Chemical Engineering Thermodynamics
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Lecture 34
Thermodynamics of Mixtures

Welcome back, in today's lecture we are going to talk about thermodynamics of mixtures. In case of pure fluid, the interaction between the components are similar. So, for example if you have only component, let us say i, so ii interactions govern the thermodynamic properties such as the internal energy, free energy and so forth, okay. However, for the case of mixtures you will have unlike introductions.

So, for example, in the case of, let us say 2 component system A and B you will have an interaction such as between aa, ab and as well as bb. So, these are the interaction which will govern the properties of the system, okay. So, that means intermolecular interactions between different components or that is interspecies interaction will affect the properties.

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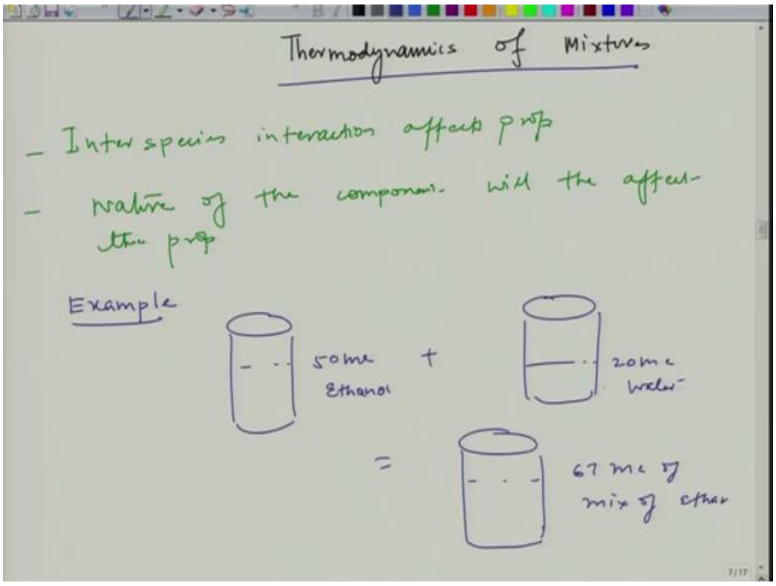

Thermodynamics of Mixtures

- Interspecies interaction affects prop
- Nature of the component will the affect the prop

Example

50ml Ethanol + 20ml water

= 67 ml of mix of ethan

Okay, so that is what I expect of it. Of course, the nature of the species or the component will also affect the properties. Okay, so let us take an example to illustrate bit of the impact of mixing 2 comments. One of the examples could be, a mixture of ethanol and water. So, let us say we have taken, let us say 50ml ethanol and we add this to 20ml water. So, what you expect the final volume of the system. Would it be 70 or will it be more 72, 73 or will it be less?

So it turns out that the final volume in this case would be 67 milliliter of mixture of ethanol with water. So what is the reason for reduction in the volume effectively? So, in this case since ethanol also has OH group and water has also OH group, so essentially it allows them to form hydrogen bond. So, due to the nature of the hydrogen bond involved in the structure, the final solution behaved differently than simple additive effects of these 2 components.

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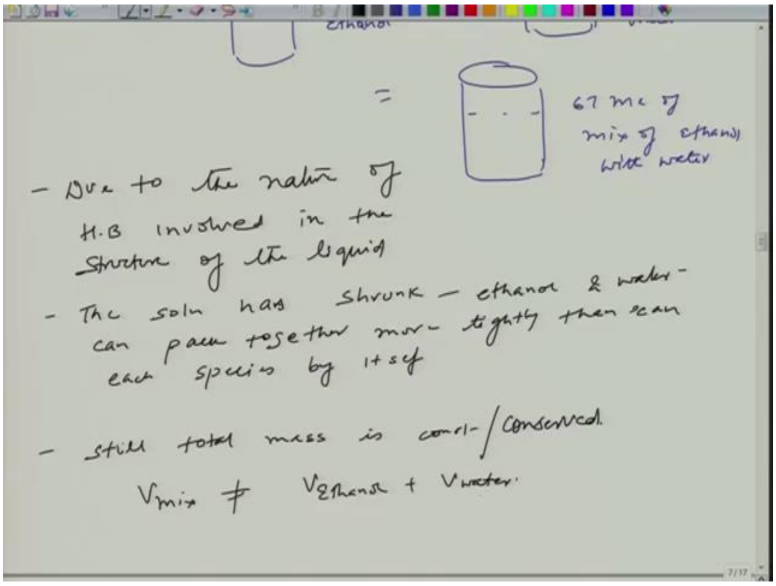

- Due to the nature of H.B involved in the structure of the liquid
- The soln has shrunk – ethanol & water – can pack together more tightly than can each species by itself
- still total mass is const/conserved.

$V_{mix} \neq V_{ethanol} + V_{water}$

So, that means the nature here, the final volume which has been reduced is due to the nature of hydrogen bond involved in the structure of the liquid, okay. This hydrogen formed bond allows specific kind of the geometry and which eventually shrinks the solution, so that means the solution has shrunk the ethanol and water that means ethanol and what can form or can pack together more tightly, right? That is why the volume has reduced. So then can each species by themselves.

Now, notice that the final mass of the final mixture still remains the same that means the total mass is conserved, right, is constant or conserved, okay. However, V mix is not equal to V of ethanol plus V of water. So, what is something which is evident from this exercise is that the properties in this case clearly depend on the interactions, okay. And, of course, it also will depend on the amount which we added here that is something which we are going to look at but interactions play a big role, okay.

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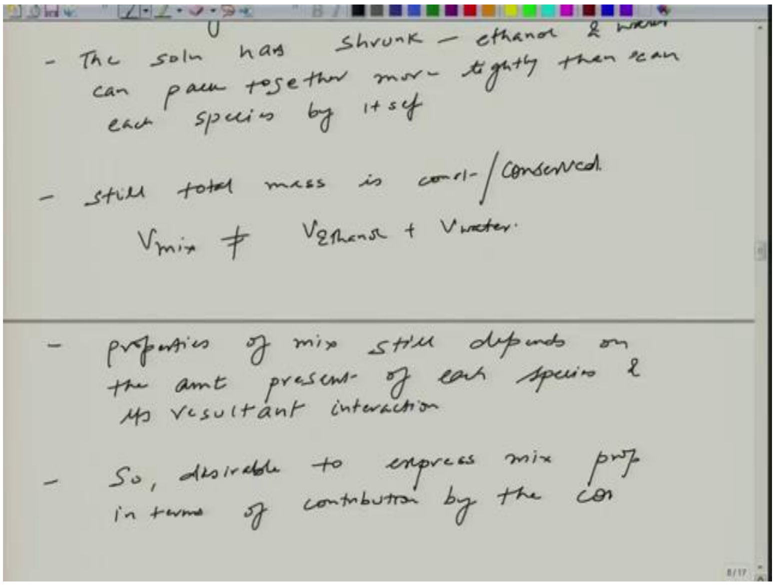
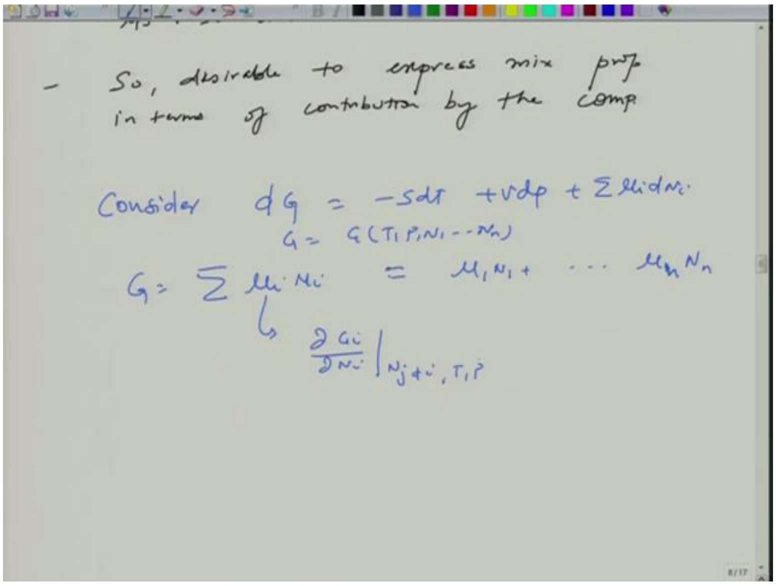


- The soln has shrunk — ethanol & water can pack together more tightly than can each species by itself
- still total mass is cons- / conserved

$V_{mix} \neq V_{ethanol} + V_{water}$.

- properties of mix still depends on the amt present of each species & its resultant interaction
- So, desirable to express mix prop in terms of contribution by the con



- So, desirable to express mix prop in terms of contribution by the comp

Consider $dG = -sdT + vdp + \sum \mu_i dN_i$

$G = G(T, P, N_1 \cdots N_n)$

$G = \sum \mu_i N_i = \mu_1 N_1 + \cdots \mu_n N_n$

$\hookrightarrow \frac{\partial G_i}{\partial N_i}\Big|_{N_{j \neq i}, T, P}$

So, properties of mixture still depend on the amount present of each species and resulted, its resultant interaction. So that is why we prefer to express the mixtures property in terms of the contribution from each component. So, this is the reason that we desire, so it is desirable to express mixture property in terms of contribution by the component, okay. So, let us little bit explore this how to express mixture properties in terms of contribution by the component, okay.

So, for that let me consider going back to the fundamentals of thermodynamic expressions.

$$dG = -sdT + vdP + \sum \mu_i dN_i$$

$$G = G(T, P, N_1, \dots N_n)$$

$$G = \sum \mu_i N_i = \mu_1 N_1 + \cdots + \mu_n N_n$$

$$\mu_i = \frac{\partial G_i}{\partial N_i}\Big|_{N_{j\neq i,T,P}}$$

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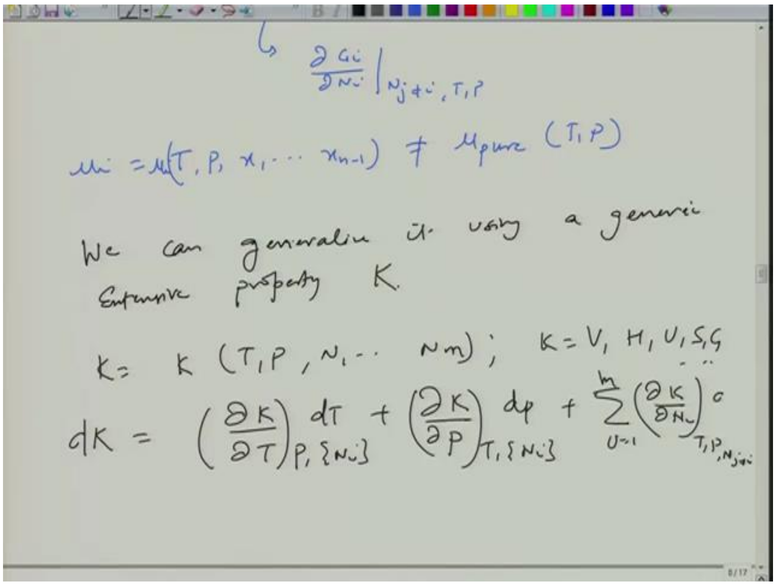

↳ $\frac{\partial G_i}{\partial N_i}\Big|_{N_{j\neq i},T,P}$

$\mu_i = \mu_i(T, P, x_1, \cdots x_{n-1}) \neq \mu_{pure}(T, P)$

We can generalize it using a generic extensive property K.

$K = K(T, P, N_1 \cdots N_m)$; $K = V, H, U, S, G$

$dK = \left(\frac{\partial K}{\partial T}\right)_{P,\{N_i\}} dT + \left(\frac{\partial K}{\partial P}\right)_{T,\{N_i\}} dp + \sum_{U=1}^{m}\left(\frac{\partial K}{\partial N_i}\right)_{T,P,N_{j\neq i}}$

$$\mu_i = \mu_i(T,P,x_1,\dots,x_{n-1}) \neq \mu_{pure}(T,P)$$

$$k \rightarrow generic\ extensive\ property$$

$$k = k(T,P,N_1,\dots,N_n)\ ;\ \ k = V,H,U,S,G$$

$$dk = \left(\frac{\partial k}{\partial T}\right)_{P,\{N_i\}} dT + \left(\frac{\partial k}{\partial P}\right)_{T,\{N_i\}} dP + \sum_{U=1}^{m}\left(\frac{\partial k}{\partial N_i}\right)_{T,P,\{N_{j\neq i}\}} dN_i$$

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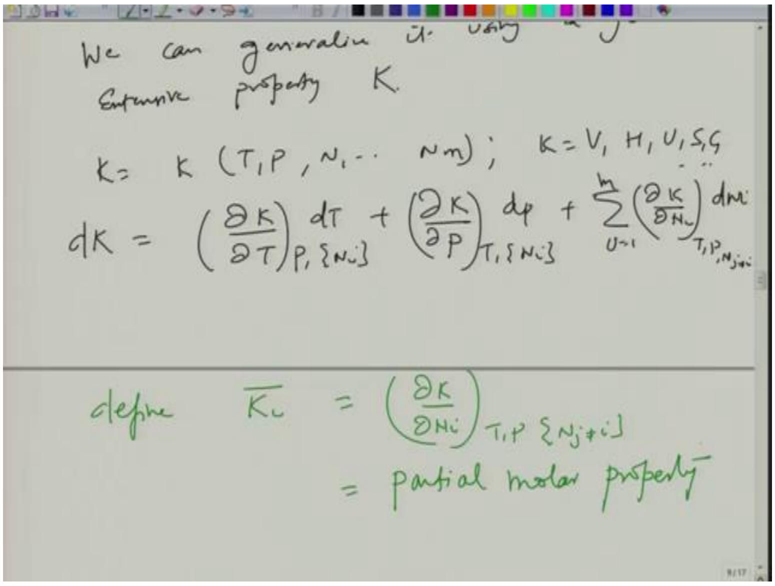


We can generalize it using a

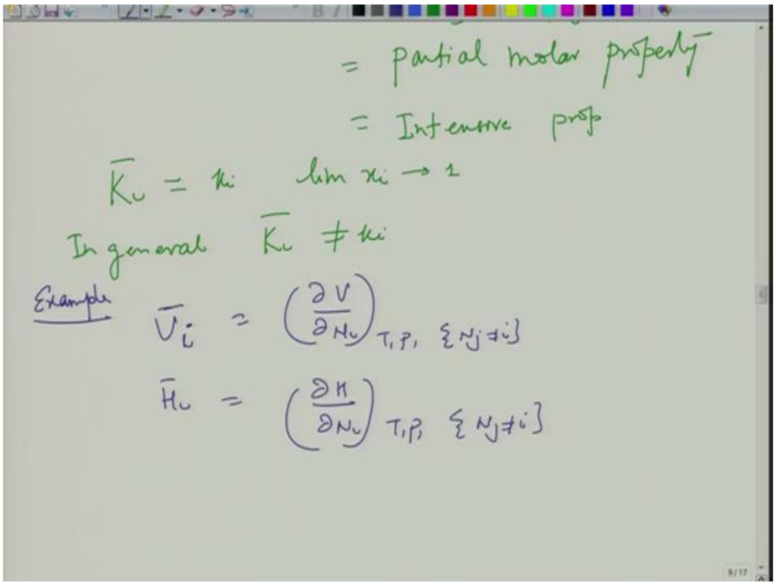
Extensive property K.

$K = K(T, P, N_1 \ldots N_m)$; $K = V, H, U, S, G \ldots$

$$dK = \left(\frac{\partial K}{\partial T}\right)_{P,\{N_i\}} dT + \left(\frac{\partial K}{\partial P}\right)_{T,\{N_i\}} dP + \sum_{i=1}^{m}\left(\frac{\partial K}{\partial N_i}\right)_{T,P,N_{j\neq i}} dN_i$$

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

= partial molar property



= partial molar property

= Intensive prop

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

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

Example

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

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

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

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

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

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

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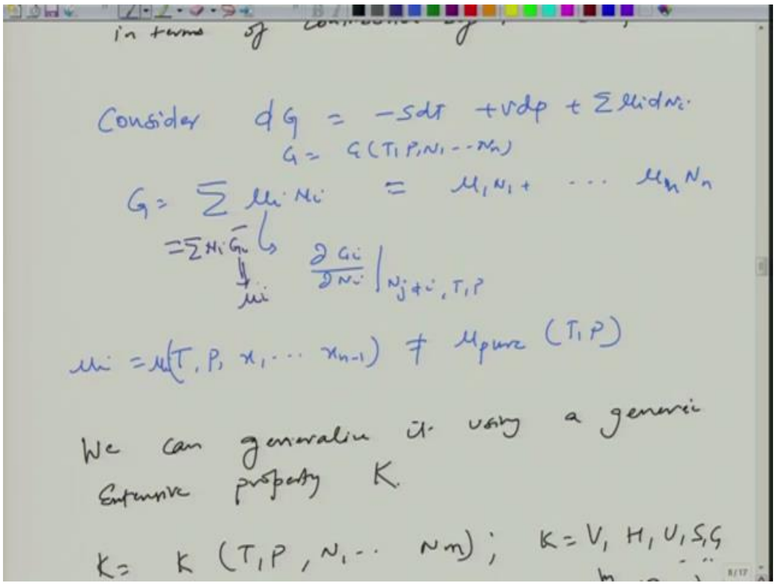

in terms of

Consider $dG = -SdT + VdP + \sum \mu_i dN_i$

$G = G(T, P, N_1 \dots N_n)$

$G = \sum \mu_i N_i = \mu_1 N_1 + \dots \mu_n N_n$

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

$\bar{G}_i \to \mu_i$ $\quad \frac{\partial G_i}{\partial N_i}\Big|_{N_{j \neq i}, T, P}$

$\mu_i = \mu(T, P, x_1, \dots x_{n-1}) \neq \mu_{pure}(T, P)$

We can generalize it using a generic extensive property K.

$K = K(T, P, N_1 \dots N_m)$; $K = V, H, U, S, G$ ...

Now, similar to the case of the Gibbs free energy when the Euler expression, Euler integration was used in order to get this expression, similarly, we can also look at that for the case of K.

$$G = \sum N_i \bar{G}_i = \sum N_i \mu_i$$

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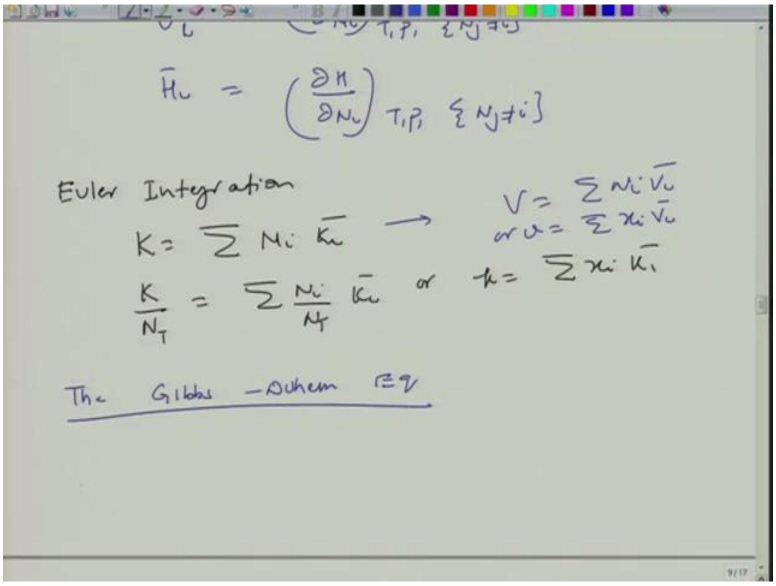

$\bar{H}_i = \left(\frac{\partial H}{\partial N_i}\right)_{T, P, \{N_j \neq i\}}$

Euler Integration

$K = \sum N_i \bar{K}_i \longrightarrow V = \sum N_i \bar{V}_i$ or $v = \sum x_i \bar{V}_i$

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

The Gibbs-Duhem Eq

So, let me now extend this thing exercise for the case of K.

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

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

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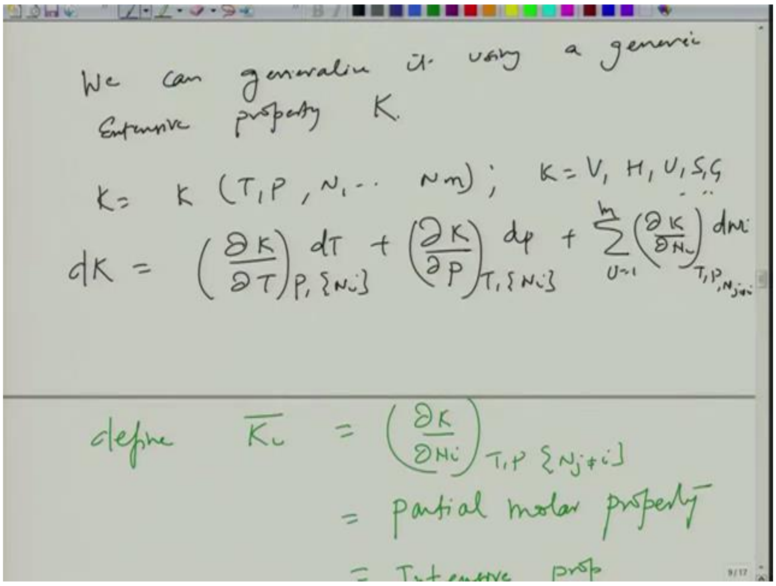

We can generalize it using a generic Extensive property K.

$$K = K(T, P, N_1 \cdots N_m); \quad K = V, H, U, S, G \ldots$$

$$dK = \left(\frac{\partial K}{\partial T}\right)_{P, \{N_i\}} dT + \left(\frac{\partial K}{\partial P}\right)_{T, \{N_i\}} dp + \sum_{i=1}^{m} \left(\frac{\partial K}{\partial N_i}\right)_{T, P, N_{j \neq i}} dN_i$$

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

= partial molar property

= Intensive prop

So, let us again look at K is nothing but summation Ki bar dn bar.

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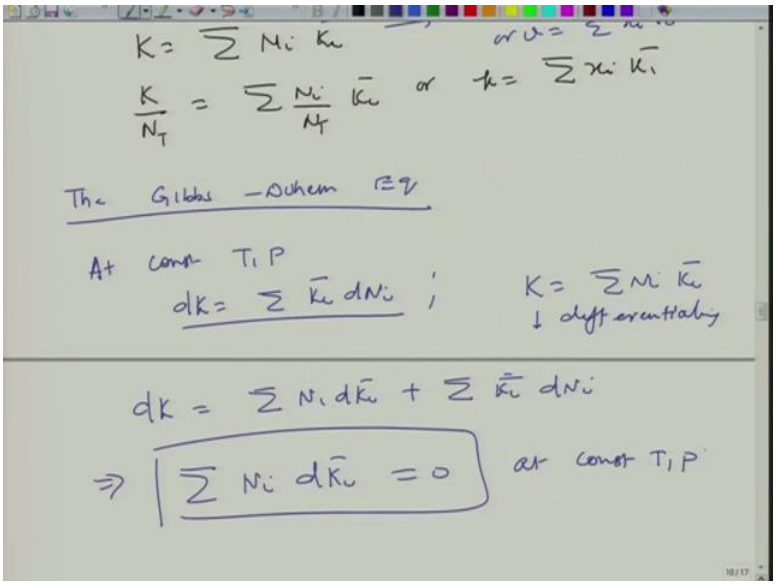

$K = \sum N_i \bar{K}_i$ or $v = \sum x_i$

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

The Gibbs-Duhem Eq

At const T, P

$dK = \sum \bar{K}_i dN_i$; $K = \sum N_i \bar{K}_i$ ↓ differentiating

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

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

$$Gibbs - Duhem\ eqn: \quad at\ const\ T, P$$

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

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

$$\sum N_i d\bar{K}_i = 0\ \ at\ const. T, P$$

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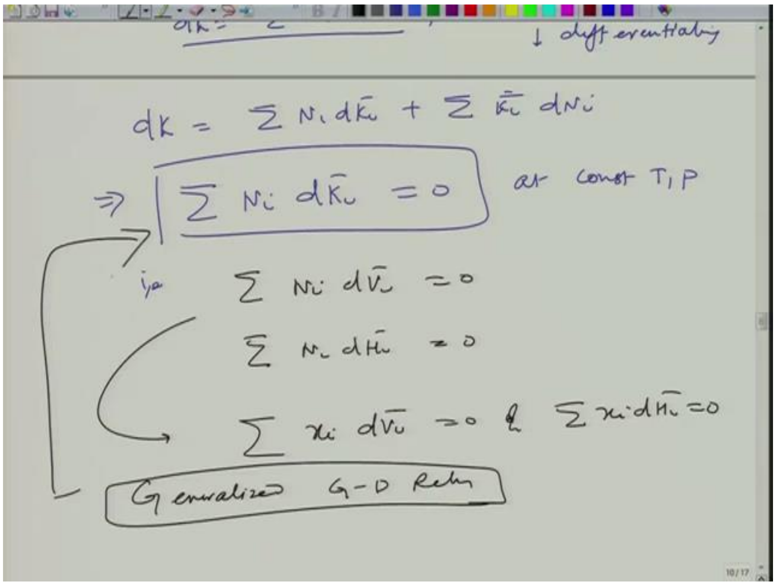

↓ differentiating

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

$\Rightarrow \boxed{\sum N_i d\bar{K}_i = 0}$ 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

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

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

$$\sum x_i d\overline{V_\iota} = 0 \; and \; \sum x_i d\overline{H_\iota} = 0$$

So, that means I can write this as Ni dvi, bar this has to be 0 at a constant temperature and pressure. Similarly, this will also hold the following, okay. I can also divide by total number of molecules, total number of moles here and I can get here in terms of composition and summation xi dHi equal to 0, okay. So, this is what we have is generalized Gibbs Duhem relation. That is something which you can say that, okay.

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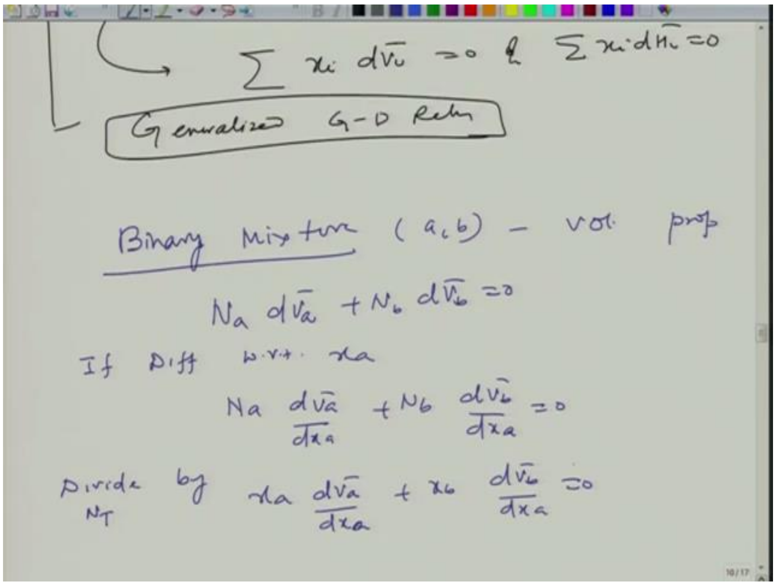

$\sum x_i d\bar{V_i} = 0$ & $\sum x_i d\bar{H_i} = 0$

Generalized G-D Reln

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 $\quad x_a \frac{d\bar{V_a}}{dx_a} + x_b \frac{d\bar{V_b}}{dx_a} = 0$

Now, let us apply for the property of volume for the binary mixtures. So, let us try to do an example for the binary mixture, okay and use this Gibbs Duhem relation. So, for the binary mixture let us say, it is a, b, okay. I can write this as N of a, okay and since, we are interested in let us say volume, property for volume, volume property.

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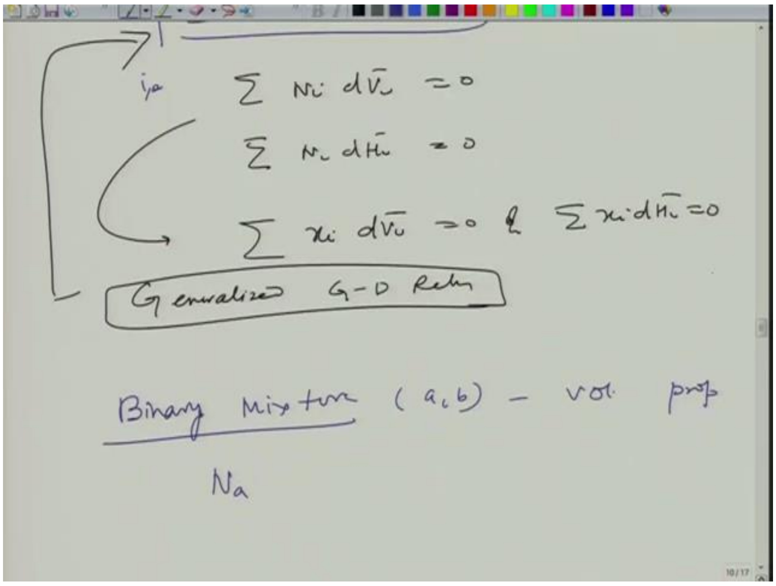

i.e. $\sum N_i d\bar{V}_i = 0$

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

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

Generalized G-D Reln

Binary Mixture (a, b) - vol. prop

N_a

We want to apply this summation expression for volume.

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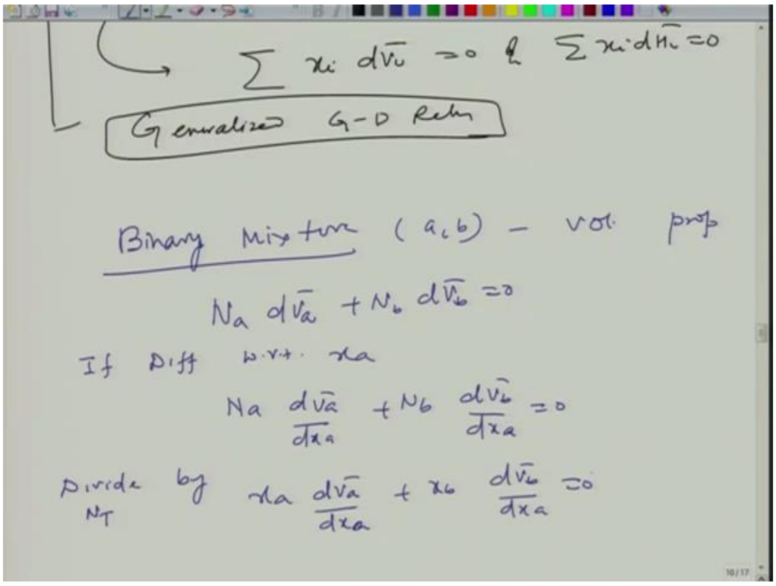

$\sum x_i d\bar{V}_i = 0$ & $\sum x_i d\bar{H}_i = 0$

Generalized G-D Reln

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

$$Binary\ Mixture:\ (a,b)$$

$$N_a d\overline{V_a} + N_b d\overline{V_b} = 0$$

$$Diff\ wrt\ x_a:\ \frac{N_a d\overline{V_a}}{dx_a} + \frac{N_b d\overline{V_b}}{dx_a} = 0$$

$$Dividing\ by\ N_T:\ \frac{x_a d\overline{V_a}}{dx_a} + \frac{x_b d\overline{V_b}}{dx_a} = 0$$

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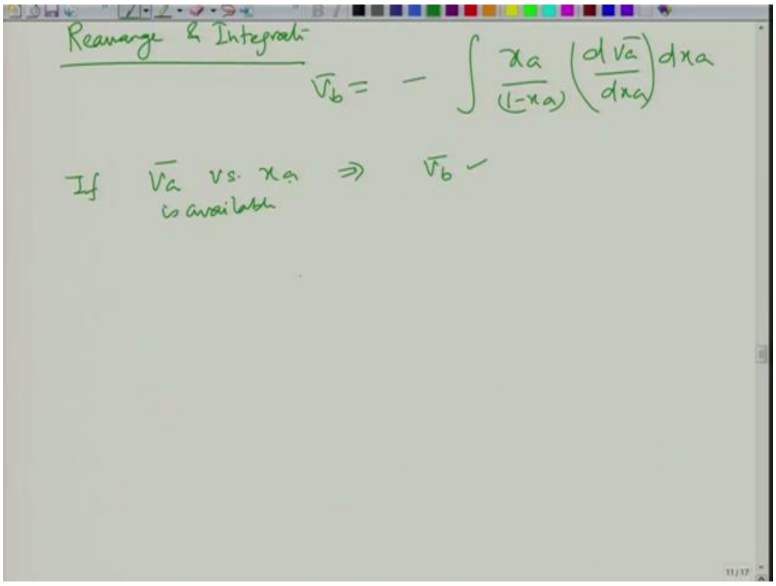

Rearrange & Integrate

$$\bar{V_b} = - \int \frac{x_a}{(1-x_a)} \left(\frac{d\bar{V_a}}{dx_a}\right) dx_a$$

If $\bar{V_a}$ vs. x_a is available $\Rightarrow$ $\bar{V_b}$ ✓

$$Rearranging\ and\ integrating\colon\ \overline{V_b} = -\int \frac{x_a}{1-x_a}\left(\frac{d\overline{V_a}}{dx_a}\right)dx_a$$

Now, let us try to simplify a bit here. Okay, so if you rearrange and integrate, okay. So, if you rearrange and integrate, I can get this expression as, let us say if you are looking at only b here then it is Vb bar is going to be minus, okay. I can write xa plus xb is equal to 1 or in other words I get xb as 1 by xa and this term as dva by dxa. So, essentially, I have this divided xb here and replace xb by 1 minus xa taking to the other side, got a negative sign here and then this is the term which I got and then we have to integrate with dxa, okay. So, this is the expression we got, okay.

So, it tells you that va bar versus xa that means partial molar property of a component A as a function of the composition of the component A if that is available then I should be able to find out the partial molar property of a Vb, okay. So, if this relation is available, I should be able to find out the Vb, okay. That is what we got from this exercise.

So, let me continue this, now we talked about typical property and in terms of molar properties, the typical property of a mixture can be expressed in terms of the molar properties. So, that is something which we have looked at but what about the change in mixing. For example you added the volumes, so what about the change in the volume which you observed upon mixing. So that is something which many times is relevant and important.

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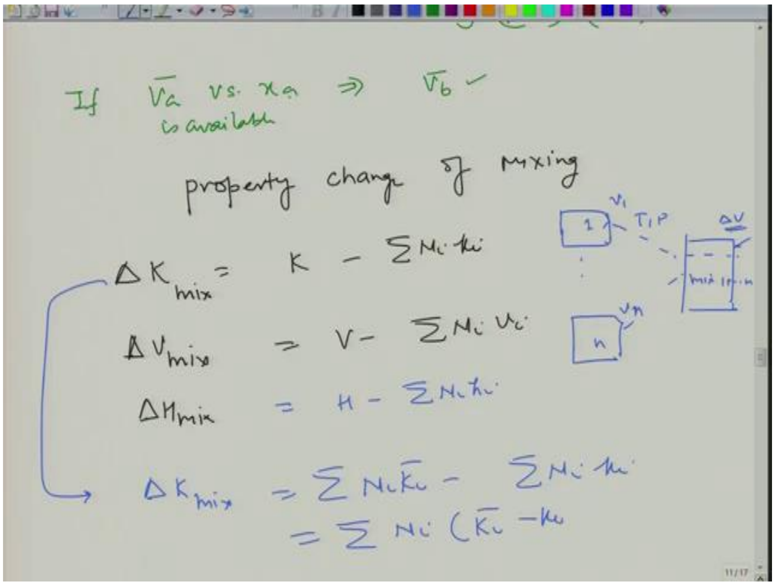

So, now let me just talk about that. So what we are interested is now is property change of mixing upon mixing, okay. So, if we are talking about generalized extensive variable K then we can use this K here, Delta K mix all we can define this as the K of the mixture minus summation and I, small ki, okay. So, it tells you that if you have added the components K and the corresponding moles here, so it is like literally the effective additive individually if you are just adding up the pure component and then you subtract that from the file property and whatever the changes there that would be a change in the mixing.

So, in other words if you are talking about let us say volume this would be your V minus summation ni, vi, okay where Vi is a pure molar volume of component i, okay. And this is the moles of a component i, okay and similarly for Delta H mix, okay. So, if you think from this point of view let us consider this that essentially, so if you have added, let us say component 1, okay.

At a constant let us say temperature and pressure, okay. And essentially what you are looking at is, for the case of let us say volume here, looking at the change here would be your Delta V, if you have had mixture of 1 plus n here. So this Delta V mix is nothing but whatever the volume it is there final, okay minus the individual volumes here multiplied by molar volumes here multiplied by ni or individual volumes, okay.

So in other words if it is V1 till Vn essentially what is there is Delta V is nothing but V minus of all this Vl till Vn, alright. So we will try to do some examples to understand this bit more. So, we can extend this understanding from V we can also extend to let us say H here, okay. So now in that case I can little bit simplified this expression, okay let us look at again the generalized variable. Now I know that K, we just did that exercise K can be written as nI partial molar property Ki minus Ni small ki. So this can be written as now summation Ni Ki minus ki, okay.

So it just tells you the difference between the molar property and the partial molar property multiplied by the moles and summing it up over all components would give you the change in the property of the mixture, okay.

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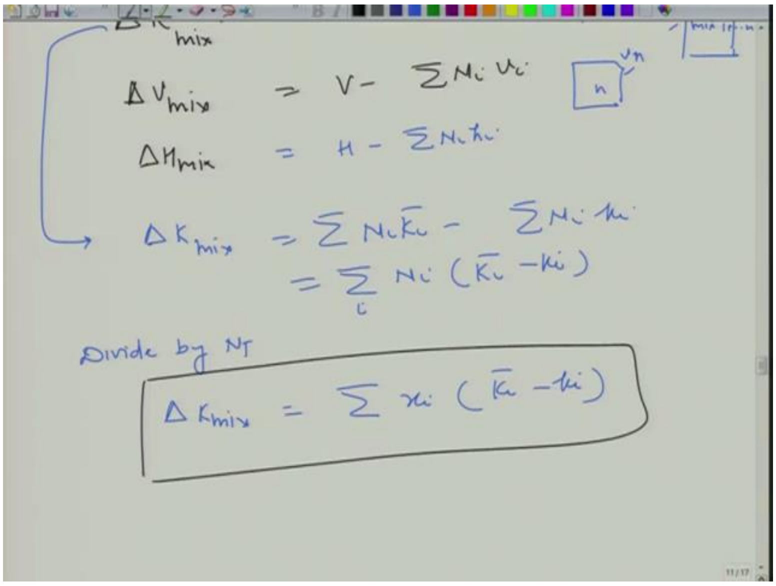

$$\Delta V_{mix} = V - \sum N_i v_i$$

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

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

$$= \sum_i N_i (\bar{K}_i - k_i)$$

Divide by N_T

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

$$Property\ change\ of\ mixing: \quad \Delta K_{mix} = K - \sum N_i k_i$$

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

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

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

$$Dividing\ by\ N_T: \ \Delta K_{mix} = \sum x_i (\bar{K}_i - k_i)$$

So if you divide by NT I get now Delta k mix as summation xi Ki bar minus Ki, so this is my final expression as far as Delta k mix is concerned, okay.

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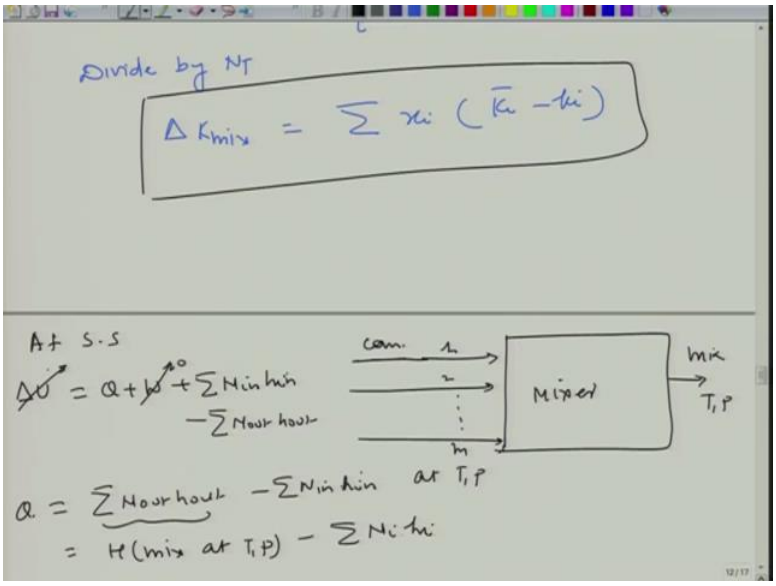

Divide by N_T

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

At S.S

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

$$Q = \underbrace{\sum N_{out} h_{out}} - \sum N_{in} h_{in}$$

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

Now, let us try to little bit of some kind of exercise here. So, let us consider case of mixture, okay. And let us say that we are giving this component, we are adding this component 1, 2 and let us say this is m here, okay. And finally, so these are component 1, 2 and 3 to the m and finally we have a mixed system which is at T and P, okay. And these are all components; let us assume that they are also at T and P.

So, at a steady-state we can apply the first law for the open system and we can write this Delta u of this system here which is the mixtures is Q plus W whatever the work related plus summation N of in h in minus summation N of out h out. Now, consider that there is, of course, a rigid mixture that means there is no boundary work. Considering, of course, the steady-state of course this has to go to 0.

What remains is now this Q. Q can be written as summation N out h out minus summation N in and small h in, okay. Now this here is nothing but single 1, okay there is only one here and essentially this is nothing but H of mix at TP and this is nothing but summation Ni small h i, right?

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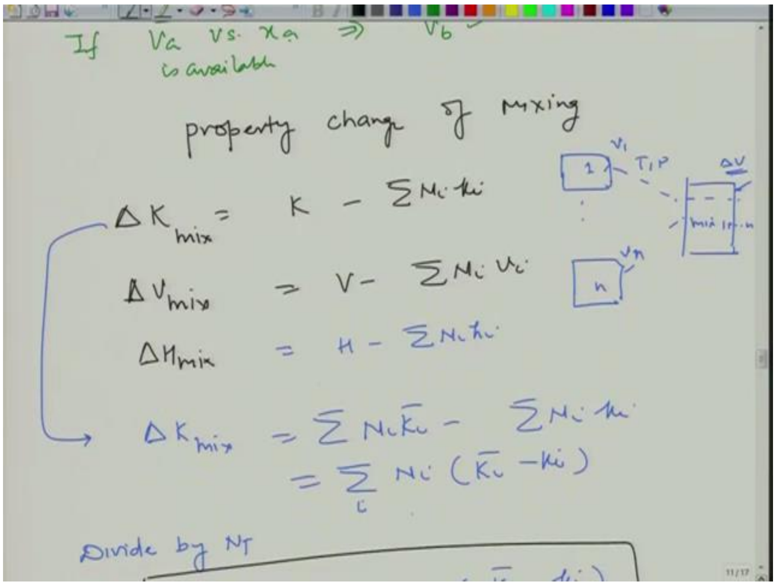


If V_a vs. x_a is available ⇒ V_b

property change of mixing

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

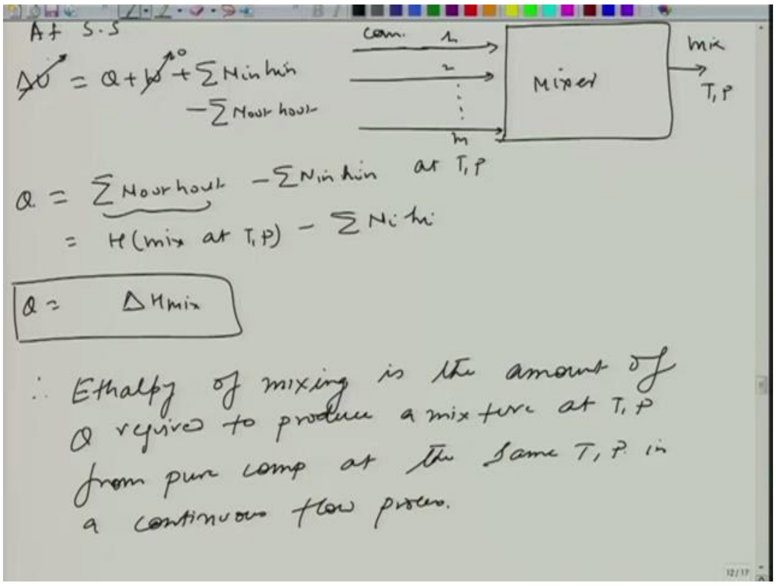
$\Delta V_{mix} = V - \sum N_i v_i$

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

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

$= \sum_i N_i (\bar{K}_i - k_i)$

Divide by N_T



At S.S

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

$Q = \underbrace{\sum N_{out} h_{out}} - \sum N_{in} h_{in}$ 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.

$$At\ steady\ state:\quad \Delta U = Q + W + \sum N_{in} h_{in} - \sum N_{out} h_{out}$$

$$Q = \sum N_{out} h_{out} - \sum N_{in} h_{in} = H(mix\ at\ T, P) - \sum N_i h_i$$

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

Now, if you look at the expression here, okay. This expression tells you that for a steady-state system function like this Q is nothing but Delta H mix. So Q is nothing but Delta H mix essentially enthalpy of mixing is the amount of Q required to produce a mixture at TP from pure component at the same temperature pressure in a continuous flow process, okay.

So this is what clearly tells out that their Delta H mix in this case is nothing but simply the Q which is required to makes the component at the same temperature and produces at the same temperature. So what we did is, we simply defined how to use the partial molar property which is the contribution given by each component towards the final property.

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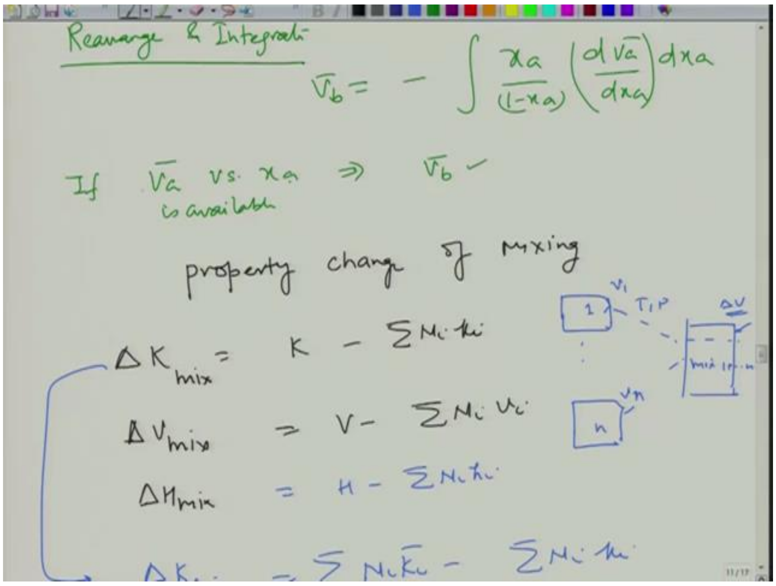

Rearrange & Integrati

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

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

property change of mixing

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

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

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

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

And now this particular definition and exercise what we have just gone through is something which you are going to now taking in the next lecture with some examples and elaborate more on this concept, okay. So that to be the end of this class.