

Chemical Engineering Thermodynamics
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Lecture 36

Examples of Partial Molar Properties for Real Processes

Welcome back. In the last lecture we were looking at partial molar properties and properties upon, change in the properties upon mixing. So, in this lecture we will start with an example to illustrate particularly how to make use of it in a real process.

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Well - insulated piston - cylinder assembly

Example

400

1 bar

$n_1 = 2 \text{ mol}$

$n_2 = 4 \text{ mol}$

$n_3 = 4 \text{ mol}$

Partition

If the partition is removed determine the final T

$$\Delta h_{mix} = 400x_1x_2 + 800x_1x_3 + 0x_2x_3 + 37.5x_1x_2x_3 \quad [\text{J/mole}]$$

$C_{p1} = 27.5 \text{ J/mol.K}$

$C_{p2} = 25 \quad \text{---}$

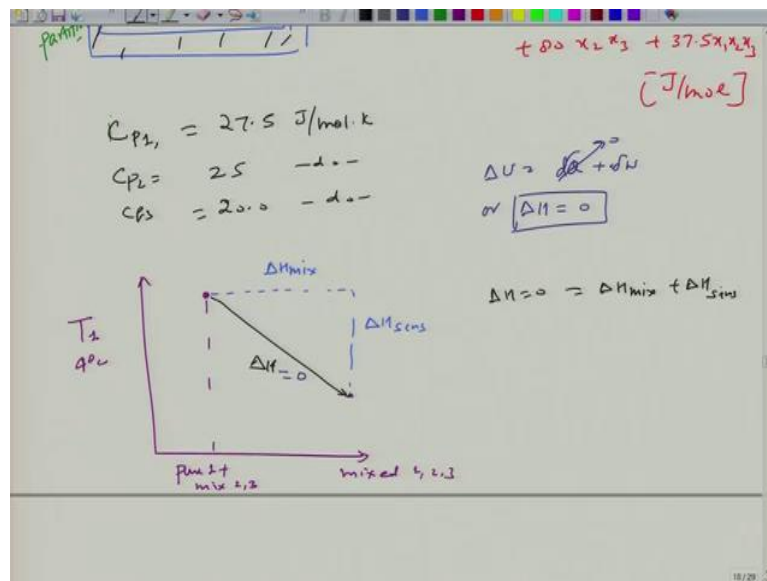
$C_{p3} = 20.0 \quad \text{---}$

So will start with a very simple problem and this is a problem on well insulated piston cylinder assembly, so what we have been given is that you have 3 components or mixture which is desirable but initially what we have is a cylinder which is well insulated and this is all maintained at 1 bar and 4 degrees Celsius, 4 degrees Celsius 1 bar. Initially, we have a partition such that the component one with moles of 2 moles is in this region and we have a mixture of 2 and 3 component with corresponding moles written here okay.

Now, the question is that if you remove the partition that is if the partition is removed determining the final temperature okay, so this is a simple question which we want to do that, we want to remove this partition and then subsequently, of course, this will get mixed but what would be the final temperature? So, what is given to us is the molar change in enthalpy of the mixture which is a function of composition.

So, this is in the units of joules per mole. In addition, we have been given the CP 1 which is 27.5 joules per mole Kelvin, CP 2 which is 25 and a CP 3 which is 20 same units. So, how do you solve this problem? So, essentially what we want to do is we want to remove this partition and then there is a mixture, so essentially the Delta h mix we need to find out, so let me just first draw schematic diagram.

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$$\Delta U = dQ + \delta W; \quad dQ = 0$$

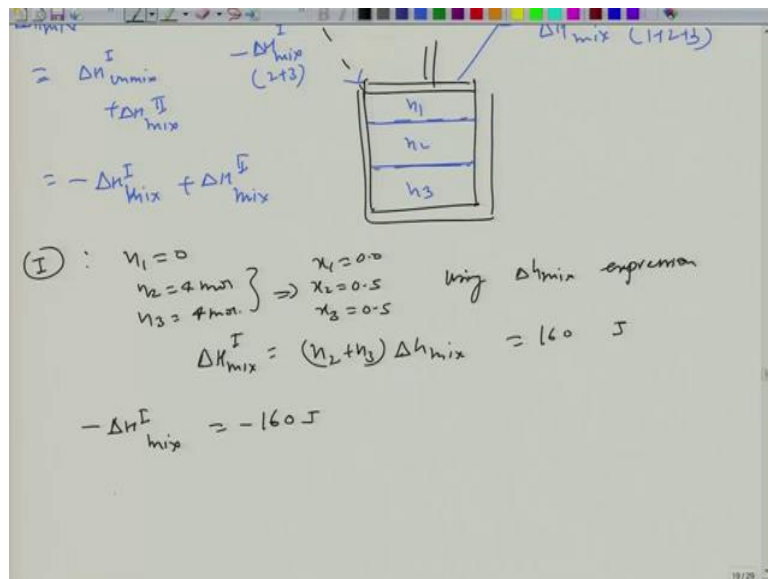
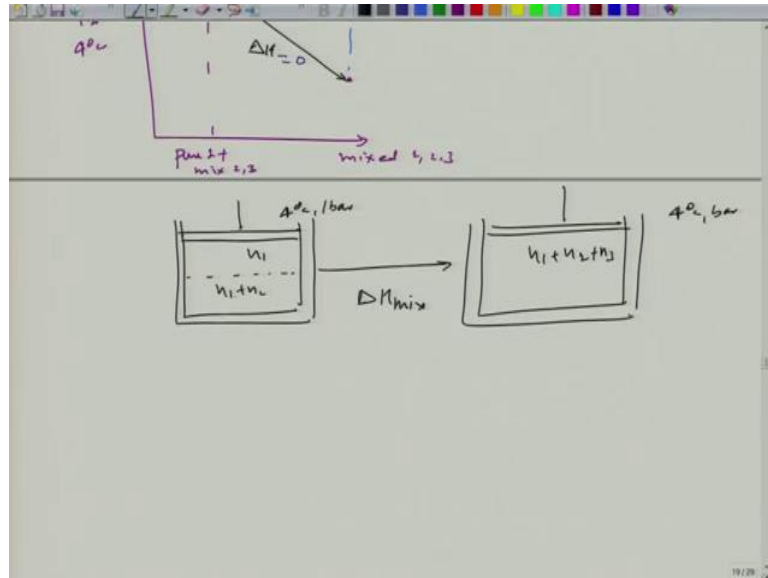
$$\Delta H = 0 = \Delta H_{mix} + \Delta H_{sens}$$

So, one can think of the following, if it is T1 the temperature which is 4 degree and this is let us say states, so initially we have base which essentially is nothing but pure one plus mixture of 2 and 3 and finally we have a state, let us say this is there, assuming the temperature is going to be lower this is going to be mixed 1, 2, 3. So, what we are interested in is some kind of Delta H which we can find it out to start with but since it is adiabatic we know that your Delta you is going to q.

Whatever the q plus the corresponding change which is basically dQ and w and essentially this is going to be 0 which means that I can say this for such a system Delta H has to be 0 and hence, this must be 0. So, I can divide this process which has occurred into 2 states first is at the mixing occurs at 4 degrees Celsius and subsequently there is a change in sensible heat, where the change temperature occurs.

So, if I do that, I can have essentially two-step process, this will be your Delta H mix and this will be your Delta H sensible and thus your Delta H 0 is nothing but Delta H mix plus Delta H sensible. Now, essentially, we would like to find out now Delta H mix.

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So, let me schematically show a bit that what we intend to do what you are talking about is that your piston cylinder which is initially here is n_1 and here is n_1 plus n_2 and this is at 4 degree Celsius 1 bar, so we would like to mix this such that we have 4 degree 1 bar with n_1 plus n_2 plus n_3 , so this is your Delta H mix, but this is what we would like to find it out. Now, this can be again broken into 2 steps, first that we can unmix n_1 plus n_2 because the fact is what we have is the delta h as the function is given in terms of x_1 , x_2 and x_3 .

$$\Delta H_{mix}^I = (n_2 + n_3)\Delta h_{mix} = 160 J$$

$$-\Delta H_{mix}^I = -160 J$$

So, if you unmixed it you can make use of that Delta H here, so I can now divide this part as 2 parts one that you unmix it, essentially it means that you have again piston cylinder geometry but with 2 partitions now, not just one. One is here and another one is here, so this is n_1 , this is n_2 and this is n_3 and then so this is unmixing it, so unmixing it would be like from here to here is Delta H, so from here to here would be minus of Delta H mix for 2 plus 3, right and from here to here this will be Delta H mix with 1 plus 2 plus 3 okay.

So, in order to segregate this I am going to say that Delta H mix is equal to Delta H one, the first step unmix plus Delta H mix the second step, so this is first step, this is second step, so I am going to identify this as this, so this is nothing but minus of, this unmix is minus of Delta H1 mix plus Delta H2 mix. Remember, this refers to only 2 and 3 and this refers or this is pertaining to only 1, 2 and 3.

So, for the case of this Delta H mix 1, we have to just worry about the component 2 and 3, so the path 1 here means that n_1 is equal to 0 okay and since n_2 is equal to 4 mole, n_3 is equal to 4 mole, so this means that your x_2 is 0.5, x_3 is 0.5. Now using Delta H mix expression, I can find out Delta H mix 1 as and 2 plus and 3 delta h mix okay with this x_2 , x_3 is equal to 0.1 and x_1 is equal to 0.

So, with this I will get an expression here, this turns out to be 160 joules. Alright so now with this I have minus of Delta H1 I mix is minus 160 joules. Now, similarly I can also obtain Delta H mix for the second path which means mixing 1, 2 and 3 from the unmixed that means from here to this here and in that case, I need to again look at for the second one.

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$$\begin{aligned}
 n_2 = 4 \text{ mol} \\
 n_3 = 4 \text{ mol} & \Rightarrow x_2 = 0.5 \\
 & \quad x_3 = 0.5 \\
 \Delta H_{\text{mix}}^I &= (n_2 + n_3) \Delta h_{\text{mix}} = 160 \text{ J} \\
 -\Delta H_{\text{mix}}^I &= -160 \text{ J} \\
 \textcircled{\text{II}}: \quad n_1 = 2 \quad x_1 = 0.2 \\
 \quad n_2 = 4 \quad x_2 = 0.4 \\
 \quad n_3 = 4 \quad x_3 = 0.4 \\
 \Delta H_{\text{mix}}^{\text{II}} &= (n_1 + n_2 + n_3) \cdot \Delta h_{\text{mix}} \\
 &= 1100 \text{ J} \\
 \therefore \Delta H_{\text{mix}} &= -160 + 1100 = 940 \text{ J}
 \end{aligned}$$

determine the process

$$\Delta h_{\text{mix}} = 400x_1x_2 + 800x_1x_3 + 80x_2x_3 + 37.5x_1x_2x_3 \quad [\text{J/mol}]$$

$C_{p,1} = 27.5 \text{ J/mol}\cdot\text{K}$
 $C_{p,2} = 25 \text{ J/mol}\cdot\text{K}$
 $C_{p,3} = 20.0 \text{ J/mol}\cdot\text{K}$

$\Delta U = \delta Q + \delta W$
 or $\Delta H = 0$

$\Delta H = 0 = \Delta H_{\text{mix}} + \Delta H_{\text{sens}}$

In this case you have 1 is equal to 2 okay and 2 is 4 and 3 is 4 these are all in moles, so this means x_1 is 0.2, x_2 is 0.4, x_3 is also 0.4. Now, using the same way as we have done earlier, as H_2 mix is equal to n_1 plus n_2 plus n_3 multiplied by a ΔH_{mix} , this turns out to be 1100 joules. You can now add this and this in order to get ΔH_{mix} .

$$\Delta h_{\text{mix}} = 400x_1x_2 + 800x_2x_3 + 80x_2x_3 + 37.5x_1x_2x_3 \quad \left[\frac{\text{J}}{\text{mol}} \right]$$

This is going to be minus 160 plus 1100, this is 940 joules okay. So, this is your ΔH_{mix} , remember again what we wanted was ΔH from here to here is ΔH_{mix} at the temperature then you take the mixture and heat it up or change it or cool it down to the temperature which is of final temperature that would be your sensible part.

$$\Delta H_{\text{mix}}^{\text{II}} = (n_1 + n_2 + n_3) \Delta h_{\text{mix}} = 1100 \text{ J}$$

$$\Delta H_{mix} = -160 + 1100 = 940 \text{ J}$$

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Handwritten derivation of the sensible enthalpy change equation:

$$\Delta H_{sens} = \int_{T^0}^{T_f} (n_1 c_{P1} + n_2 c_{P2} + n_3 c_{P3}) dT$$

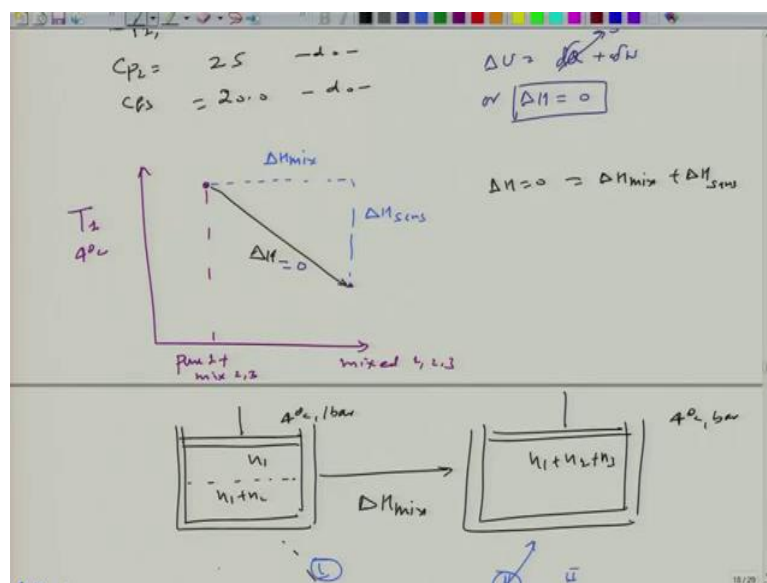
$$= 235 (T_f - 277) \text{ J}$$

To determine the final T

$$\Delta H = 0 = \Delta H_{mix} + \Delta H_{sens}$$

$$= 940 + 235 (T_f - 277)$$

$$\Rightarrow T_f = 273 \text{ K}$$



So, now we can look at the sensible part, so Delta H sensible would be from the T0, whatever the T0 at which mixing to the T final, and this would be your n1 CP 1, plus n2 CP 2, plus n3 CP 3 dt, so this is already known to us and n1, n2 and n3 we know, so if you plug-in here we are going to get 2, 3, 5 T2 minus 277 joules, so T2 is the T final, T final minus 277 joules. So, now in order to determine the final temperature with revert back to the old expression which is your Delta H is equal to 0.

$$\Delta H_{sens} = \int_{T^0}^{T_f} (n_1 c_{P1} + n_2 c_{P2} + n_3 c_{P3}) dT = 235(T_f - 277) \text{ J}$$

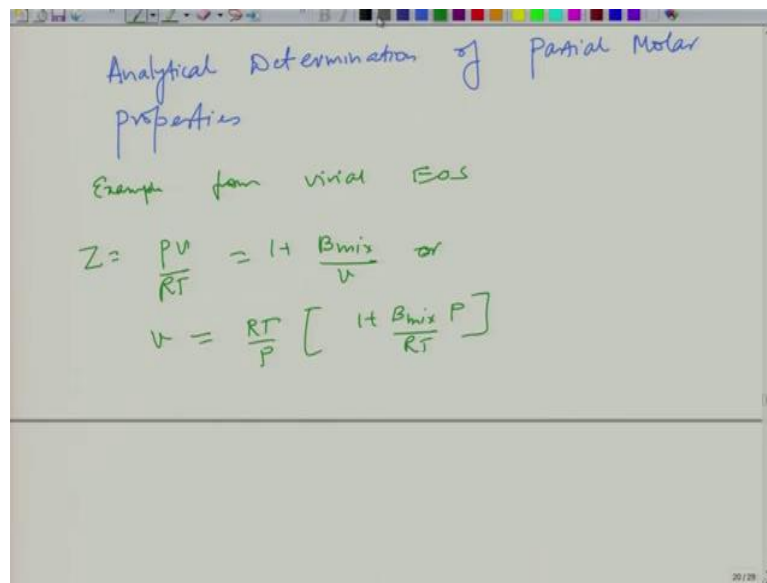
To determine final T: $\Delta H = 0 = \Delta H_{mix} + \Delta H_{sens} = 940 + 235(T_f - 277)$

$$T_f = 273 K$$

This is nothing but Delta H mix plus Delta H sensible, and then you can put 940 plus 235 T final minus 277 and here the T final is going to be 273 Kelvin that is how you get from this exercise. So a very simple operation here where we just made use of Delta H mix that is something which was the only thing which was given to us besides the CP and then we consider the process and we divided the process into steps in order to simplify the problem and subsequently we will solve this thing.

Okay, so this is a bit on this Delta H mix. Now, we can go back again and ask the question can be determining partial molar property using analytical ways or using equations, so that is something which I would like to elaborate it, we will take an example of virial coefficient to illustrate this analytical ways to obtain partial molar property.

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Analytical Determination of Partial Molar Properties

Example for virial EOS

$$Z = \frac{PV}{RT} = 1 + \frac{B_{mix}}{v} \text{ or}$$
$$v = \frac{RT}{P} \left[1 + \frac{B_{mix} P}{RT} \right]$$

So, let us now look at simple virial equation as I said we will take example from virial equation of state. So, we will take a case again being a partial molar property essentially means we have to take equation still relevant for the mixtures, so we will take a case of virial equation truncated to the second virial coefficient.

$$Z = \frac{PV}{RT} = 1 + \frac{B_{mix}}{v}$$

$$v = \frac{RT}{P} \left[1 + \frac{B_{mix} P}{RT} \right]$$

Now here B mix for the case of binary mixture can be written as following.

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The image shows handwritten mathematical derivations on a digital whiteboard. The top section shows the derivation of molar volume v from compressibility factor Z . It starts with $Z = \frac{Pv}{RT} = 1 + \frac{B_{mix}}{v}$ or $v = \frac{RT}{P} \left[1 + \frac{B_{mix} P}{RT} \right]$. The middle section defines the mixture second virial coefficient as $B_{mix} = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22}$. The bottom section shows the total volume $V = (n_1 + n_2)v = \frac{(n_1 + n_2)RT}{P} + \frac{n_1^2 B_{11} + 2n_1 n_2 B_{12} + n_2^2 B_{22}}{(n_1 + n_2)}$ and defines the mole fractions $y_1 = n_1/n_T$ and $y_2 = n_2/n_T$.

$$B_{mix} = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22}$$

$$V = (n_1 + n_2)v = \frac{(n_1 + n_2)RT}{P} + \frac{(n_1^2 B_{11} + 2n_1 n_2 B_{12} + n_2^2 B_{22})}{n_1 + n_2}$$

$$y_1 = \frac{n_1}{n_T}; y_2 = \frac{n_2}{n_T}$$

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$$\bar{V}_1 = \left(\frac{\partial V}{\partial n_1} \right)_{T,P,n_2} = \frac{RT}{P} + \frac{2n_1 B_{11} + 2n_2 B_{12}}{(n_1+n_2)} - \frac{n_1^2 B_{11} + 2n_1 n_2 B_{12} + n_2^2 B_{22}}{(n_1+n_2)^2}$$

$$\bar{V}_1 = \frac{RT}{P} + (y_1^2 + 2y_1 y_2) B_{11} + 2y_2^2 B_{12} - y_2^2 B_{22}$$

$$\bar{V}_2 = \frac{RT}{P} - y_1^2 B_{11} + 2y_1^2 B_{12} + (y_2^2 + 2y_1 y_2) B_{22}$$

To obtain make vs. $v_1 = ?$ $y_2 = 0$

$$V_1 = \frac{RT}{P} + B_{11}$$

$$\bar{V}_1 = \frac{RT}{P} + (y_1^2 + 2y_1 y_2) B_{11} + 2y_2^2 B_{12} - y_2^2 B_{22}$$

$$\bar{V}_2 = \frac{RT}{P} - y_1^2 B_{11} + 2y_1^2 B_{12} + (y_2^2 + 2y_1 y_2) B_{22}$$

To obtain make vs. $v_1 = ?$ $y_2 = 0$

$$V_1 = \frac{RT}{P} + B_{11} = \bar{V}_1$$

$$\bar{V}_1 = \left(\frac{\partial V}{\partial n_1} \right)_{T,P,n_2} = \frac{RT}{P} + \frac{2n_1 B_{11} + 2n_2 B_{12}}{n_1 + n_2} - \frac{n_1^2 B_{11} + 2n_1 n_2 B_{12} + n_2^2 B_{22}}{(n_1 + n_2)^2}$$

$$\bar{V}_1 = \frac{RT}{P} + (y_1^2 + 2y_1 y_2) B_{11} + 2y_2^2 B_{12} - y_2^2 B_{22}$$

$$\bar{V}_2 = \frac{RT}{P} - y_1^2 B_{11} + 2y_1^2 B_{12} + (y_2^2 + 2y_1 y_2) B_{22}$$

$$V_1 = \frac{RT}{P} + B_{11} = \bar{V}_1$$

Now this expression for the V_1 bar similarly you can do the same exercise for V_2 bar and without writing down the detail derivation I can simply write here the following. So now you

have both partial molar property, now to obtain let us say that you would like to obtain molar volume for pure species, to obtain molar volume let us say for V_1 then we will put y_2 is equal to 0 and here \bar{V}_1 would become V_1 .

And we can get this V_1 is nothing but $\frac{RT}{P}$ plus B_{11} that is what you expect. If you put y_2 is equal to 0 here and y_1 naturally will be 1 hence \bar{V}_1 by is equal to V_1 , molar volumes small 1, molar volume for the pure case and that will be your expression for the component 1. So, this is something which you expect anyway, so this is something which you can get from this expression right.

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To obtain molar vol., $v_i \rightarrow ?$ $y_2 = 0$

$$\bar{V}_1 = \frac{RT}{P} + B_{11} = V_1$$

$$\Delta V_{mix} = V - \underbrace{(y_1 v_1 + y_2 v_2)}_{\sum y_i \bar{v}_i}$$

Substituting in for v_1 & v_2

$$\Delta V_{mix} = \left[\frac{RT}{P} + y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \right] - \left[y_1 \left(\frac{RT}{P} + B_{11} \right) + y_2 \left(\frac{RT}{P} + B_{22} \right) \right]$$

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$$\bar{V}_1 = \frac{RT}{P} + B_{11}$$

$$\Delta V_{mix} = V - (y_1 v_1 + y_2 v_2)$$

$$\downarrow \sum y_i \bar{v}_i$$

Substituting in for v_1 & v_2

$$\Delta V_{mix} = \left[\frac{RT}{P} + y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \right] - \left[y_1 \left(\frac{RT}{P} + B_{11} \right) + y_2 \left(\frac{RT}{P} + B_{22} \right) \right]$$

$$\Delta V_{mix} = 2y_1 y_2 \left[B_{12} - \frac{B_{11} + B_{22}}{2} \right]$$

$$\Delta V_{mix} = V - (y_1 V_1 + y_2 V_2)$$

$$\Delta V_{mix} = \left[\frac{RT}{P} + y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \right] - \left[y_1 \left(\frac{RT}{P} + B_{11} \right) + y_2 \left(\frac{RT}{P} + B_{22} \right) \right]$$

$$\Delta V_{mix} = 2y_1 y_2 \left[B_{12} - \frac{B_{11} + B_{22}}{2} \right]$$

I mean if you look at it y_1 and y_2 is going to be positive, so the sign of V_{mix} whether it is positive.

And it depends upon the competitive behaviour here for the case of POPO and with pure with like and unlike, so essentially you have a term here 1, 2. If interaction between the component 1 and 2 is extremely strong then that corresponds to POPO case. So that means if this value, because usually this B is going to be negative, so the interactions are strong then essentially this will become more negative, so that means they would like to come closer.

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Handwritten slide content showing the derivation of the mixing volume change equation and a note on its sign and magnitude.

$$\Delta V_{mix} = 2y_1 y_2 \left[B_{12} - \frac{B_{11} + B_{22}}{2} \right]$$

Sign & magnitude is determined by comparing the strength of unlike interaction B_{12}

$$B_{12} > \frac{1}{2} (B_{11} + B_{22}) \Rightarrow \Delta V_{mix} < 0$$

(large negative no)

So, let me just write down some salient features based on this expression. So that means the sign here and magnitude is determining by comparing the strength of unlike interaction B_{12} . So, if the unlike interaction this B_{12} it is much stronger than the average B_{11} plus B_{22} , this would mean that ΔV_{mix} is negative. Now usually this means stronger because this is usually, the value would be large negative number, that is what it means because if it is stronger it means you will have large negative numbers here because B_{12} is kind of interaction strength.

So, this essentially V_{mix} negative would indicate that 12 particles will be closer it will be more compact arrangements will be there between the unlike particles. If it is positive or if V

mix is greater than 0 it remains like like interactions are stronger compared to unlike interaction and they would be more expanded because essentially they will not like to mix in that case. So, the signs gives you a very interesting way to understand the interaction strength between the particles without knowing the molecule nature you could get a better feeling that what kind of system you are talking about here. So, let us take an example to listed a bit more on this.

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Example
 Consider a binary mix of 10 mol% of chloroform (1)
 in acetone (2) at 333K & 10 bar

$B_{11} = -910$
 $B_{22} = -1330$
 $B_{12} = -205$

$\left. \begin{array}{l} B_{11} = -910 \\ B_{22} = -1330 \\ B_{12} = -205 \end{array} \right\} \text{ cm}^3/\text{mol}$ Determine v_1, \bar{V}_1 & ΔV_{mix}

$v_1 = \frac{RT}{P} + B_{11} = 1840 \text{ cm}^3/\text{mol}$

$\bar{V}_1 = 991 \text{ cm}^3/\text{mol}$

$\Delta V_{\text{mix}} = 2x_1x_2 \left[B_{12} - \frac{B_{11} + B_{22}}{2} \right]$

$B_{11} = -910$
 $B_{22} = -1330$
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$\left. \begin{array}{l} B_{11} = -910 \\ B_{22} = -1330 \\ B_{12} = -205 \end{array} \right\} \text{ cm}^3/\text{mol}$ Determine v_1, \bar{V}_1 & ΔV_{mix}

$v_1 = \frac{RT}{P} + B_{11} = 1840 \text{ cm}^3/\text{mol}$

$\bar{V}_1 = 991 \text{ cm}^3/\text{mol}$

$\Delta V_{\text{mix}} = 2x_1x_2 \left[B_{12} - \frac{B_{11} + B_{22}}{2} \right]$

or
 $\Delta V_{\text{mix}} = x_1x_2 \left[2B_{12} - B_{11} - B_{22} \right] = -372 \text{ cm}^3/\text{mol}$

$$V_1 = \frac{RT}{P} + B_{11}$$

$$\Delta V_{\text{mix}} = 2x_1x_2 \left[B_{12} - \frac{B_{11} + B_{22}}{2} \right]$$

$$\Delta V_{\text{mix}} = x_1x_2 [2B_{12} - B_{11} - B_{22}] = -372 \frac{\text{cm}^3}{\text{mol}}$$

So let us consider binary mixture of 10 mole percent of chloroform which we are saying it is component 1 in acetone which is component 2, so it is a solution basically at some temperature which is 333 Kelvin and 10 bar, so the second...so what we have given as second coefficients are given to us and what is known is B_{11} is minus 910 B_{22} is minus 1330 B_{12} is minus 205 all in centimetre cube per mole.

So what is being asked that we should find out small V molar volume of component 1 V_1 bar and ΔV small v mix, so this is the question we have been asked, so we can make use of the virial equation of state for the mixture truncated till the second virial coefficients because second virial coefficients is the one which is given to us, so will start with that okay so we know the expression already for V_1 bar, V_1 is nothing but RT/B_{11} .

So we know the expression v_1 , so we can directly use that here so this comes out to be 1860 centimetre cube per mole. Similarly V_1 bar we calculated it, so V_1 bar is this expression, so instead of y we are going to put x because of the solution and we are saying that virial equation of state is still valid here for this liquid phase.

So if you put there it comes out to be 991 centimetre cube per mole. Then the last thing is your ΔV mix which we said 2 so instead of y I am going to write $x_1 x_2$ B_{12} minus B_{11} plus B_{22} or ΔV mix can be written as $x_1 x_2$ B_{12} minus B_{11} minus B_{22} . So we know x_1 and x_2 we know the B , so with this comes out to be minus 372 centimetre per mole okay. Now what you should note is that the pure component of chloroform in acetone is 1860 centimetre per mole that is pure for molar volume for component one. On the other hand the partial molar volume for component one that is chloroform is almost half of this amount, so why is that?

That means the contribution to the total is reduced and this is due to the strong hydrogen bond between the chloroform and the carbonyl group of the acetone. And because of the strong hydrogen bond that means your B_{12} is very strong, so B_{12} is very large negative so this should have been 05, so because of this B_{12} which is extremely large this indicates also that there is a strong binding or attraction between component 1 and 2 which pulls the species in the mixture closer to each other and this results in reduction in the solution volume and that is why your Δv mix is negative.

So usually this kind of interactions are not very common in most of the mixture, hydrogen bonds are very specific set of component which allows you to have such kind of a strong

binding leading to reduction in the volume but clearly this gives you indicative particularly the wave coefficients can be an indicative of what kind of interaction, what you expect and leading to the facts on the volumetric properties.

So, I hope that with this 2 examples we got to learn a bit that how do we make use of equation of state, analytical ways to solve problems related to the mixtures using virial equation for example or you could also come up with other equation of state. So that would be the end of today's class, so we will see you next time and we will elaborate more on this particularly from the graphical approach, so I will see you in the next lecture.