Course on Phase Equilibrium Thermodynamics
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Lecture No 41
Non Ideal solutions(Contd.)

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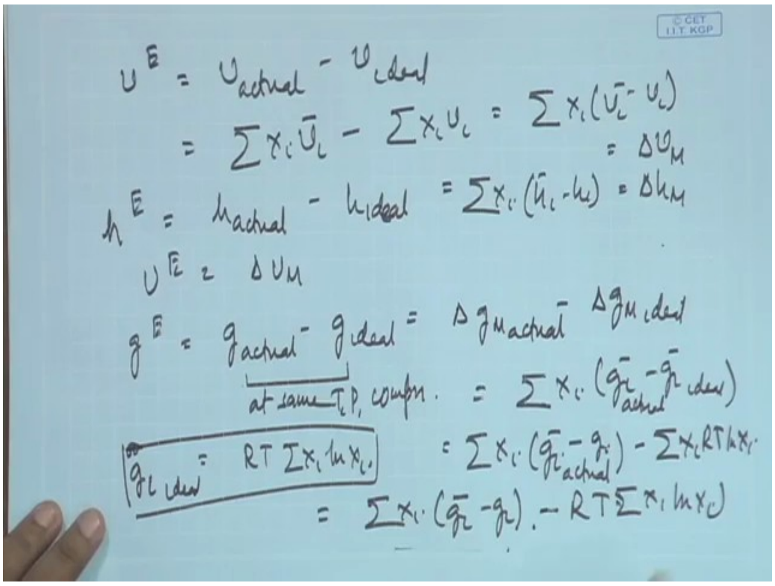

$$v^E = v_{actual} - v_{ideal}$$

$$= \sum x_i \bar{v}_i - \sum x_i v_i = \sum x_i (\bar{v}_i - v_i) = \Delta v_M$$

$$h^E = h_{actual} - h_{ideal} = \sum x_i (\bar{h}_i - h_i) = \Delta h_M$$

$$u^E = \Delta u_M$$

$$g^E = \underbrace{g_{actual} - g_{ideal}}_{\text{at same T, P, compn.}} = \Delta g_{M\,actual} - \Delta g_{M\,ideal}$$

$$= \sum x_i (\bar{g}_{i\,actual} - \bar{g}_{i\,ideal})$$

$$\boxed{g_{i\,ideal} = RT \sum x_i \ln x_i}$$

$$= \sum x_i (\bar{g}_{i\,actual} - g_i) - \sum x_i RT \ln x_i$$

$$= \sum x_i (\bar{g}_i - g_i) - RT \sum x_i \ln x_i$$

So therefore let us see what are the excess properties that we were dealing with? Just as I have told you, so therefore if we go to the previous slide it will be clear to you that what do we have then in this particular case? We have v excess what is v excess it is v actual minus v ideal. Actual ideal everything refers to solution. What is v actual then? It is Sigma xi vi bar, what is v ideal you know? It is xi vi, so therefore this should be xi vi bar minus vi had the solution been ideal vi bar would have been equal to vi and vE would have been equal to 0.

This case this is not equal to 0, therefore what is this? It is actually the volume change on mixing of the solution. Same way we can write down hE just the same way we can repeat it h actual minus h ideal, right? Which is nothing but equal to Sigma xi hi bar minus hi which is nothing but equal to Delta h mixing for a real solution same thing uE will be equal to U delta U mixing. Let us see what is gE equals to?

For gE, what is this? Again in the same way it should be g actual minus g ideal, okay. So therefore what is this remember one thing this is the Gibbs free energy of the solution actual or the real solution, this is the Gibbs free energy of the ideal solution both at same T, P, composition. Now remember one thing as I had already mentioned we cannot define absolute values of any properties we always define the property changes, right?

So therefore this actual Gibbs free energy of the solution is better expressed as the actual change in Gibbs free energy on forming the solution, isn't it? So we had 2 components ab we mixed them due to this mixture there was a change in Gibbs free energy, what is this Gibbs free energy change for a real solution? What is this Gibbs free energy change for an ideal solution? The difference between the 2 should be a better measure of the excess property as compared to the Gibbs free energy of actual solution minus the Gibbs free energy of the ideal solution, why?

Because we cannot define absolute value of Gibbs free energy for any particular substance in any particular state we always need a datum as you remember. So therefore this can be expressed as Delta gM actual minus Delta gM of mixing ideal, agreed? Which can also be referred to as Xi gi bar minus gi bar ideal this is actual. Now if you recollect what was Delta gM bar ideal? If you recollect, so therefore gi for an ideal solution what was this? Your gi bar ideal or rather gi ideal. Let us take it; it was RT Sigma xi ln xi that we have already derived.

So therefore what should this become? This should become xi gi bar actual minus Sigma Xi RT ln, so we can we can take this out or else we can define this as Sigma xi gi bar minus gi minus RT Sigma xi ln xi. This should have been gi bar actual minus gi, agreed?

Okay, so therefore what did I do this Delta gM actual that that is actually the Delta gM change for the actual solution which is given by this the , what happens during formation of the solution? The molar Gibbs free energy changes to the partial molar Gibbs free energy for each component i. So this is for the actual solution and this is for the real solution, right?

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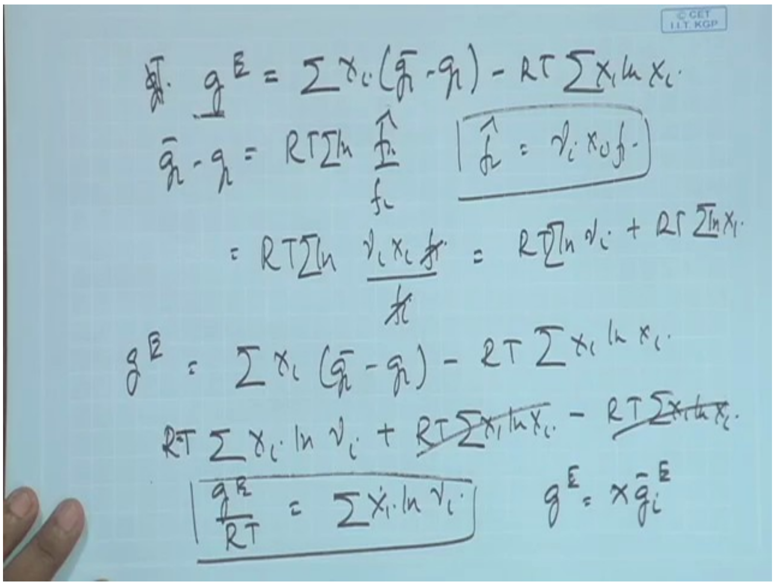

$$g^E = \sum x_i(\bar{g}_i - g_i) - RT\sum x_i \ln x_i$$

$$\bar{g}_i - g_i = RT\sum \ln \frac{\hat{f}_i}{f_i} \qquad \boxed{\hat{f}_i = \gamma_i x_i f_i}$$

$$= RT\sum \ln \frac{\gamma_i x_i \cancel{f_i}}{\cancel{f_i}} = RT\sum \ln \gamma_i + RT\sum \ln x_i$$

$$g^E = \sum x_i(\bar{g}_i - g_i) - RT\sum x_i \ln x_i$$

$$RT\sum x_i \ln \gamma_i + \cancel{RT\sum x_i \ln x_i} - \cancel{RT\sum x_i \ln x_i}$$

$$\boxed{\frac{g^E}{RT} = \sum x_i \ln \gamma_i} \qquad g^E = x\bar{g}_i^E$$

Now tell me one thing, how is this gi bar minus gi related? This so I will just repeat it once more, so that it is easier for you to understand g excess this is equal to Sigma Xi gi bar minus gi minus RT sigma Xi ln Xi, fine. What is this gi bar minus gi? This is why because the pure component i was taken into a solution that is why this particular change occured. Can we not write it down as RT ln fi bar by fi? What does it show?

The fugacity change of pure component i when it is taken into solution. So what is my standard state in this particular case pure component i. So from there and the standard states as same for both the left inside and right-hand side of the equation, so from the pure component i, I am taking it to the solution state as a result of which it’s Gibbs free energy is changing to gi bar and its fugacity is changing to fi cap, agreed?

So therefore this particular equation this particular exact equation can be written relating the molar Gibbs free energy or the partial molar Gibbs free energy with the fugacity and the partial molar fugacity, agreed? I can do this, so what is this again what is this fi bar equals to? For a real solution this is equals to gamma i Xi fi. So therefore can I not write it down as RT gamma i Xi fi by fi? Both the cases remember the fi are the same it is the pure component fugacity at temperature, pressure of the solution.

This was the fugacity of the pure component and this is also the fugacity of the pure component, can I not write it down in this particular way? So therefore what is my gi bar minus gi then in this case this is RT ln, Sigma gamma i plus RT sigma ln xi. I can write it down in this particular way, fine. And so therefore if I substitute this in this particular equation, what do I get? Excess Gibbs is nothing but Sigma Xi gi bar minus gi minus RT sigma Xi ln Xi.

What is, I just substitute gi bar minus gi so what do I get? This is equal to Sigma Xi RT can be taken outside ln gamma I plus RT sigma Xi ln Xi minus RT sigma Xi ln Xi. What do I get as a result of this? I find that the gamma i can be related in a very simple way with this is the relationship of excess Gibbs free energy with gamma, right? And remember one thing just because the solution is not ideal. So therefore there will be some excess Gibbs free energy and that decides whether the solution forms spontaneously or not and as a result of this non-ideality gamma has come into picture.

So therefore we find that that the gamma of the of each and every component can be related to the molar Gibbs free energy change of the solution in this particular summation form. Now what is this gE tell me? gE is nothing but equals to your X into gi bar E, yes or no? Agreed?

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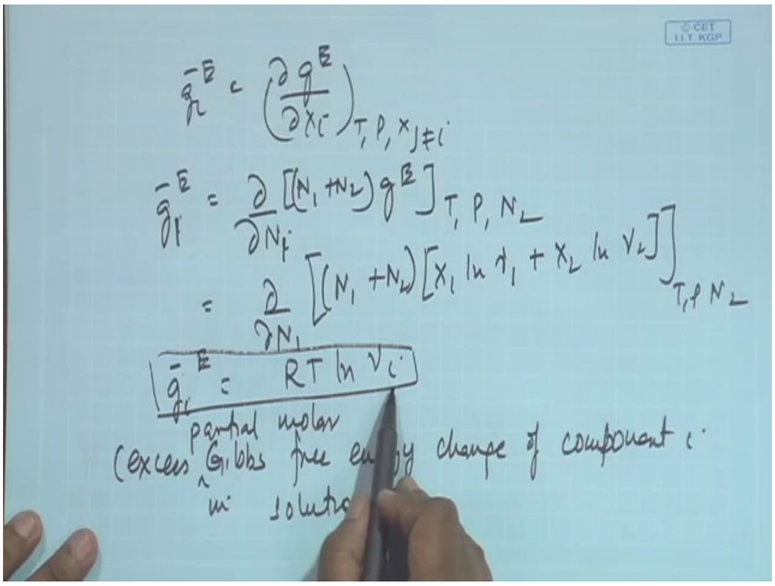

$$\bar{g}_i^E = \left(\frac{\partial g^E}{\partial x_i}\right)_{T,P,x_{j\neq i}}$$

$$\bar{g}_1^E = \frac{\partial}{\partial N_1}\left[(N_1+N_2)g^E\right]_{T,P,N_2}$$

$$= \frac{\partial}{\partial N_1}\left[(N_1+N_2)\left[x_1 \ln \gamma_1 + x_2 \ln \gamma_2\right]\right]_{T,P,N_2}$$

$$\boxed{\bar{g}_i^E = RT \ln \gamma_i}$$

(excess partial molar Gibbs free energy change of component i in solutio

So therefore how can I get this gi bar E? This gi bar E it is nothing but equal to del gE del xi at constant T, P xj not equal to i, agreed. Or in other words can I not write it down in this particular way del del Ni of? Say suppose it is a your binary mixtures. So therefore del del this is g1 E is del del N1, N1 plus N2 into gE at constant T, P, N2. And and what is this gE equals to? This is nothing but equal to del del N1, N1 plus N2 X1 ln gamma1 plus X2 ln Gamma2 constant T, P, N2.

Simply differentiate this and what do you get? You just differentiate it you are going to get g by gi bar E that is the excess, I will write it down excess Gibbs free energy change, excess E excess partial molar, why? The bar is there excess partial molar Gibbs free energy change of component i in solution, what does what is this? This is gi bar E equals to RT ln gamma i. So if you can calculate the excess Gibbs free energy the partial molar excess its free energy of component I then you should be in a position to calculate the activity coefficient of that particular component, agreed?

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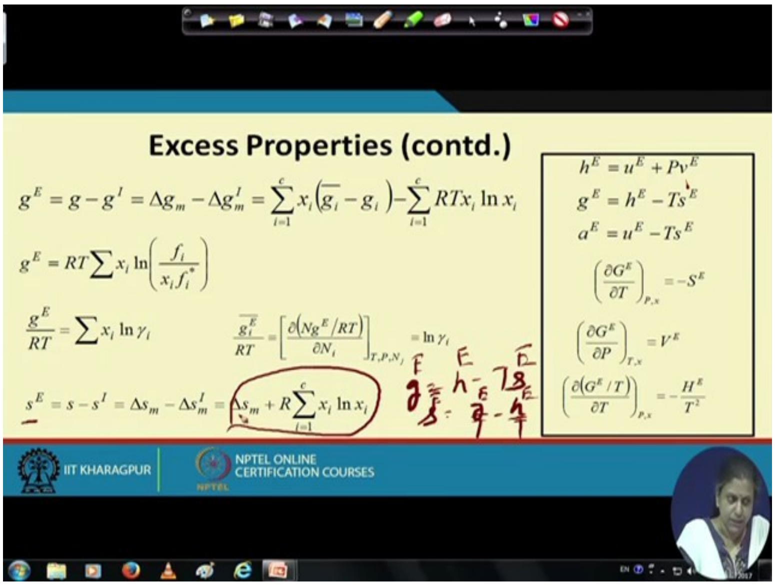

Excess Properties (contd.)

$$g^E = g - g^I = \Delta g_m - \Delta g_m^I = \sum_{i=1}^{c} x_i\left(\overline{g_i} - g_i\right) - \sum_{i=1}^{c} RTx_i \ln x_i$$

$$g^E = RT\sum x_i \ln\left(\frac{f_i}{x_i f_i^*}\right)$$

$$\frac{g^E}{RT} = \sum x_i \ln \gamma_i \qquad \frac{\overline{g_i^E}}{RT} = \left[\frac{\partial\left(Ng^E/RT\right)}{\partial N_i}\right]_{T,P,N_j} = \ln \gamma_i$$

$$s^E = s - s^I = \Delta s_m - \Delta s_m^I = \boxed{\Delta s_m + R\sum_{i=1}^{c} x_i \ln x_i}$$

$$g^E = h^E - Ts^E$$

$$s^E = \frac{g^E}{T} - \frac{h^E}{T}$$

$$h^E = u^E + Pv^E$$

$$g^E = h^E - Ts^E$$

$$a^E = u^E - Ts^E$$

$$\left(\frac{\partial G^E}{\partial T}\right)_{P,x} = -S^E$$

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

$$\left(\frac{\partial\left(G^E/T\right)}{\partial T}\right)_{P,x} = -\frac{H^E}{T^2}$$

So therefore we find that we have come across these 2 equations which I have already written down here if you observe. We find the molar Gibbs excess Gibbs free energy of the solution is given in terms of composition or activity coefficient by this equation and the partial molar excess Gibss free energy change of component i in solution is nothing but equal to ln of gamma i, right? So therefore this should be one particular way of finding out gE of finding out gamma i and it it's important for you to recollect that just like we had done for ideal solutions we can always write down or rather we can always find out the excess entropy change of the solution.

What it is going to be? This is nothing but equals to hE minus, if I write it down what is s equals to? Recollect g equals to h minus Ts. So therefore s will be equal to g by T minus h by T, right? And therefore once this equation was written for a for a molar quantity we can always add a superscript s for the in extensive properties and this is the relationship between the excess properties. So therefore we can easily find out Gibbs free energy excess entropy in terms of excess Gibbs free energy and excess enthalpy and once we do it we find that the excess entropy is given by this particular equation, right?

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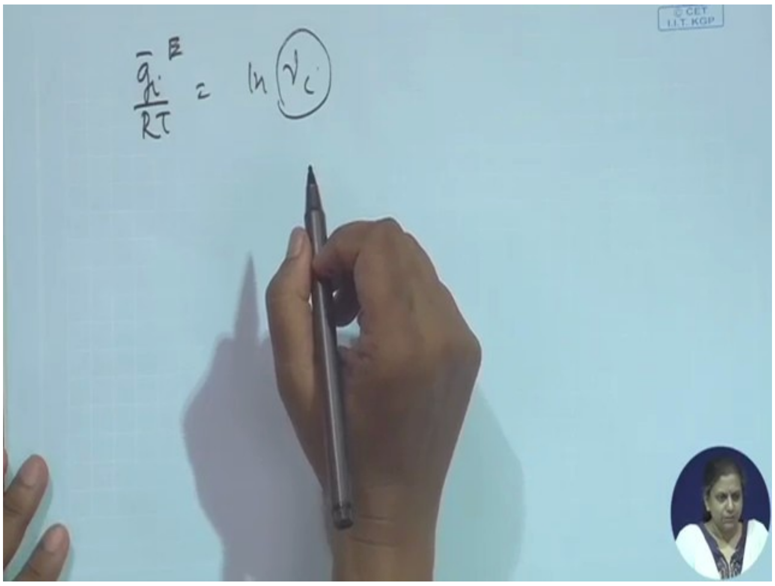

$$\frac{\bar{g}_i^E}{RT} = \ln \gamma_i$$

So therefore the interesting part which we found out was the first thing which we found out gi bar E by RT equals to ln gamma i gamma should also be related to other excess properties, how would is related let us see?

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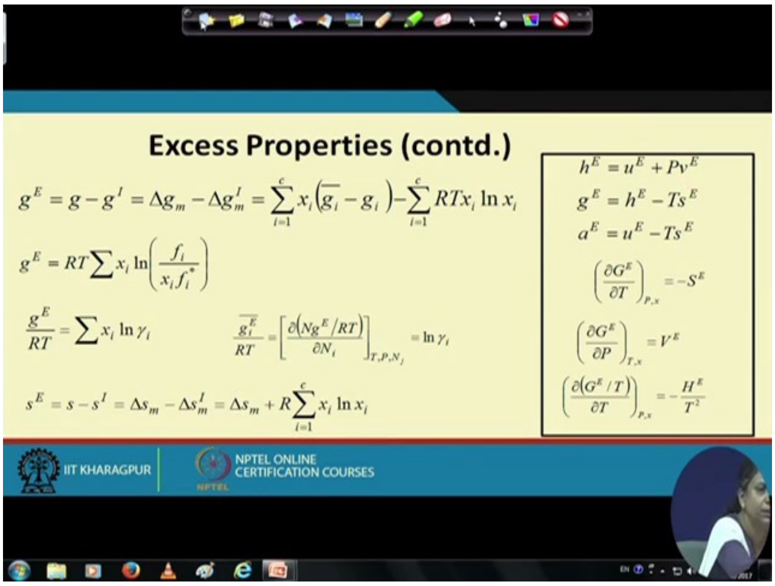

Excess Properties (contd.)

$$g^E = g - g^I = \Delta g_m - \Delta g_m^I = \sum_{i=1}^{c} x_i \left(\overline{g_i} - g_i\right) - \sum_{i=1}^{c} RT x_i \ln x_i$$

$$g^E = RT \sum x_i \ln\left(\frac{f_i}{x_i f_i^*}\right)$$

$$\frac{g^E}{RT} = \sum x_i \ln \gamma_i \qquad \frac{\overline{g_i^E}}{RT} = \left[\frac{\partial\left(N g^E / RT\right)}{\partial N_i}\right]_{T,P,N_j} = \ln \gamma_i$$

$$s^E = s - s^I = \Delta s_m - \Delta s_m^I = \Delta s_m + R \sum_{i=1}^{c} x_i \ln x_i$$

$$h^E = u^E + P v^E$$

$$g^E = h^E - T s^E$$

$$a^E = u^E - T s^E$$

$$\left(\frac{\partial G^E}{\partial T}\right)_{P,x} = -S^E$$

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

$$\left(\frac{\partial (G^E / T)}{\partial T}\right)_{P,x} = -\frac{H^E}{T^2}$$

How gamma varies with temperature pressure and composition etc. Just try to do it yourself and then see what do you get?

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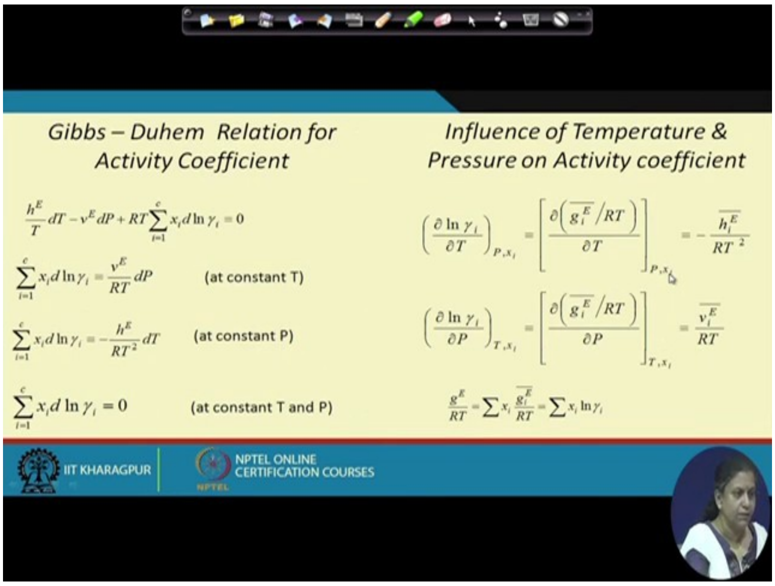

Gibbs – Duhem Relation for Activity Coefficient

$$\frac{h^E}{T}dT - v^E dP + RT\sum_{i=1}^{c} x_i d\ln\gamma_i = 0$$

$$\sum_{i=1}^{c} x_i d\ln\gamma_i = \frac{v^E}{RT}dP$$ (at constant T)

$$\sum_{i=1}^{c} x_i d\ln\gamma_i = -\frac{h^E}{RT^2}dT$$ (at constant P)

$$\sum_{i=1}^{c} x_i d\ln\gamma_i = 0$$ (at constant T and P)

Influence of Temperature & Pressure on Activity coefficient

$$\left(\frac{\partial \ln\gamma_i}{\partial T}\right)_{P,x_i} = \left[\frac{\partial\left(\overline{g_i^E}/RT\right)}{\partial T}\right]_{P,x_i} = -\frac{\overline{h_i^E}}{RT^2}$$

$$\left(\frac{\partial \ln\gamma_i}{\partial P}\right)_{T,x_i} = \left[\frac{\partial\left(\overline{g_i^E}/RT\right)}{\partial P}\right]_{T,x_i} = \frac{\overline{v_i^E}}{RT}$$

$$\frac{g^E}{RT} = \sum x_i \frac{\overline{g_i^E}}{RT} = \sum x_i \ln\gamma_i$$

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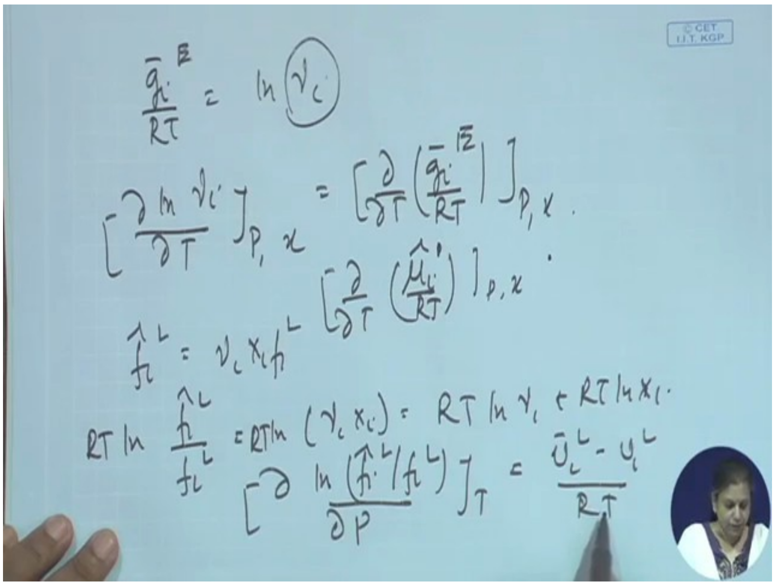

$$\frac{\bar{g}_i^E}{RT} = \ln \boxed{\gamma_i}$$

$$\left[\frac{\partial \ln\gamma_i}{\partial T}\right]_{P,x} = \left[\frac{\partial}{\partial T}\left(\frac{\bar{g}_i^E}{RT}\right)\right]_{P,x}.$$

$$\left[\frac{\partial}{\partial T}\left(\frac{\hat{\mu}_i}{RT}\right)\right]_{P,x}.$$

$$\hat{f}_i^L = \gamma_i x_i f_i^L$$

$$RT\ln\frac{\hat{f}_i^L}{f_i^L} = RT\ln(\gamma_i x_i) = RT\ln\gamma_i + RT\ln x_i.$$

$$\left[\frac{\partial \ln(\hat{f}_i^L/f_i^L)}{\partial P}\right]_T = \frac{\bar{v}_i^L - v_i^L}{RT}$$

Suppose you try to find out del ln gamma I del T, right? At constant pressure and composition, what is this equals to? You already know what is ln gamma i? It is nothing but equals to gi bar E, please do not forget there are 3 things which have to be mentioned at constant P and x, right? And what is this gi bar E this is nothing but equals to del del T of mu i cap by RT at constant P and x, right? We can write it down in this particular way.

So therefore from here what do we get then? From here we find out or in other words this can also be written down as, we can start it in a slightly different way and which will be easier for you to understand. Let us start from the basics then it will be easier for you to understand. This we have already found out, right? So therefore what is ln fi L by fi L? Pure component nothing but equal to ln gamma i Xi. Now this is equal to RT, so if we have a RT here you have a RT here you have ln gamma i plus RT ln X Xi, agreed? So what is del ln fi L by fi L.

Say del P if we take at constant temperature, recollect what is this equal to? This will be equal to vi bar L minus vi L by RT, if you remember dg equals to minus sdT plus vdP. So therefore this is what precisely we have done.

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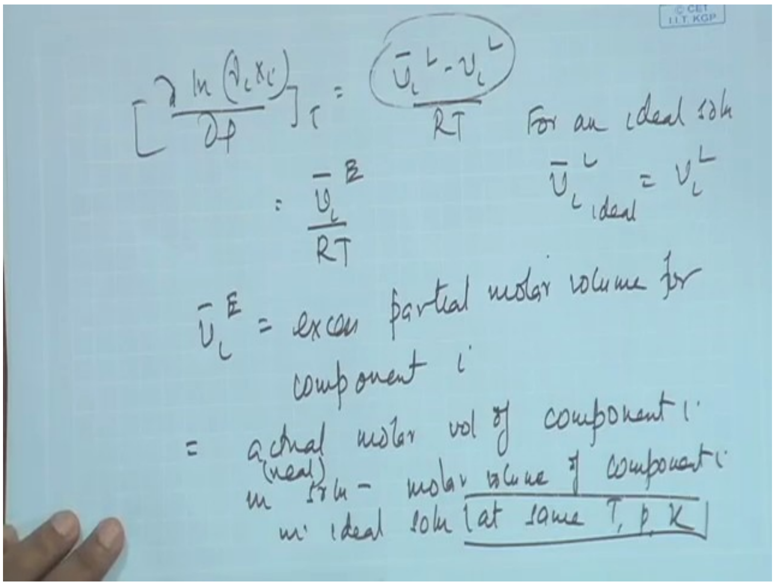

$$\left[\frac{\partial \ln(\gamma_i x_i)}{\partial P}\right]_T = \frac{\boxed{\bar{v}_i^L - v_i^L}}{RT}$$

For an ideal soln

$$\bar{v}^L_{i\,\text{ideal}} = v_i^L$$

$$= \frac{\bar{v}_i^E}{RT}$$

$\bar{v}_i^E$ = excess partial molar volume for component i

= actual molar vol of component i in (real) soln − molar volume of component i in ideal soln $\underline{\text{at same } T, P, x}$

So in the same way we, can you not write it down as l, del ln gamma I Xi del P? This should be equal to vi bar L minus Vi L by RT. What is vi bar L? It is the partial molar excess volume of component i in the liquid solution. What is this? It is the molar volume of component i in the liquid state for an ideal solution we know that if the for an ideal solution what do we know? For an ideal solution vi bar L ideal is nothing but equal to Vi L.

So therefore what is this then in that case? It is the partial molar volume change for the case of a real solution minus the partial molar volume change for an ideal solution. So therefore what is it then? This is nothing but vi excess by RT vi bar excess by RT, agreed? Which is what? This vi bar E excess, what is this? Excess partial excess E bar means partial molar volume, agreed? For component i which is nothing but actual molar volume of component i in solution minus the, in real solution real is within bracket minus molar volume of component i in ideal solution, very important at same T, P, x. This you have to keep on adding because the standards states have to be the same, right?

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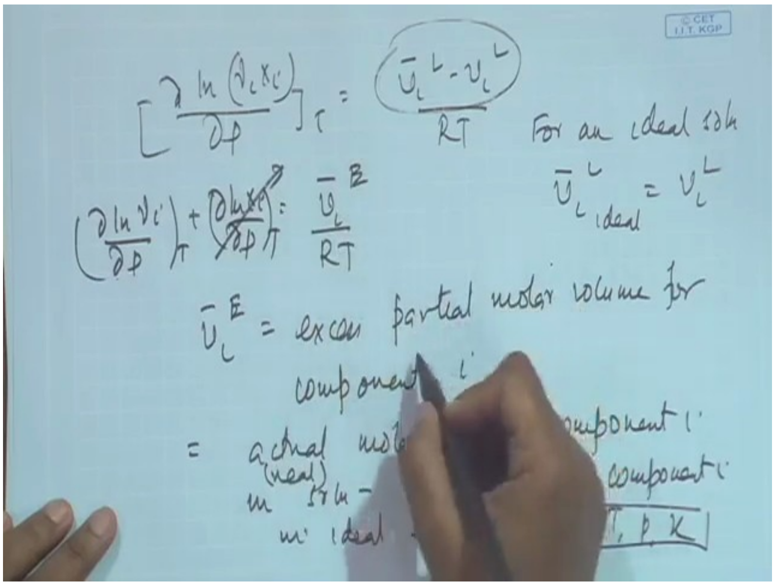

$$\left[\frac{\partial \ln(\gamma_i x_i)}{\partial P}\right]_T = \frac{\bar{v}_i^L - v_i^L}{RT}$$

For an ideal soln

$$\bar{v}^L_{i\,\text{ideal}} = v_i^L$$

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_T + \cancel{\left(\frac{\partial \ln x_i}{\partial P}\right)_T} = \frac{\bar{v}_i^E}{RT}$$

$\bar{v}_i^E$ = excess partial molar volume for component i

= actual mol … component i
(real)
in soln − … component i
in ideal … T, P, x

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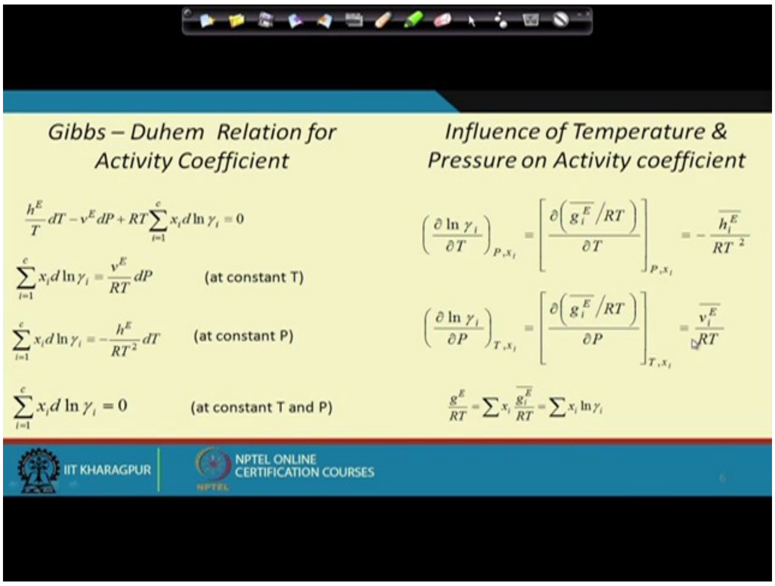

Gibbs – Duhem Relation for Activity Coefficient

$$\frac{h^E}{T}dT - v^E dP + RT\sum_{i=1}^{c} x_i d\ln\gamma_i = 0$$

$$\sum_{i=1}^{c} x_i d\ln\gamma_i = \frac{v^E}{RT}dP \qquad \text{(at constant T)}$$

$$\sum_{i=1}^{c} x_i d\ln\gamma_i = -\frac{h^E}{RT^2}dT \qquad \text{(at constant P)}$$

$$\sum_{i=1}^{c} x_i d\ln\gamma_i = 0 \qquad \text{(at constant T and P)}$$

Influence of Temperature & Pressure on Activity coefficient

$$\left(\frac{\partial \ln\gamma_i}{\partial T}\right)_{P,x_i} = \left[\frac{\partial\left(\overline{g_i^E}/RT\right)}{\partial T}\right]_{P,x_i} = -\frac{\overline{h_i^E}}{RT^2}$$

$$\left(\frac{\partial \ln\gamma_i}{\partial P}\right)_{T,x_i} = \left[\frac{\partial\left(\overline{g_i^E}/RT\right)}{\partial P}\right]_{T,x_i} = \frac{\overline{v_i^E}}{RT}$$

$$\frac{g^E}{RT} = \sum x_i \frac{\overline{g_i^E}}{RT} = \sum x_i \ln\gamma_i$$

And therefore and what is this Del ln gamma I by del P? So we can we not write it down as del ln gamma I del P at constant T plus del ln xi del P at constant T. We know that Xi the mole fraction does not change with pressure. So therefore del ln gamma I del P is nothing but it can be related to the excess partial molar volume for component i which I have also written down. Same way suppose we would like to find out the temperature, the dependence of gamma i on temperature. It should again go on in the same way.

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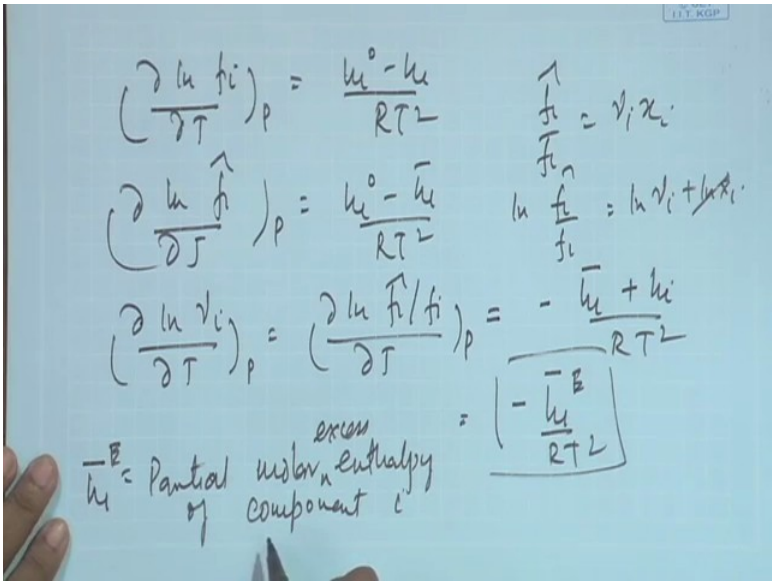

$$\left(\frac{\partial \ln f_i}{\partial T}\right)_P = \frac{h_i^0 - h_i}{RT^2} \qquad \frac{\hat{f}_i}{f_i} = \gamma_i x_i$$

$$\left(\frac{\partial \ln \hat{f}_i}{\partial T}\right)_P = \frac{h_i^0 - \bar{h}_i}{RT^2} \qquad \ln \frac{\hat{f}_i}{f_i} = \ln \gamma_i + \cancel{\ln x_i}$$

$$\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_P = \left(\frac{\partial \ln \hat{f}_i/f_i}{\partial T}\right)_P = \frac{-\bar{h}_i + h_i}{RT^2} = \boxed{-\frac{\bar{h}_i^E}{RT^2}}$$

$\bar{h}_i^E$ = Partial molar excess enthalpy of component i

It should be del ln fi del T at constant P this is nothing, if you recollect hi 0 minus hi by RT square . Same way, can we not write down for the partial molar fugacity hi 0 minus hi bar by RT square? So therefore can I not write and what do I know? I know fi bar by fi equals to gamma i Xi, right? So therefore ln fi bar by fi is nothing but equal to ln gamma i plus ln Xi agreed? So therefore can I not write this down as del ln gamma i?

Again I know that Xi is not a function of temperature it been composition does not depend on temperature. So can I not write this down as del ln fi bar by fi del T at constant P? Is this not equal to minus of hi bar plus hi by RT square hi0 is the same for both the equations. What is this equal to? Isn't it equal to minus hi bar excess by RT square? What is this? This is nothing but the partial, I will write it down hi bar E it is the partial molar enthalpy of component i. For partial there is a bar partial molar excess, See I am also missing a lot of things partial molar excess enthalpy of component i which is nothing but the partial molar enthalpy of i minus the molar enthalpy of component i at the same conditions of temperature and pressure, right?

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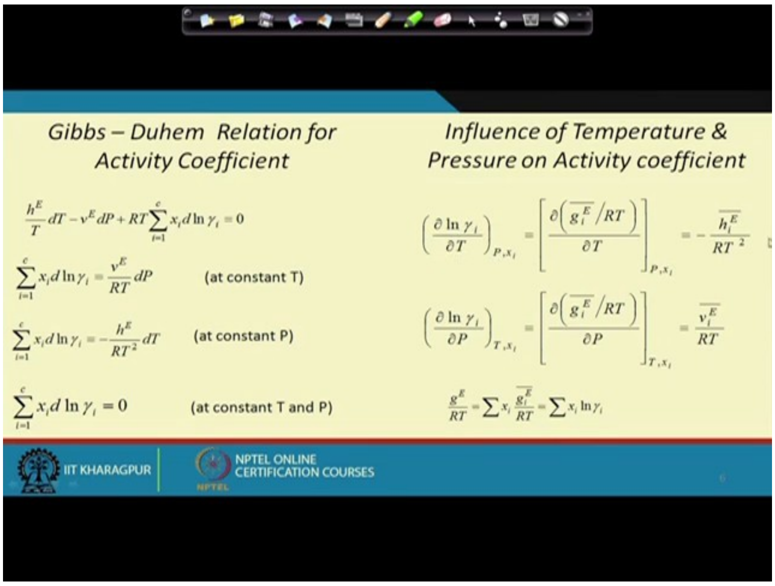

Gibbs – Duhem Relation for Activity Coefficient

$$\frac{h^E}{T}dT - v^E dP + RT\sum_{i=1}^{c} x_i d\ln\gamma_i = 0$$

$$\sum_{i=1}^{c} x_i d\ln\gamma_i = \frac{v^E}{RT}dP$$ (at constant T)

$$\sum_{i=1}^{c} x_i d\ln\gamma_i = -\frac{h^E}{RT^2}dT$$ (at constant P)

$$\sum_{i=1}^{c} x_i d\ln\gamma_i = 0$$ (at constant T and P)

Influence of Temperature & Pressure on Activity coefficient

$$\left(\frac{\partial \ln\gamma_i}{\partial T}\right)_{P,x_i} = \left[\frac{\partial\left(\overline{g_i^E}/RT\right)}{\partial T}\right]_{P,x_i} = -\frac{\overline{h_i^E}}{RT^2}$$

$$\left(\frac{\partial \ln\gamma_i}{\partial P}\right)_{T,x_i} = \left[\frac{\partial\left(\overline{g_i^E}/RT\right)}{\partial P}\right]_{T,x_i} = \frac{\overline{v_i^E}}{RT}$$

$$\frac{g^E}{RT} = \sum x_i \frac{\overline{g_i^E}}{RT} = \sum x_i \ln\gamma_i$$

So variation with temperature can be related with the partial molar excess enthalpy of the of the solution and the gamma variation with pressure can be related with partial molar excess volume of component i in the solution and we know that the you’re the gamma i it is related with the with the excess Gibbs free energy of each and every partial molar Gibbs free energy of each and every component in the mixture by this equals to ln gamma i and the excess molar Gibbs free energy of the mixture by this particular equation.

So therefore we find as we have anticipated that excess properties arising to the real the deviation of the solution from the ideal behaviour and we have used gamma to account for this particular deviation. So therefore gamma can be related with the excess properties and we have shown how it is related to excess molar Gibbs free energy of the solutin excess molar the partial molar enthalpy of each component, partial excess partial molar volume of each particular component.

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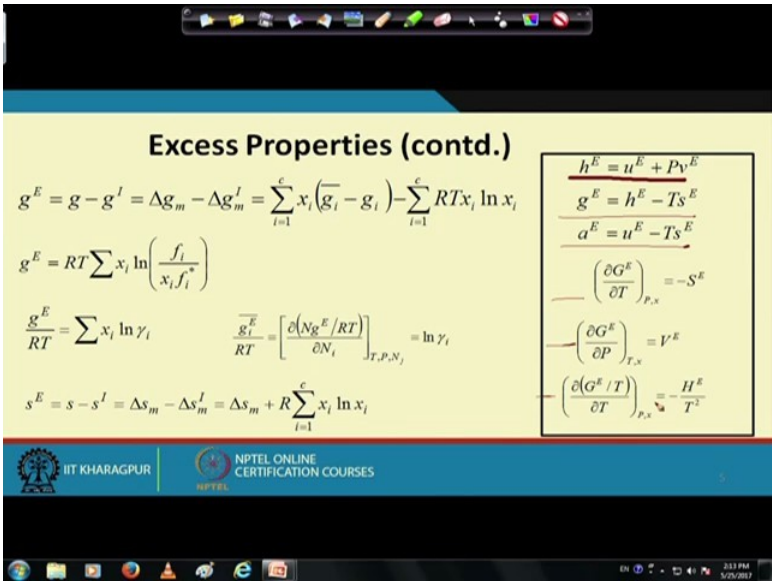

Excess Properties (contd.)

$$g^E = g - g^I = \Delta g_m - \Delta g_m^I = \sum_{i=1}^{c} x_i\left(\overline{g_i} - g_i\right) - \sum_{i=1}^{c} RTx_i \ln x_i$$

$$g^E = RT\sum x_i \ln\left(\frac{f_i}{x_i f_i^*}\right)$$

$$\frac{g^E}{RT} = \sum x_i \ln \gamma_i \qquad \frac{\overline{g_i^E}}{RT} = \left[\frac{\partial\left(Ng^E/RT\right)}{\partial N_i}\right]_{T,P,N_j} = \ln \gamma_i$$

$$s^E = s - s^I = \Delta s_m - \Delta s_m^I = \Delta s_m + R\sum_{i=1}^{c} x_i \ln x_i$$

$$h^E = u^E + Pv^E$$

$$g^E = h^E - Ts^E$$

$$a^E = u^E - Ts^E$$

$$\left(\frac{\partial G^E}{\partial T}\right)_{P,x} = -S^E$$

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

$$\left(\frac{\partial\left(G^E/T\right)}{\partial T}\right)_{P,x} = -\frac{H^E}{T^2}$$

Now since we have defined another set of excess properties it is very interesting to find out that these particular excess properties they also obey the same equations as that of the the molar properties as that of the total properties whatever equations we have defined in terms of total properties in terms of molar properties you just add a superscript E and you find that each and every particular relationship is applicable and all these equations you can actually derive and you can find it out that all these equations which you have derived for the your molar and total properties are applicable for total excess properties, for partial molar excess properties for molar excess properties, right?

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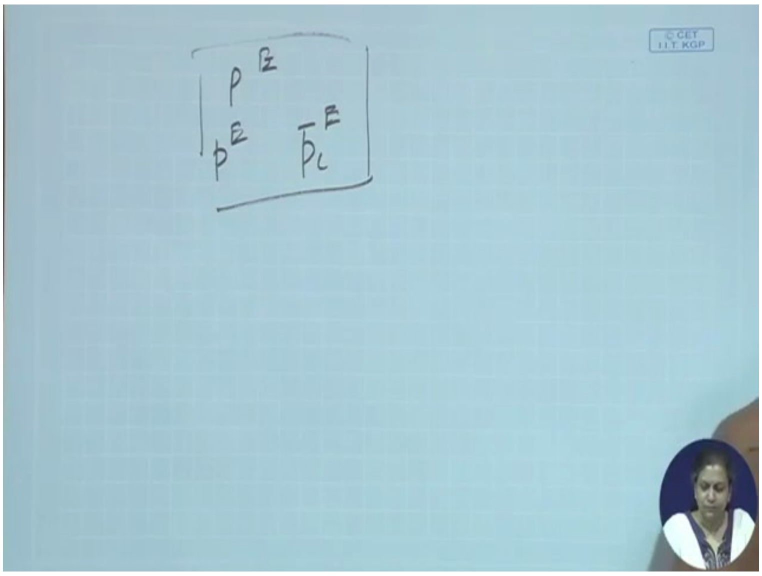

P^E

p^E $\quad \bar{p}_i^E$

Total excess properties given by this, your molar excess property is given by this, partial molar excess property for each component is given by this. So these are the 3 symbols that we will be using we just should be little careful about the symbols since we are dealing with a large number of properties, right?

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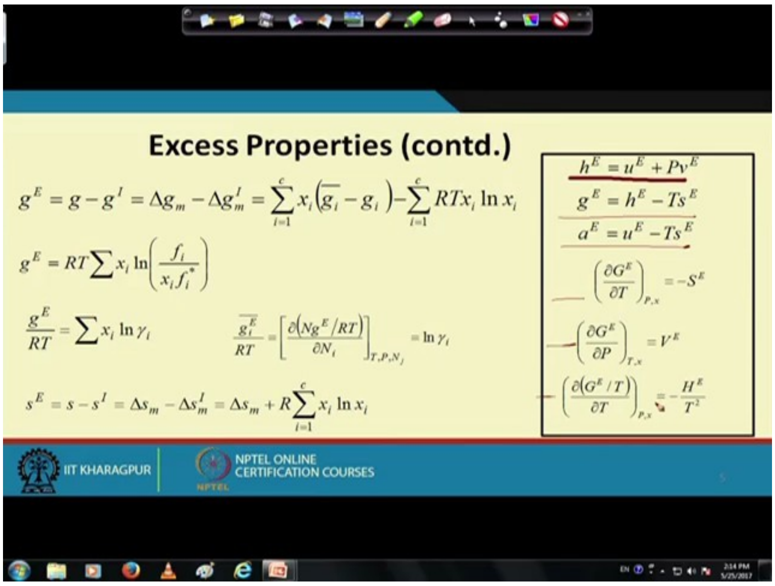

Excess Properties (contd.)

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$$g^E = RT\sum x_i \ln\left(\frac{f_i}{x_i f_i^*}\right)$$

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$$s^E = s - s^I = \Delta s_m - \Delta s_m^I = \Delta s_m + R\sum_{i=1}^{c} x_i \ln x_i$$

$$h^E = u^E + Pv^E$$

$$g^E = h^E - Ts^E$$

$$a^E = u^E - Ts^E$$

$$\left(\frac{\partial G^E}{\partial T}\right)_{P,x} = -S^E$$

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

$$\left(\frac{\partial\left(G^E/T\right)}{\partial T}\right)_{P,x} = -\frac{H^E}{T^2}$$

There is one more thing which is very interesting we have defined rather we have tried to incorporate the non ideal behaviour by incorporating gamma we have related to the excess properties of the solution. Now whenever we have been dealing with solutions we found out that for mixtures there is a very important relation which tells us that all properties of the mixtures are not ideal, what was that particular equation?

It was the Gibbs Duhem equation; we have derived the Gibbs Duhem equation in terms of chemical potential, right? The same can be derived for in terms of fugacity and we should be also in a position to derive Gibbs Duhem equation for activity coefficient, why do we need to do it? We need to do it because we have seen that if Gibbs Duhem equation gives us one particular clue by which we can find out any property of component a if the same property for component b is known provided it is a binary mixture. If it is a N component mixture if we know the property for N minus 1 components we will be in a position to find the same property for other nth component provided the entire thing is being performed under the conditions of same temperature, pressure and composition.

So therefore since finding out gamma is so very important gamma is so very important as far as vapor liquid equilibrium for nonideal solution are concerned and we come across nonideal solutions very frequently so therefore it is important to find out gamma or rather to express Gibbs Duhem equation in terms of gamma. So that for a binary solution which we usually come across is we know gamma 1 we will be in a position to find out gamma 2.

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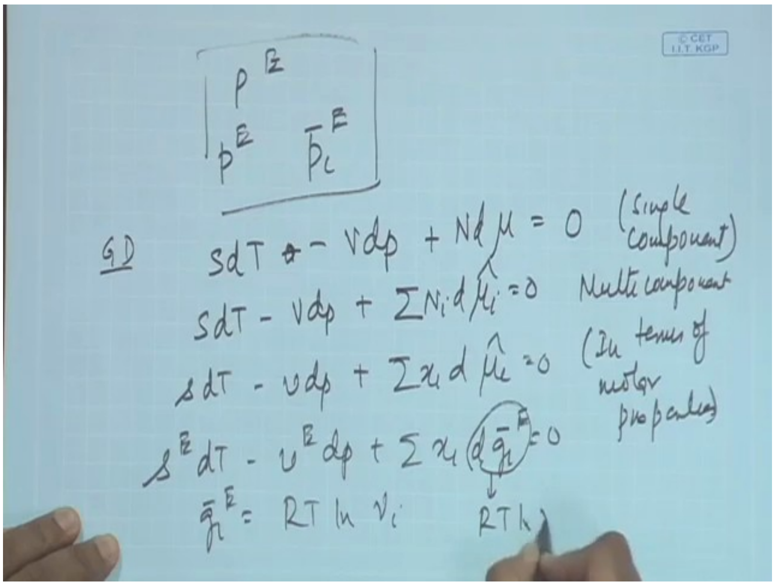

P^E

$p^E \quad \bar{p}_i^E$

GD $SdT \cancel{+} - Vdp + Nd\hat{\mu} = 0$ (Single component)

$SdT - Vdp + \sum N_i d\hat{\mu}_i = 0$ Multi component

$sdT - vdp + \sum x_i d\hat{\mu}_i = 0$ (In terms of molar properties)

$s^E dT - v^E dp + \sum x_i \underset{\substack{\downarrow \\ RT\ln}}{\boxed{d\bar{g}_i^E}} = 0$

$\bar{g}_i^E = RT\ln\gamma_i$

Let us start from the beginning and see how we can derive the Gibbs Duhem equation in terms of gamma? Remember the basic equation it was SdT minus Vdp plus Ndmui equals to 0 this we had found out for single component, agreed? For multi-component what should what should happen? The same equation but this should be Sigma should come up Nidmu i equals to 0, this is for multi-component case.

In terms of molar property everything becomes small, plus Sigma xi d mu i equals to 0 in terms of molar properties, agreed? So therefore in terms of excess molar properties again let us write down, can I not write it down as mu i is nothing but gb gi bar E equals to 0, right? And again I know what is this gi bar E. We have derived it it is nothing but RT ln gamma i, agreed? So therefore instead of this di bar g I can just write down RT ln gamma i then what happens to the Gibbs Duhem equation?

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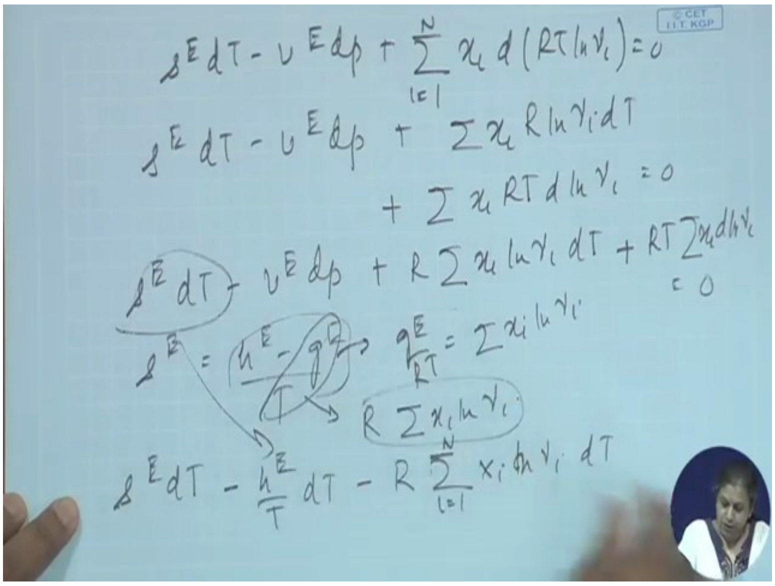

$$s^E dT - v^E dp + \sum_{i=1}^{N} x_i\, d(RT \ln \gamma_i) = 0$$

$$s^E dT - v^E dp + \sum x_i R \ln \gamma_i dT + \sum x_i RT\, d \ln \gamma_i = 0$$

$$s^E dT - v^E dp + R \sum x_i \ln \gamma_i dT + RT \sum x_i\, d \ln \gamma_i = 0$$

$$s^E = \frac{h^E - g^E}{T} \rightarrow \frac{g^E}{RT} = \sum x_i \ln \gamma_i$$

$$R \sum x_i \ln \gamma_i$$

$$s^E dT - \frac{h^E}{T} dT - R \sum_{i=1}^{N} x_i \ln \gamma_i dT$$

The Gibbs Duhem equation then becomes sEdT minus vE dp plus Sigma i equals to 1 to N of whatever xi d RT ln gamma i equals to 0, agreed? We can write it down in this particular way, so therefore and now if we expand this part what do we get? We get sEdT minus vEdp I am just deriving it so that it will be easier for you xi R ln gamma i dT plus Sigma xi RT d ln gamma i equals to 0, agreed? So therefore what do I get finally sEdT minus vEdp plus R written in a proper shape xi ln gamma i dT plus RT Sigma xid ln gamma i this is equals to 0, fine.

What is sE equals to? It is nothing but equals to hE minus gE by T we have already done it. What is this gE? Again I would like to (re) recollect gE by RT it is equal to Sigma xi ln gamma i, right? So therefore this particular term gE by T, can this not be written down as R Sigma xi ln gamma i? Let us substitute it here what do we get? Do we not get sEdT minus hE by T dT minus R? Then this term and this term they cancel these 2 terms this and this they cancel out and we get minus R Sigma i equals to 1 to N Xi ln gamma i dT, fine.This particular term, this term then can be written down as this term can be written in this particular form, okay. And so therefore on substituting this particular this and this in this equation, what do we get?

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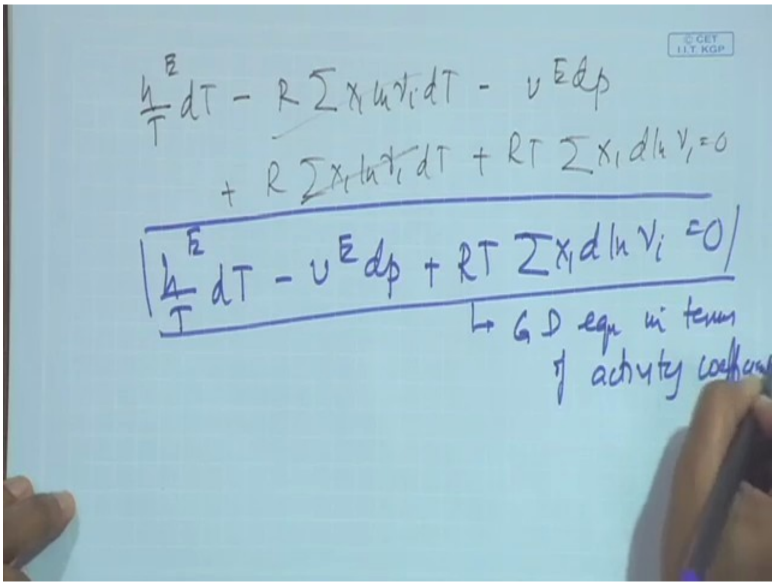

$$\frac{h^E}{T}dT - R\sum x_i \ln\gamma_i dT - v^E dp$$

$$+ \cancel{R\sum x_i \ln\gamma_i dT} + RT\sum x_i d\ln\gamma_i = 0$$

$$\boxed{\frac{h^E}{T}dT - v^E dp + RT\sum x_i d\ln\gamma_i = 0}$$

↳ G D eqn in terms of activity coeffic

We get equation like this hE by T dT minus R I have just substituted Xi ln gamma i dT minus vEdp plus R sigma Xi ln gamma i dT plus RT Sigma Xi d Ln gamma i equals to 0. We immediately find that this and this and this they cancels out and when all these cancels out, what is the final equation that we get? Final equation it becomes hE by T dT minus vE dp plus Rt Sigma Xid ln gamma i equals to 0. This is the final equation this is the Gibbs Duhem equation in terms of activity coefficient gamma, right?

So therefore this is the equation that that we get under this particular condition.

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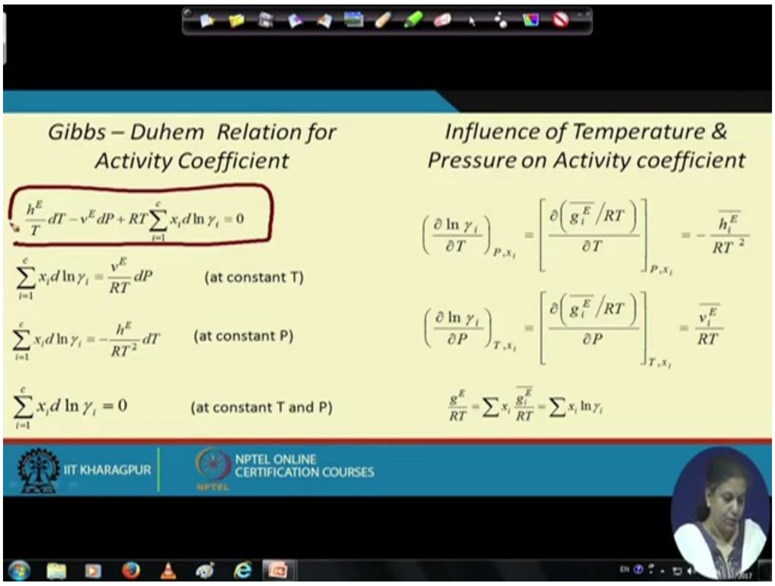

Gibbs – Duhem Relation for Activity Coefficient

$$\frac{h^E}{T}dT - v^E dP + RT\sum_{i=1}^{c} x_i d\ln\gamma_i = 0$$

$$\sum_{i=1}^{c} x_i d\ln\gamma_i = \frac{v^E}{RT}dP$$ (at constant T)

$$\sum_{i=1}^{c} x_i d\ln\gamma_i = -\frac{h^E}{RT^2}dT$$ (at constant P)

$$\sum_{i=1}^{c} x_i d\ln\gamma_i = 0$$ (at constant T and P)

Influence of Temperature & Pressure on Activity coefficient

$$\left(\frac{\partial \ln\gamma_i}{\partial T}\right)_{P,x_i} = \left[\frac{\partial\left(\overline{g_i^E}/RT\right)}{\partial T}\right]_{P,x_i} = -\frac{\overline{h_i^E}}{RT^2}$$

$$\left(\frac{\partial \ln\gamma_i}{\partial P}\right)_{T,x_i} = \left[\frac{\partial\left(\overline{g_i^E}/RT\right)}{\partial P}\right]_{T,x_i} = \frac{\overline{v_i^E}}{RT}$$

$$\frac{g^E}{RT} = \sum x_i \frac{\overline{g_i^E}}{RT} = \sum x_i \ln\gamma_i$$

And then remember one thing that when we are dealing with properties this is what I have written down this is the final equation that I have written down so this is the equation that we have obtained, right? Now here I would like to mention one more thing before I go further. Since this is a property therefore we can have this particular derivation in an alternative form as well.

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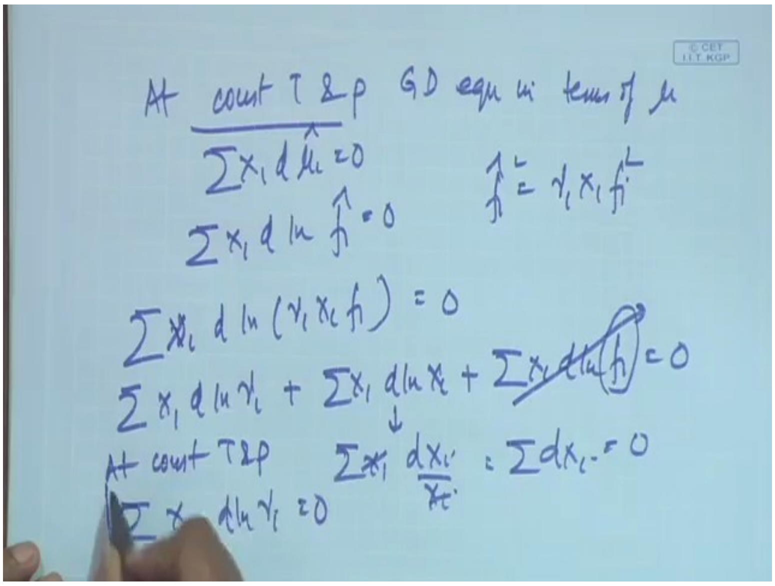

At const T & p GD equ in terms of μ

$$\sum x_i d\hat{\mu}_i = 0 \qquad \hat{f}_i^L = \gamma_i x_i f_i^L$$

$$\sum x_i d\ln\hat{f}_i = 0$$

$$\sum x_i d\ln(\gamma_i x_i f_i) = 0$$

$$\sum x_i d\ln\gamma_i + \sum x_i d\ln x_i + \cancel{\sum x_i d\ln f_i} = 0$$

At const T & p $\quad \sum x_i \frac{dx_i}{x_i} = \sum dx_i = 0$

$$\sum x_i d\ln\gamma_i = 0$$

Instead of starting from this particular way we could have also started the Gibbs Duhem equation in terms of mui and we could have proceeded. At constant temperature and pressure Gibbs Duhem equation in terms of mui, in this particular case we have started with gi bar in terms of fugacity or in terms of mu, suppose we write we can also start with this particular equation, okay. In terms of fugacity this becomes Xi d ln fi bar equals to 0, right?

We know fi bar is nothing but equal to gamma I Xifi everything is for is for the liquid phase if you take, so therefore can I not write it down in this particular way gamma i d, Xi d ln gamma i Xi fi Sigma this is equals to 0, right? So therefore we if you break it down what happen? This is Xi d ln gamma i plus sigma Xi d ln Xi plus Sigma Xi d ln fi equals to 0 this is a easier derivation. So that is why I am just doing it for you.

Now try to understand we have started with constant temperature and pressure. At constant temperature and pressure, what is fi equals to? It is a fugacity of the pure component liquid at the same conditions of temperature and pressure and we know that from low to moderate pressure it is a saturated vapor pressure. So when T and P are constant fi automatically becomes constant. So therefore even if it is at low to moderate pressure or at any pressure we know that this component becomes equal to 0.

What about this part? This is nothing but equal to Sigma Xi dXi by Xi, isn't it? Or in other words this is Sigma dXi. What is this? This Sigma of dXi means the variation of the total number of moles we know the total number of moles of the component is constant. So therefore automatically this becomes equal to 0. So therefore what does it imply? It implies that at constant T and P automatically Xi d ln gamma i equals to 0.

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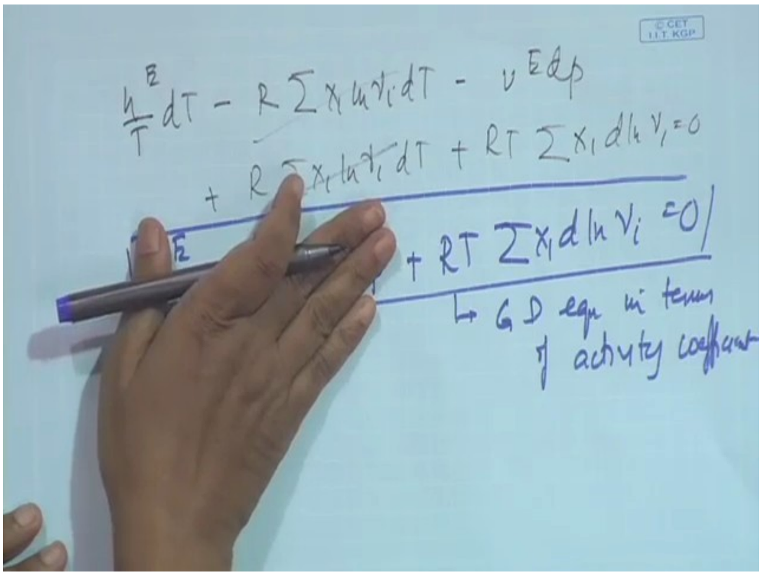

Just the same equation which I have derived here but this was the generalized expression at constant T and P this goes out. So therefore this is the equation which I have derived in this particular case as well, right?

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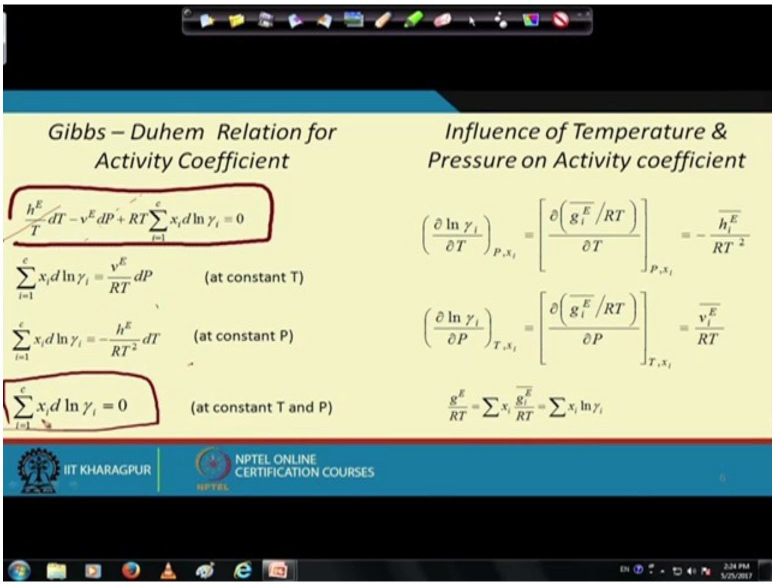

Gibbs – Duhem Relation for Activity Coefficient

$$\boxed{\frac{h^E}{T}dT - v^E dP + RT\sum_{i=1}^{c} x_i d\ln\gamma_i = 0}$$

$$\sum_{i=1}^{c} x_i d\ln\gamma_i = \frac{v^E}{RT}dP$$ (at constant T)

$$\sum_{i=1}^{c} x_i d\ln\gamma_i = -\frac{h^E}{RT^2}dT$$ (at constant P)

$$\boxed{\sum_{i=1}^{c} x_i d\ln\gamma_i = 0}$$ (at constant T and P)

Influence of Temperature & Pressure on Activity coefficient

$$\left(\frac{\partial \ln\gamma_i}{\partial T}\right)_{P,x_i} = \left[\frac{\partial\left(\overline{g_i^E}/RT\right)}{\partial T}\right]_{P,x_i} = -\frac{\overline{h_i^E}}{RT^2}$$

$$\left(\frac{\partial \ln\gamma_i}{\partial P}\right)_{T,x_i} = \left[\frac{\partial\left(\overline{g_i^E}/RT\right)}{\partial P}\right]_{T,x_i} = \frac{\overline{v_i^E}}{RT}$$

$$\frac{g^E}{RT} = \sum x_i \frac{\overline{g_i^E}}{RT} = \sum x_i \ln\gamma_i$$

So therefore this is the generalized equation which we have we find that at constant temperature naturally this term goes off and this is the equation at constant pressure this term goes off and therefore this is the equation at constant temperature and pressure I have derived this equation in two particular ways and we find that this is the equation. Now this equation just like I had told you previously this equation is very important particular importance or can be better appreciated if we can write it down in terms of a binary mixture.

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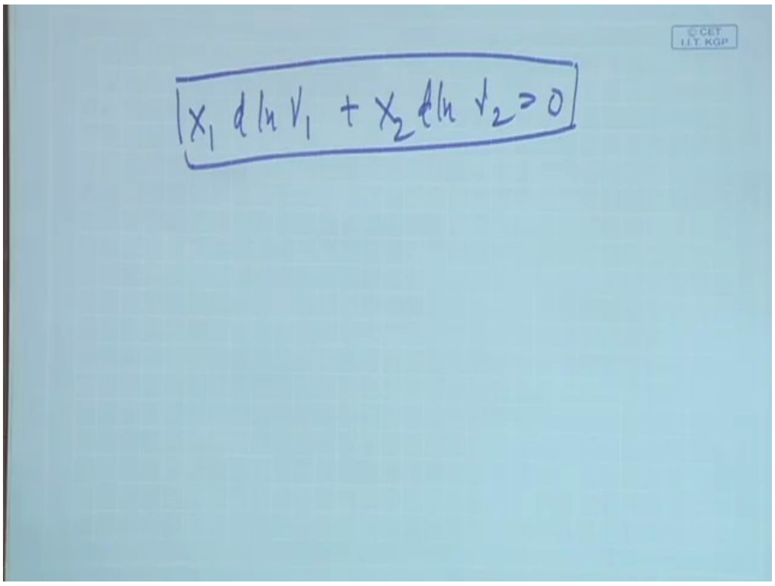

$$\boxed{x_1\, d\ln \gamma_1 + x_2\, d\ln \gamma_2 = 0}$$

In terms of a binary mixture what do how can we write down the equation it is X1 d ln gamma 1 plus X2 d ln gamma 2 equals to 0, agree? So therefore from this particular equation there are a number of important information that we can get which you are going to discuss in the next class.