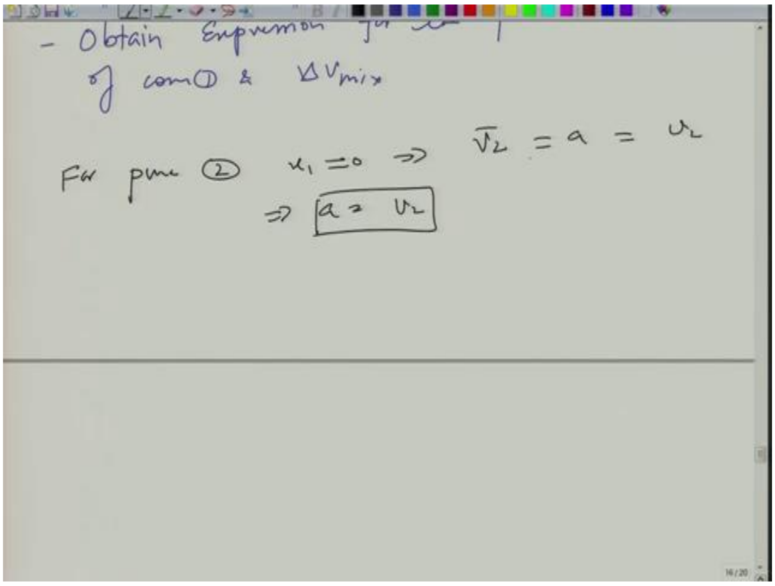


Example

The partial molar vol of comp 2 in a binary mix at T,P is given

$$\bar{V}_2 = a + bx_1^3$$

- find a in terms of molar vol. of pure component.
- Obtain Expression for the partial mol. vol of com① & ΔV_{mix}



- Obtain Expression

of com① & ΔV_{mix}

For pure ② $x_1 = 0 \Rightarrow \bar{V}_2 = a = v_2$

$$\Rightarrow \boxed{a = v_2}$$

So, this is again an example, okay, so in this case what we have is a partial molar volume of component 2 in a binary mixture at T and P is given by the following expression. So,

$$V_2 = a + bx_1^3$$

So, what is being asked is to relate the constant A, so find A in terms of molar volume of pure component and obtain an expression for the partial molar volume of component A1 and volume of mixing, okay.

So, you have to find out by partial molar of component of volume 1 and volume of mixing, okay. So, looking at this expression, you can clearly tell one aspect that,

$$x_1 = 0\,; \bar{V}_2 = a = U_2$$

$$\therefore a = U_2$$

So, A is nothing but, so that is something which we can clearly come out we can write down this from the expression. Now, we need to find out the partial molar volume of component 1, so we will start with the Gibbs-Duhem relation because this is the one which relates both the partial molar properties with the composition.

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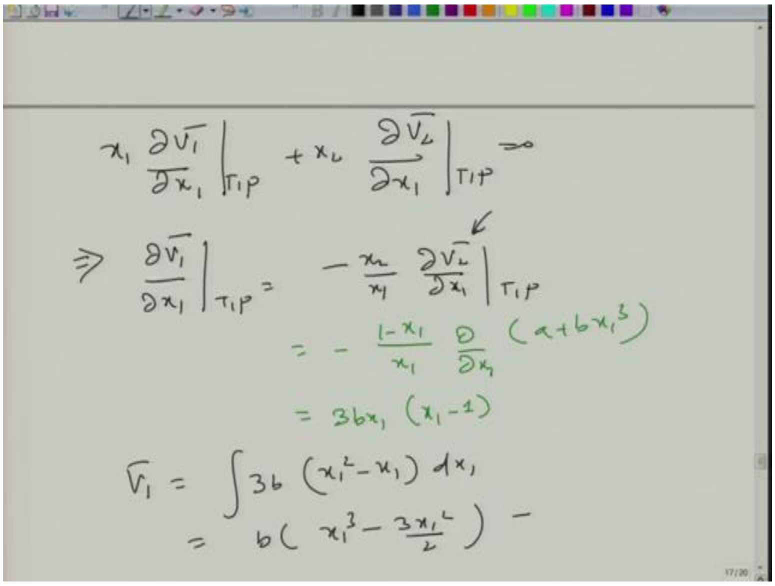

$$x_1 \frac{\partial \bar{V}_1}{\partial x_1}\Big|_{T,P} + x_2 \frac{\partial \bar{V}_2}{\partial x_1}\Big|_{T,P} = 0$$

$$\Rightarrow \frac{\partial \bar{V}_1}{\partial x_1}\Big|_{T,P} = -\frac{x_2}{x_1} \frac{\partial \bar{V}_2}{\partial x_1}\Big|_{T,P}$$

$$= -\frac{1-x_1}{x_1} \frac{\partial}{\partial x_1}(a+bx_1^3)$$

$$= 3bx_1(x_1-1)$$

$$\bar{V}_1 = \int 3b(x_1^2 - x_1)\,dx_1$$

$$= b\left(x_1^3 - \frac{3x_1^2}{2}\right) -$$

$$\frac{x_1 \delta \bar{V}_1}{\delta x_1}|_{T,P} + \frac{x_2 \delta \bar{V}_2}{\delta x_1}|_{T,P} = 0$$

$$Or, \frac{\delta \bar{V}_1}{\delta x_1}|_{T,P} = -\frac{x_2}{x_1}\frac{\delta \bar{V}_2}{\delta x_1}|_{T,P} = -\frac{1-x_1}{x_1}\frac{\delta(a+bx_1^3)}{\delta x_1} = 3bx_1(x_1-1)$$

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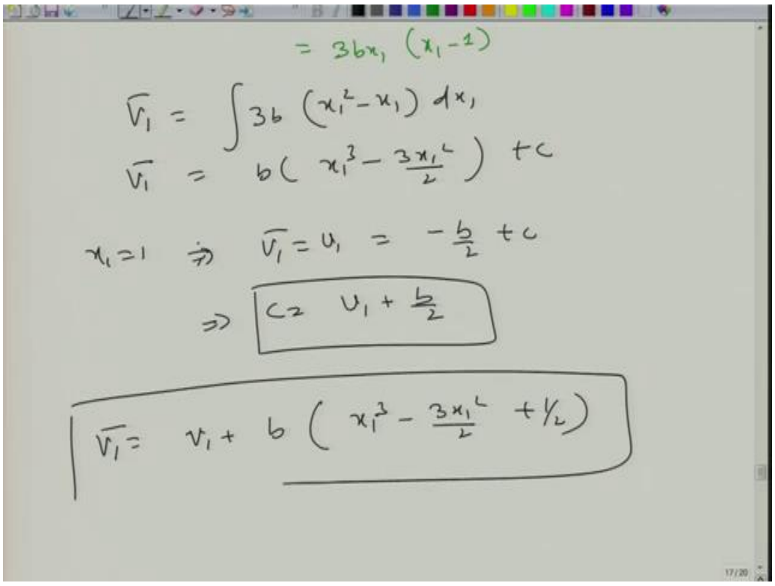

$$= 3bx_1(x_1-1)$$

$$\bar{V}_1 = \int 3b(x_1^2 - x_1)\,dx_1$$

$$\bar{V}_1 = b\left(x_1^3 - \frac{3x_1^2}{2}\right) + c$$

$$x_1 = 1 \Rightarrow \bar{V}_1 = v_1 = -\frac{b}{2} + c$$

$$\Rightarrow \boxed{c = v_1 + \frac{b}{2}}$$

$$\boxed{\bar{V}_1 = v_1 + b\left(x_1^3 - \frac{3x_1^2}{2} + \frac{1}{2}\right)}$$

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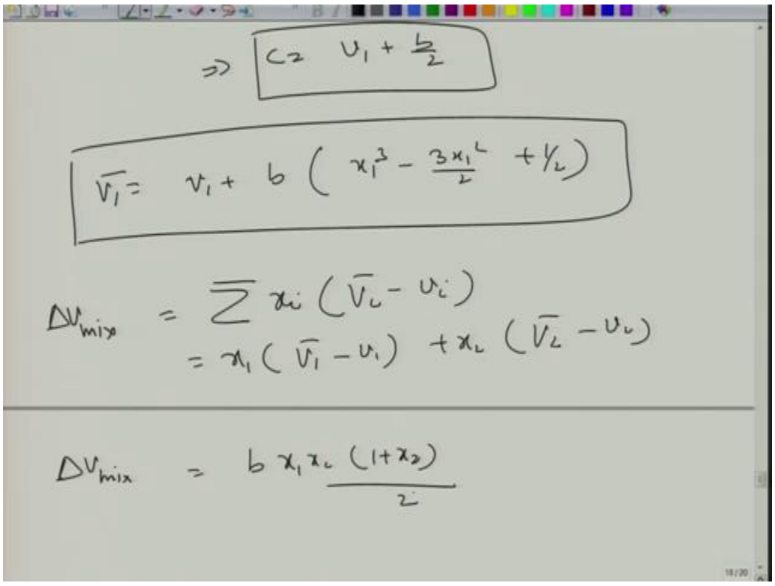

$$\Rightarrow \boxed{c = v_1 + \frac{b}{2}}$$

$$\boxed{\bar{V}_1 = v_1 + b\left(x_1^3 - \frac{3x_1^2}{2} + \frac{1}{2}\right)}$$

$$\Delta V_{mix} = \sum x_i(\bar{V}_i - v_i)$$

$$= x_1(\bar{V}_1 - v_1) + x_2(\bar{V}_2 - v_2)$$

$$\Delta V_{mix} = \frac{b\,x_1 x_2(1+x_2)}{2}$$

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$$\bar{V}_1 = \int (3b(x_1^2 - x_1)dx_1) = b\left(x_1^3 - \frac{3x_1^2}{2}\right) + C$$

$$x_1 = 1 \quad \bar{V}_1 = U_1 = -\frac{b}{2} + C$$

$$C = U_1 + \frac{b}{2}$$

$$\bar{V}_1 = V_1 + b\left(x_1^3 - \frac{3x_1^2}{2} + \frac{1}{2}\right)$$

$$\Delta V_{mix} = \sum x_i(\bar{V}_i - U_i) = x_1(\bar{V}_1 - U_1) + x_2(\bar{V}_2 - U_2)$$

$$\Delta V_{mix} = \frac{b x_1 x_2 (1 + x_2)}{2}$$

So, this was a very simple mathematical exercise which we have used in order to obtain the relevant information and the key element was that we use the limiting conditions and Gibbs-Duhem relations in order to find the unknown information.

So, that will be the end of today's class and we will continue this exercise in the next class as well, okay, so I will see you in the next class.