Chemical Engineering Thermodynamics
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Lecture 37
Obtaining the Partial Molar Properties from Experimental Data

Welcome back. In the last class we were discussing about how to find partial molar properties using analytical equation of state. In today's class we will start with obtaining partial molar properties through experimental data. So, we will start with that and later on we will move into finding out the mixture property for ideal solution on first with the gas and then followed by solution.

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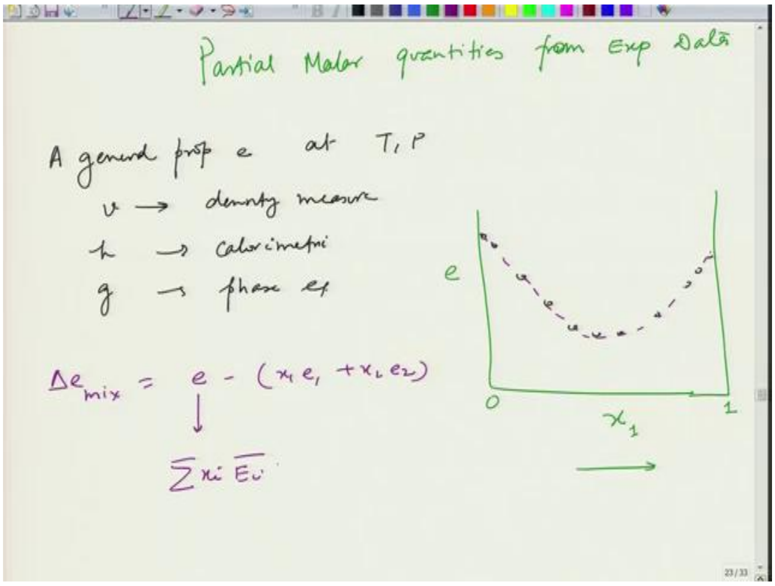

So, in case you have molar properties then you can as a function of composition then you can find partial molar quantities from the experimental data. So, let us assume that we are concerned or we have information of general, let us say property e at a given temperature and pressure. So, e could be volume, could be enthalpy could be free energy so this comes from your density measurement, this comes from calorimetry and this comes from phase diagram.

So, let me just draw a schematic presentation of e as a function of x, let us say component 1 and we are talking from here 0 to 1 and the data which are let us say assuming this starts pure component here. So these are the data, so let me draw kind of a dash line which follows this data. So our interest is to find out partial molar properties. So, let me start with definition again for e mix here and let us consider it as binary mixture.

So, it would be e x1 e1 plus x2 e2, e is for the mixture this is again we are considering the molar properties so it is delta e of mixture, the change in the molar properties of e in the mixture is the e of the mixture minus that of the pure component and e here is nothing but summation xi ei that is the partial molar properties, so what we are interested is to find out e1 bar and e2 bar for the binary mixture.

$$\Delta e_{mix} = e - (x_1 e_1 + x_2 e_2)$$

$$e = \sum x_i \overline{E_\iota}$$

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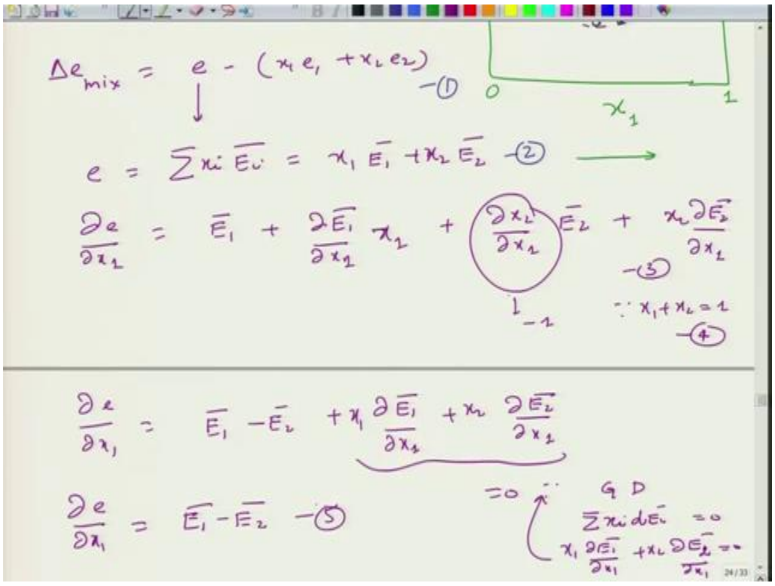

$$\Delta e_{mix} = e - (x_1 e_1 + x_2 e_2) \quad -①$$

$$e = \sum x_i \overline{E_i} = x_1 \overline{E_1} + x_2 \overline{E_2} \quad -②$$

$$\frac{\partial e}{\partial x_1} = \overline{E_1} + \frac{\partial \overline{E_1}}{\partial x_1} x_1 + \underset{-1}{\boxed{\frac{\partial x_2}{\partial x_1}}} \overline{E_2} + \frac{x_2 \partial \overline{E_2}}{\partial x_1} \quad -③$$

$$\because x_1 + x_2 = 1 \quad -④$$

$$\frac{\partial e}{\partial x_1} = \overline{E_1} - \overline{E_2} + \underbrace{x_1 \frac{\partial \overline{E_1}}{\partial x_1} + x_2 \frac{\partial \overline{E_2}}{\partial x_1}}_{=0}$$

$\because$ G D

$$\sum x_i d\overline{E_i} = 0$$

$$x_1 \frac{\partial \overline{E_1}}{\partial x_1} + x_2 \frac{\partial \overline{E_2}}{\partial x_1} = 0$$

$$\frac{\partial e}{\partial x_1} = \overline{E_1} - \overline{E_2} \quad -⑤$$

24/33

$$e = x_1 \overline{E_1} + x_2 \overline{E_2}$$

$$\frac{\partial e}{\partial x_1} = \overline{E_1} + \frac{\partial \overline{E_1}}{\partial x_1} x_1 + \frac{\partial x_2}{\partial x_1} \overline{E_2} + \frac{x_2 \partial \overline{E_2}}{\partial x_2} ; \quad x_1 + x_2 = 1;\ hence, \frac{\partial x_2}{\partial x_1} = -1$$

$$\frac{\partial e}{\partial x_1} = \overline{E_1} - \overline{E_2} + \frac{\partial \overline{E_1}}{\partial x_1} x_1 + \frac{x_2 \partial \overline{E_2}}{\partial x_2}$$

$$Gibbs\ Duhem\ eqn{:} \sum x_i d\overline{E_\iota} = 0$$

$$Thus, \qquad \frac{\partial e}{\partial x_1} = \overline{E_1} - \overline{E_2}$$

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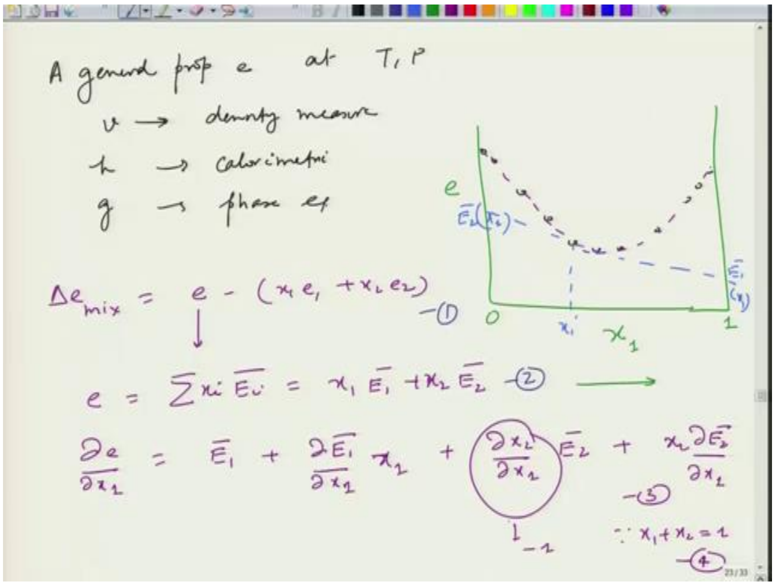


A general prop e at T, P

v → density measure

h → calorimetric

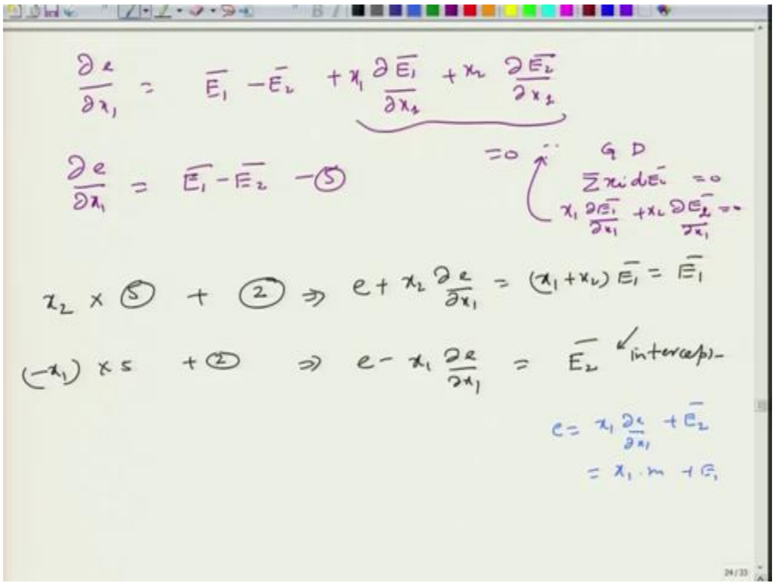
g → phase eq

$$\Delta e_{mix} = e - (x_1 e_1 + x_2 e_2) \quad -①$$

$$e = \sum x_i \bar{E}_i = x_1 \bar{E}_1 + x_2 \bar{E}_2 \quad -②$$

$$\frac{\partial e}{\partial x_1} = \bar{E}_1 + \frac{\partial \bar{E}_1}{\partial x_1} x_1 + \underset{-1}{\boxed{\frac{\partial x_2}{\partial x_1}}} \bar{E}_2 + x_2 \frac{\partial \bar{E}_2}{\partial x_1} \quad -③$$

$$\because x_1 + x_2 = 1 \quad -④$$



$$\frac{\partial e}{\partial x_1} = \bar{E}_1 - \bar{E}_2 + \underbrace{x_1 \frac{\partial \bar{E}_1}{\partial x_1} + x_2 \frac{\partial \bar{E}_2}{\partial x_1}}_{=0}$$

$\because$ G D

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

$$x_1 \frac{\partial \bar{E}_1}{\partial x_1} + x_2 \frac{\partial \bar{E}_2}{\partial x_1} = 0$$

$$\frac{\partial e}{\partial x_1} = \bar{E}_1 - \bar{E}_2 \quad -⑤$$

$$x_2 \times ⑤ + ② \Rightarrow e + x_2 \frac{\partial e}{\partial x_1} = (x_1 + x_2)\bar{E}_1 = \bar{E}_1$$

$$(-x_1) \times 5 + ② \Rightarrow e - x_1 \frac{\partial e}{\partial x_1} = \bar{E}_2 \swarrow \text{intercept}$$

$$e = x_1 \frac{\partial e}{\partial x_1} + \bar{E}_2$$
$$= x_1 \cdot m + \bar{E}_1$$

Now, what I am going to do is I am going to use this equation to simplify this expression because our interest is to find out E1 bar and E2 bar, so I am going to use equation, 5 multiply x2 with that plus I will add equation 2, so equation 5 plus equation 2, this is what I am saying and this would lead to x2 multiplied by equation 2 is, so it is going to be e plus x2 del e by del x1 and right hand side this is x2 E1 minus x2 E2 so I am going to get x1 plus x2 E1 that is your E1 okay, so this is one equation which we got.

Similarly, I can do minus of x1 plus 2, so this will give us e minus x1 del e by del x1 is equal to e2 bar. This is basically nothing but equation of line and we suggest that this is nothing but an intercept here okay. Now this is basically nothing but why x is here this is a slope so if you take a slope at a given value of x, so if you take a slope let us say here at a given value of x, so let us say this is the value of x given here and if you take a slope that would be the de by dx at a given value of x1 okay.

This slope will tell you that on one hand it is going to be even bar and on the other hand it is going to be e2 bar so think about this as nothing but e is equal to x1 del e by del x1 plus e2 bar and this is nothing but some slope plus e2 bar, so this comes from here so essentially e2 bar is in the positive side so this is the e2 bar which we are going to get at that specific x1 and this is going to be e1 bar at that specific x1.

$$e + x_2 \frac{\partial e}{\partial x_1} = (x_1 + x_2)\overline{E_1} = \overline{E_1}$$

$$e - x_1 \frac{\partial e}{\partial x_1} = \overline{E_2}$$

So this is how I am going to obtain the partial molar properties of the let us say e here if you have a data, so I take a slope at a given value of x1 and we look at the intercept at both the ends and obtain the value e1 or e2 bar okay. Similar, to this if data are available not for the molar properties but Delta of e mix then I can use similar kind of exercise to obtain a relation.

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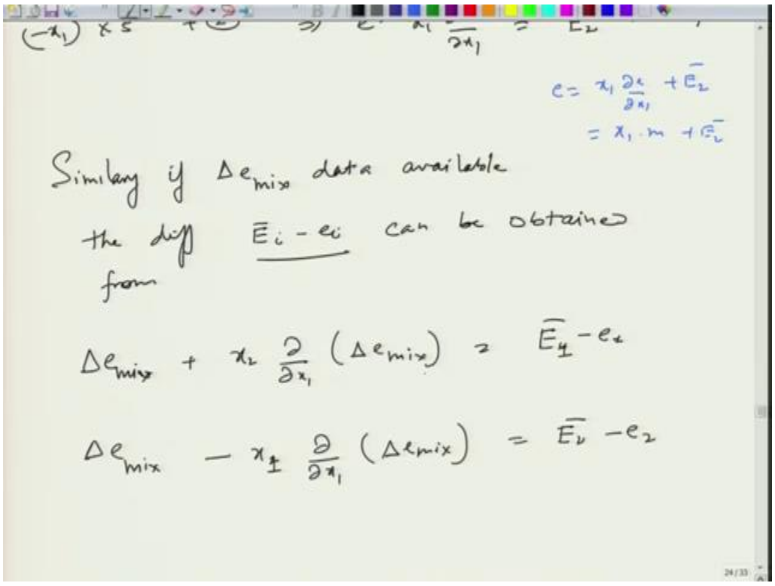
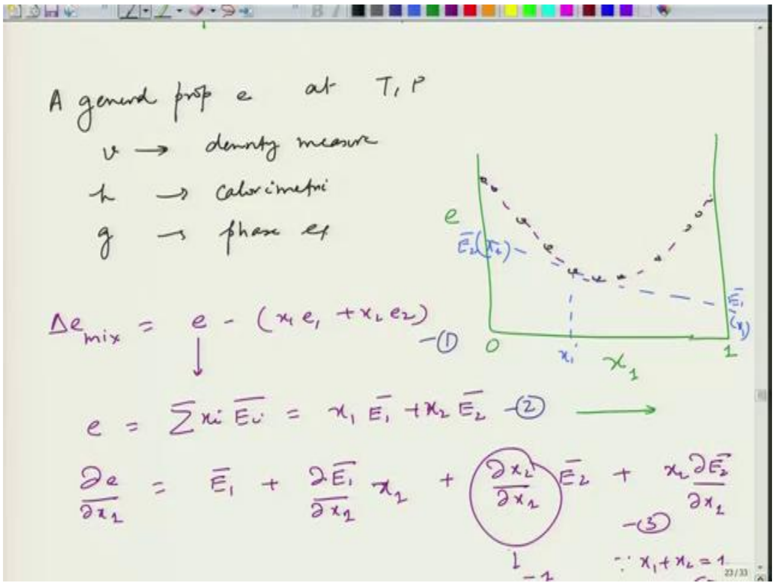


$$e = x_1 \frac{\partial e}{\partial x_1} + \bar{E}_2$$
$$= x_1 \cdot m + \bar{E}_2$$

Similary if Δe_{mix} data available the diff $\underline{\bar{E}_i - e_i}$ can be obtained from

$$\Delta e_{mix} + x_2 \frac{\partial}{\partial x_1}(\Delta e_{mix}) = \bar{E}_1 - e_1$$

$$\Delta e_{mix} - x_1 \frac{\partial}{\partial x_1}(\Delta e_{mix}) = \bar{E}_2 - e_2$$



A general prop e at T, P

v → density measure

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$\Delta e_{mix} = e - (x_1 e_1 + x_2 e_2)$ —①

↓

$e = \sum x_i \bar{E}_i = x_1 \bar{E}_1 + x_2 \bar{E}_2$ —② →

$$\frac{\partial e}{\partial x_1} = \bar{E}_1 + \frac{\partial \bar{E}_1}{\partial x_1} x_1 + \underset{\substack{1\\-1}}{\boxed{\frac{\partial x_2}{\partial x_1}}} \bar{E}_2 + x_2 \frac{\partial \bar{E}_2}{\partial x_1} \quad -③$$

∵ $x_1 + x_2 = 1$

So, similarly if delta e mix is available or data is there, the difference Ei minus small ei can be obtain from the following relation, so it is Delta e mix plus x2 del x1 delta e mix is equal to Ei minus e, so this is let us say 1 so it will be 1. Similarly, delta E mix minus x1 del x1 delta e mix okay so this is going to be 1, this was 2 and this is going to be E2 minus E2 okay so this is the way to obtain the information which is given to you is Delta E mix. So that is the kind of explanation or rather the way we wanted to describe particularly using the data given to us in the form of the E or Delta E as a function of the composition.

$$\Delta e_{mix} + \frac{x_2 \partial}{\partial x_1}(\Delta e_{mix}) = \overline{E_1} - e_1$$

$$\Delta e_{mix} + \frac{x_1 \partial}{\partial x_1}(\Delta e_{mix}) = \overline{E_2} - e_2$$

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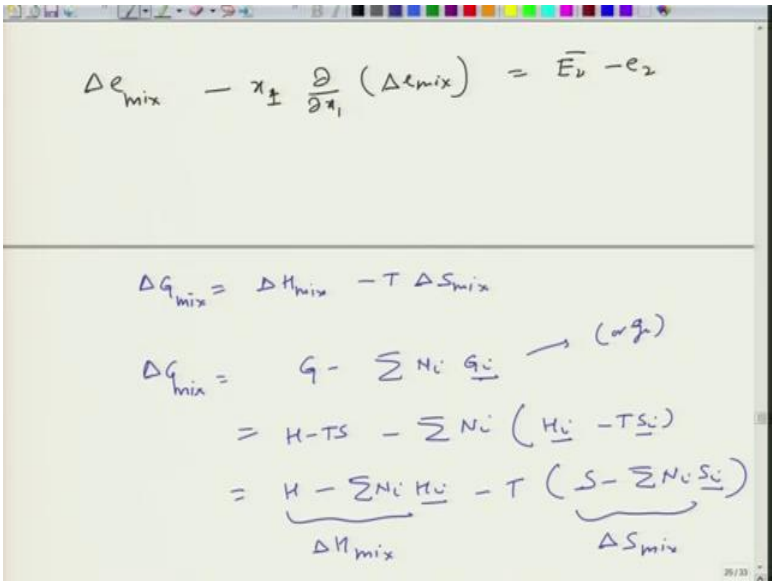


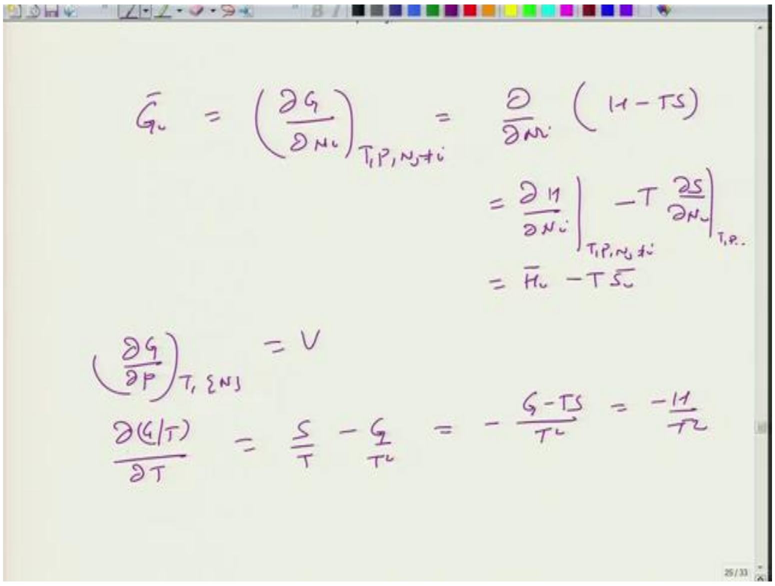
$$\Delta e_{mix} - x_1 \frac{\partial}{\partial x_1}(\Delta e_{mix}) = \bar{E_2} - e_2$$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

$$\Delta G_{mix} = G - \sum N_i \underline{G_i} \longrightarrow (\text{avg.})$$

$$= H - TS - \sum N_i(\underline{H_i} - T\underline{S_i})$$

$$= \underbrace{H - \sum N_i \underline{H_i}}_{\Delta H_{mix}} - T(\underbrace{S - \sum N_i \underline{S_i}}_{\Delta S_{mix}})$$



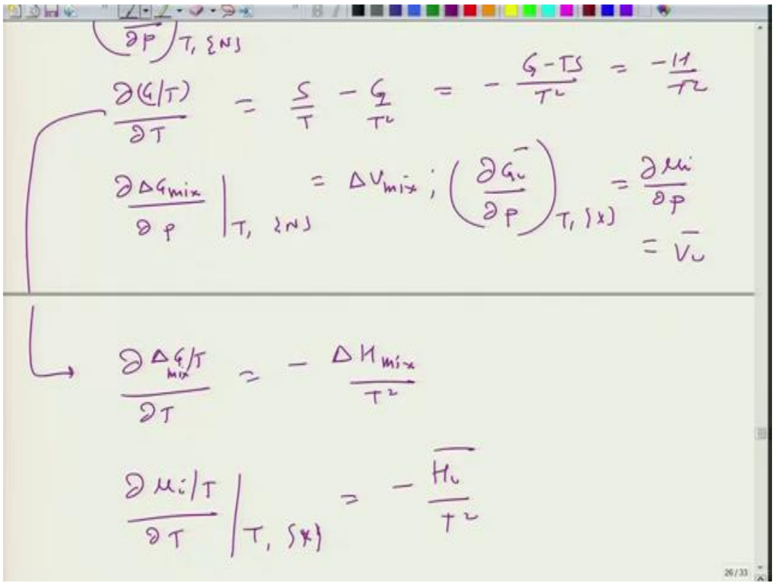
$$\bar{G_i} = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j \neq i} = \frac{\partial}{\partial N_i}(H - TS)$$

$$= \frac{\partial H}{\partial N_i}\Big|_{T,P,N_j \neq i} - T\frac{\partial S}{\partial N_i}\Big|_{T,P..}$$

$$= \bar{H_i} - T\bar{S_i}$$

$$\left(\frac{\partial G}{\partial P}\right)_{T,\{N\}} = V$$

$$\frac{\partial (G/T)}{\partial T} = \frac{S}{T} - \frac{G}{T^2} = -\frac{G - TS}{T^2} = -\frac{H}{T^2}$$



$$\left(\frac{\partial G}{\partial P}\right)_{T,\{N\}}$$

$$\frac{\partial (G/T)}{\partial T} = \frac{S}{T} - \frac{G}{T^2} = -\frac{G - TS}{T^2} = -\frac{H}{T^2}$$

$$\frac{\partial \Delta G_{mix}}{\partial P}\Big|_{T,\{N\}} = \Delta V_{mix}; \left(\frac{\partial \bar{G_i}}{\partial P}\right)_{T,\{x\}} = \frac{\partial \mu_i}{\partial P} = \bar{V_i}$$

$$\frac{\partial \Delta G_{mix}/T}{\partial T} = -\frac{\Delta H_{mix}}{T^2}$$

$$\frac{\partial \mu_i/T}{\partial T}\Big|_{T,\{x\}} = -\frac{\bar{H_i}}{T^2}$$

Now let me try to further summarise the information of mixture property, so we talked about Delta E in general but let me just be very specific now, you can talk about delta G here, so Delta G for mix can be shown as simply delta H mix for given temperature, so this is something which we can show and that you can prove in the following way that your delta G mix is nothing but G minus summation Ni Gi bar for the pure case.

This I can write as H minus TS minus summation Ni this is nothing but since it is molar property because G is nothing but H minus TS, so I can write, so instead of writing small I am just writing the molar property, I can also write G bar and here I can write this as summation Ni Hi bar or small g this is also good for us, so this is for pure case and then I am trying to rearrange the second term he is going to be S minus summation Ni Si bar and this is nothing but Delta H mix and this is nothing but Delta S mix.

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

$$\Delta G_{mix} = G - \sum N_i\overline{G_i} = H - TS - \sum N_i(\overline{H_i} - T\overline{S_i}) = H - \sum N_i\overline{H_i} - T(S - \sum N_i\overline{S_i})$$

So we can show this and similarly we can show other things also let me just quickly try to write it down for the sake of reference, For example Gi bar, you can show Gi bar to be simply Hi bar minus T Si bar so Gi bar which is a partial molar this free energy is nothing but del G by del Ni at a constant temperature P, T and J is not equal to I and this I can write as now H minus TS I am ignoring the constraints here this I can write DH by del Ni again the Constance are same T, P, N, J is not equal to I minus T del S by del Ni again T, P and this is nothing but Hi bar minus T Si bar. Now we know that del G by del P at a constant temperature and almost constant is nothing but V.

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

$$\left(\frac{\partial G}{\partial P}\right)_{T,\{N\}} = V$$

$$\frac{\partial\left(\frac{G}{T}\right)}{\partial T} = \frac{S}{T} - \frac{G}{T^2} = -\frac{(G - TS)}{T^2} = -\frac{H}{T^2}$$

Similarly, del G by T by del T is nothing but S by T minus G by t square this you can show is nothing but minus G minus TS by T square and is nothing but minus H by T square. Now I can extend this exercise for all partial and delta G mixtures for example I can write this as without proving it I can say that del of G mix by del p at T and all other components fixed and most of the components fixed is nothing but del x mix, so this is what I can show, so you can just use this information extent directed to the mixtures. Similarly I can write here as del Gi bar del p T and x constant is del mu i because Gi bar is nothing but mu I, del p this is nothing but Vi bar, the same thing.

So we are using here bar and what you are getting is another bar here so we are extending simple expression directly for delta term or bar term okay so that means the mixture change in the properties or it is the partial molar properties. Similarly here I can write do the extent here also for the mixtures with respect to their temperature, so that means I can write this as simply mix here divided by del T this is nothing but Delta H mix.

Similarly you can extend this also in terms of del mu I by T you can show that this is also nothing but this minus Hi bar divided by T square. So this is something which would be useful for you to remember or how this expressions you can make use of it in various different conditions particularly if you are interested to find out delta mu For example you can make use of this expression integrated with respect to temperature and you can obtain it.

$$\frac{\partial \Delta G_{mix}}{\partial P}\Big|_{T,\{N\}} = \Delta V_{mix}\,;\left(\frac{\partial \overline{G}_i}{\partial P}\right)_{T,\{x\}} = \frac{\partial \mu_i}{\partial P} = \overline{V}_i$$

$$\frac{\partial\left(\frac{\Delta G_{mix}}{T}\right)}{\partial T} = -\frac{\Delta H_{mix}}{T^2}$$

$$\frac{\partial\left(\frac{\mu_i}{T}\right)}{\partial T}\Big|_{T,\{x\}} = -\frac{\overline{H}_i}{T^2}$$

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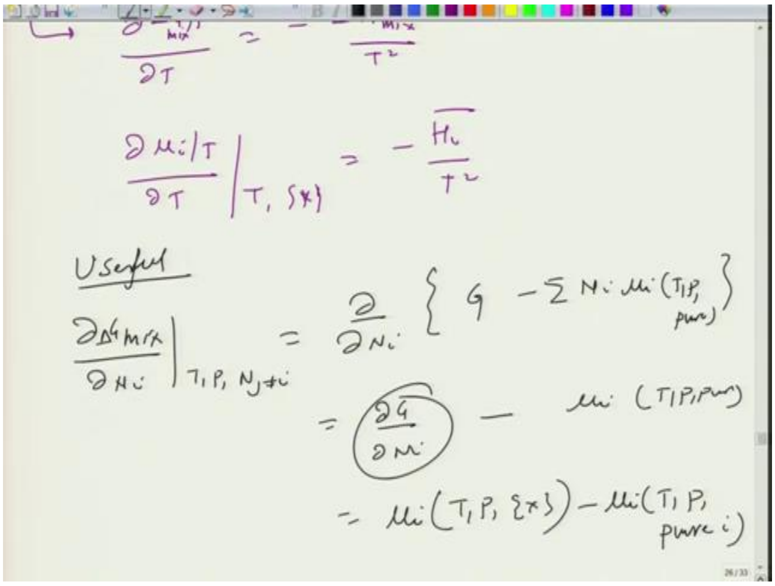

$$\frac{\partial \;{}_{mix}}{\partial T} = - \frac{{}_{mix}}{T^2}$$

$$\left.\frac{\partial \mu_i/T}{\partial T}\right|_{T,\{x\}} = - \frac{\overline{H_i}}{T^2}$$

Useful

$$\left.\frac{\partial \Delta G_{mix}}{\partial N_i}\right|_{T,P,N_{j\neq i}} = \frac{\partial}{\partial N_i}\left\{ G - \sum N_i \mu_i(T,P,\text{pure}) \right\}$$

$$= \boxed{\frac{\partial G}{\partial N_i}} - \mu_i(T,P,\text{pure})$$

$$= \mu_i(T,P,\{x\}) - \mu_i(T,P,\text{pure } i)$$

So let me close this part by just writing down the final expression which is very useful this Delta G mix with respect to del Ni at a constant TP and J not equal to I and this can be written or can be shown that it is related to nothing but delta mu but let me just write down 1st the expansion of that G mix this should be delta here, so this is G minus summation Ni mu I T, P pure.

Now I can expand this G here but since we are interested only in Ni I can write this directly as del G by del Ni minus simply mu I TP pure right and this is nothing but mu I we do not have to use bar any more so it is going to be mu I because the partial molar property with respect to Ni when you take the differentiation this is just mu I but for the mixture where temperature and pressure are same but compositions are there minus here that is for the case of the pure I, so the reason why I am writing it to emphasise that this is nothing but the pure.

$$\frac{\partial \Delta G_{mix}}{\partial N_i}|_{T,P,N_{j\neq i}} = \frac{\partial}{\partial N_i}\{G - \sum N_i \mu_i(T,P,pure) = \frac{\partial G}{\partial N_i} - \mu_i(T,P,pure)$$
$$= \mu_i(T,P,\{x\}) - \mu_i(T,P,pure\ i)$$

So you can clearly see that the partial derivative of delta G mix with respect to Ni is nothing but the difference in the chemical potential of that particular component. So we want to use this information little later. Now this is something which I would like to add as far as the partial molar properties is concerned. We will take up the next topic which will be ideal mixtures and then again we will try to connect that to the fugacity part in the next lecture. So with that I would like to close it and see you next time.