Chemical Engineering Thermodynamics
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Lecture 42 - Fugacity coefficient for ideal mixtures

Welcome back. So, let me just recap what we have done in the last few lectures and then subsequently, we will discuss about ideal mixtures. So if you look at it how we shaped up the discussion in the last few lectures, we just talked about the mixtures of the gases and we particularly looked at ideal gas mixtures, basically where the interactions between the particles are negligible.

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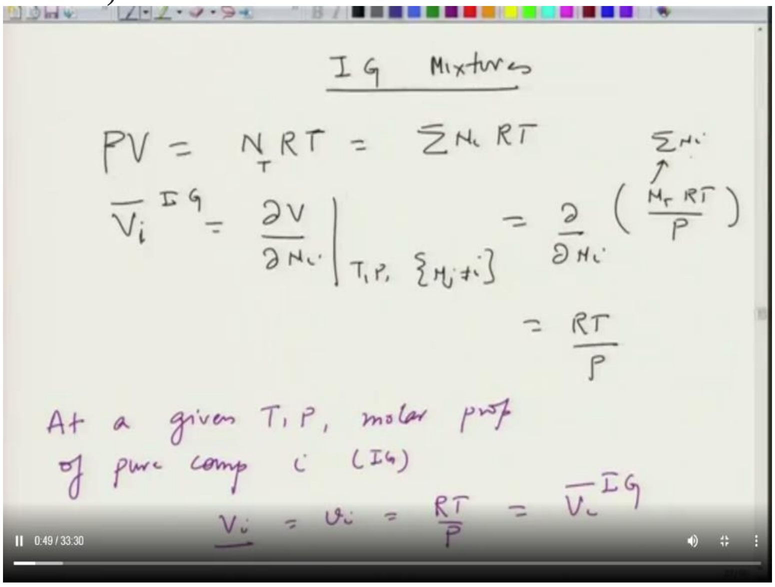

IG Mixtures

$$PV = N_T RT = \sum N_i RT \qquad \uparrow \sum N_i$$

$$\bar{V}_i^{IG} = \left.\frac{\partial V}{\partial N_i}\right|_{T,P,\{N_{j\neq i}\}} = \frac{\partial}{\partial N_i}\left(\frac{N_T RT}{P}\right) = \frac{RT}{P}$$

At a given T, P, molar prop of pure comp i (IG)

$$\underline{V_i} = v_i = \frac{RT}{P} = \bar{V}_i^{IG}$$

So if you look at the way we derived the property, so let me just quickly go through this. So essentially what we wrote is that if for a given mixture if they behave ideal gas, then the ideal gas equation of state is valid and we can write this partial molar property, partial molar volume in this case as simply RT by P.

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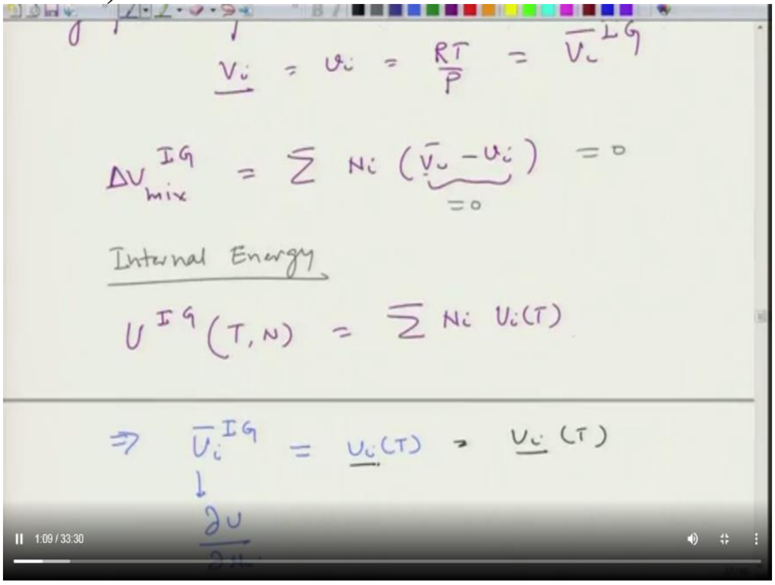

$\underline{V_i} = v_i = \frac{RT}{P} = \bar{V}_i^{IG}$

$\Delta V_{mix}^{IG} = \sum N_i (\underbrace{\bar{V}_i - v_i}_{=0}) = 0$

Internal Energy

$U^{IG}(T, N) = \sum N_i U_i(T)$

$\Rightarrow \bar{U}_i^{IG} = \underline{U_i}(T) \rightarrow \underline{U_i}(T)$

$\downarrow$

$\frac{\partial U}{\partial N_i}$

And we try to derive the change in the property of the mixtures such as delta V makes ideal, we show that is equal to 0.

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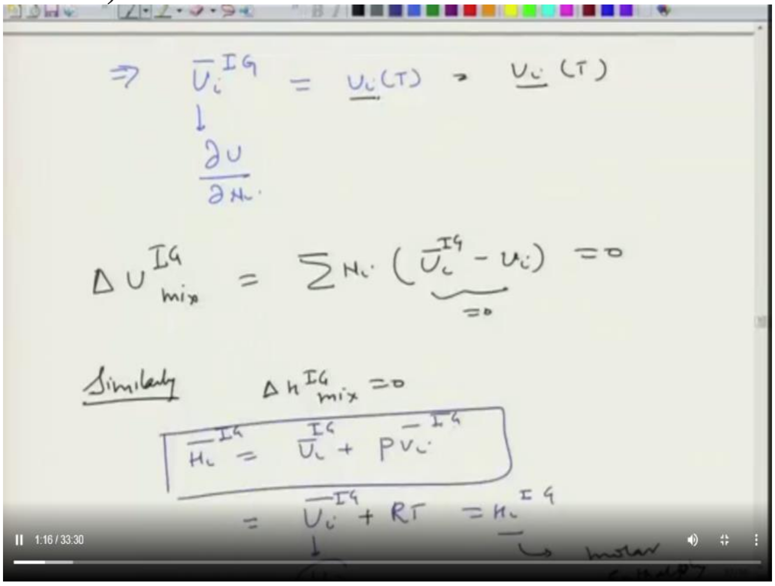


$\Rightarrow \bar{U}_i^{IG} = \underline{U_i}(T) \rightarrow \underline{U_i}(T)$

$\downarrow$

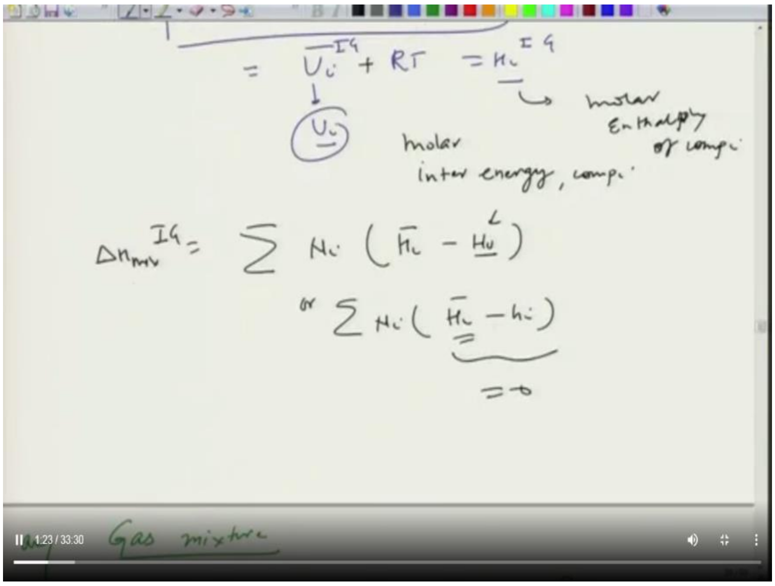
$\frac{\partial U}{\partial N_i}$

$\Delta U_{mix}^{IG} = \sum N_i (\underbrace{\bar{U}_i^{IG} - u_i}_{=0}) = 0$

Similarly $\Delta h_{mix}^{IG} = 0$

$\boxed{\bar{H}_i^{IG} = \bar{U}_i^{IG} + P\bar{V}_i^{IG}}$

$= \bar{U}_i^{IG} + RT = \underline{h_i}^{IG}$ ↪ molar



$$= \bar{U}_i^{IG} + RT = \bar{H}_i^{IG}$$

$\underline{U}_i$ molar inter energy, comp. i

molar Enthalpy of comp. i

$$\Delta H_{mix}^{IG} = \sum N_i \left(\bar{H}_i - \underline{H}_i \right)$$

$$\text{or } \underbrace{\sum N_i \left(\bar{H}_i - h_i \right)}_{= 0}$$

Gas mixture

Similarly, we showed that delta U ideal gas mixture is equal to 0 and so on. We also showed that delta H mix ideal gas is also equal to 0.

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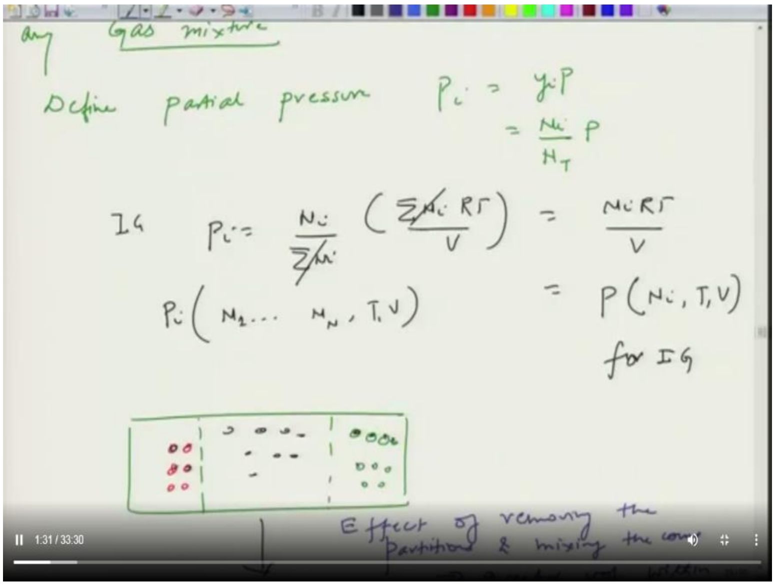

any Gas mixture

Define partial pressure $P_i = y_i P = \frac{N_i}{N_T} P$

$$\text{IG} \quad P_i = \frac{N_i}{\cancel{\sum N_i}} \left(\frac{\cancel{\sum N_i} RT}{V} \right) = \frac{N_i RT}{V}$$

$$P_i(N_1 \ldots N_N, T, V) = P(N_i, T, V) \text{ for IG}$$

Effect of removing the partitions & mixing the comp.

Then we talked about entropy that what will be the change in entropy and we realized that you know, if you take two different containers containing ideal gas and mix, then each particle individual particle will have more volume accessible and subsequently the entropy of each of the component will increase and thus since entropy is an extensive property we can just add it up the change in entropy for each component. And that is what we try to derive here if you look at it carefully.

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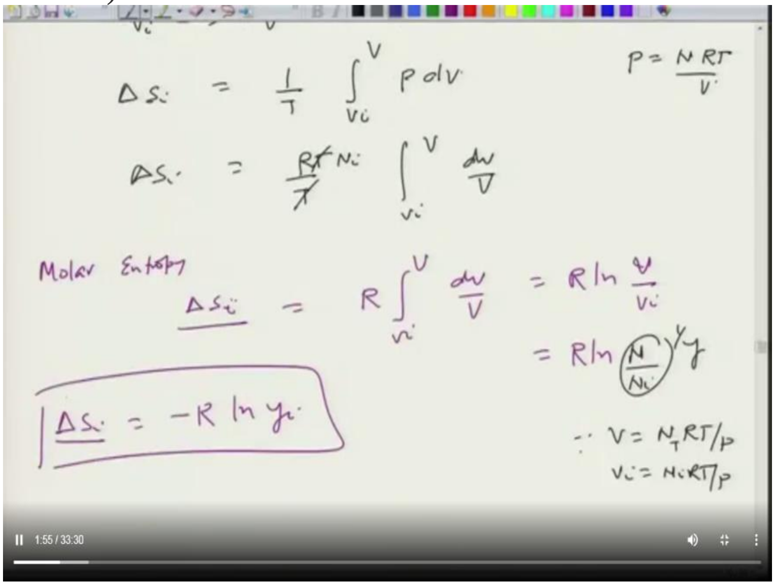


$$\Delta S_i = \frac{1}{T}\int_{V_i}^{V} P\,dV \qquad P = \frac{NRT}{V}$$

$$\Delta S_i = \frac{R\cancel{T}N_i}{\cancel{T}}\int_{V_i}^{V}\frac{dV}{V}$$

Molar Entropy

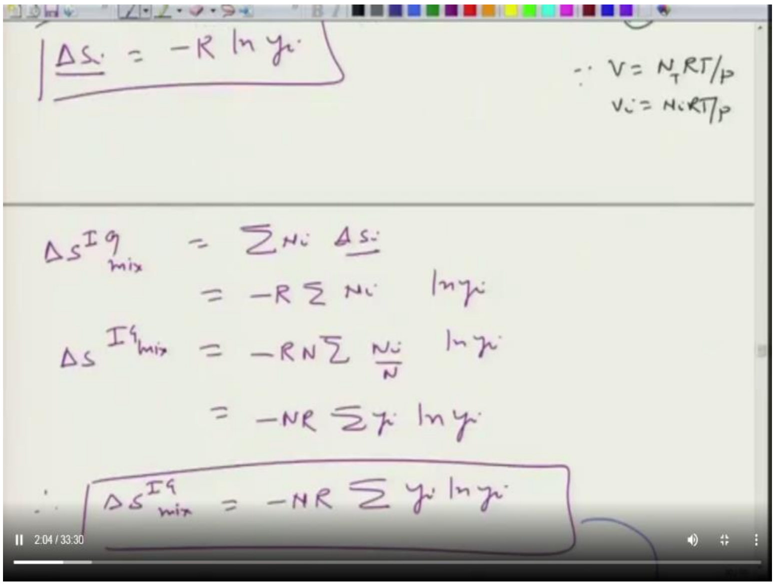
$$\underline{\Delta S_i} = R\int_{V_i}^{V}\frac{dV}{V} = R\ln\frac{V}{V_i}$$

$$= R\ln\left(\frac{N}{N_i}\right)^{1/y}$$

$$\boxed{\underline{\Delta S_i} = -R\ln y_i}$$

$$\because V = N_T RT/P$$

$$V_i = N_i RT/P$$



$$\boxed{\underline{\Delta S_i} = -R\ln y_i}$$

$$\because V = N_T RT/P$$

$$V_i = N_i RT/P$$

$$\Delta S^{IG}_{mix} = \sum N_i\,\underline{\Delta S_i}$$

$$= -R\sum N_i \ln y_i$$

$$\Delta S^{IG}_{mix} = -RN\sum\frac{N_i}{N}\ln y_i$$

$$= -NR\sum y_i \ln y_i$$

$$\therefore \boxed{\Delta S^{IG}_{mix} = -NR\sum y_i\ln y_i}$$

So if we add it up all of them, it turns out for molar excess, molar change in entropy for each individual component is nothing but minus R ln y i and hence if you add it up for the mixtures, it turns out to be simply minus NR summation y i ln y i in terms of the total change here.

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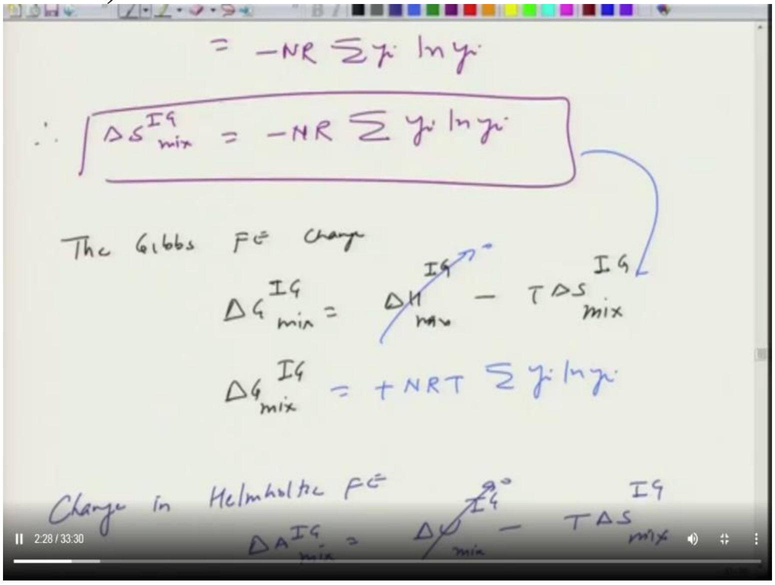

$= -NR \sum y_i \ln y_i$

$\therefore \boxed{\Delta S^{IG}_{mix} = -NR \sum y_i \ln y_i}$

The Gibbs FE change

$\Delta G^{IG}_{mix} = \overset{0}{\cancel{\Delta H^{IG}_{mix}}} - T\Delta S^{IG}_{mix}$

$\Delta G^{IG}_{mix} = +NRT \sum y_i \ln y_i$

Change in Helmholtz FE

$\Delta A^{IG}_{mix} = \overset{0}{\cancel{\Delta U^{IG}_{mix}}} - T\Delta S^{IG}_{mix}$

So this is what we derived. And this was extended to delta G mix ideal which also will have will be nonzero and it will be NRT summation y i ln y i because of the simple fact that the entropy change of ideal gas mixture is nonzero.

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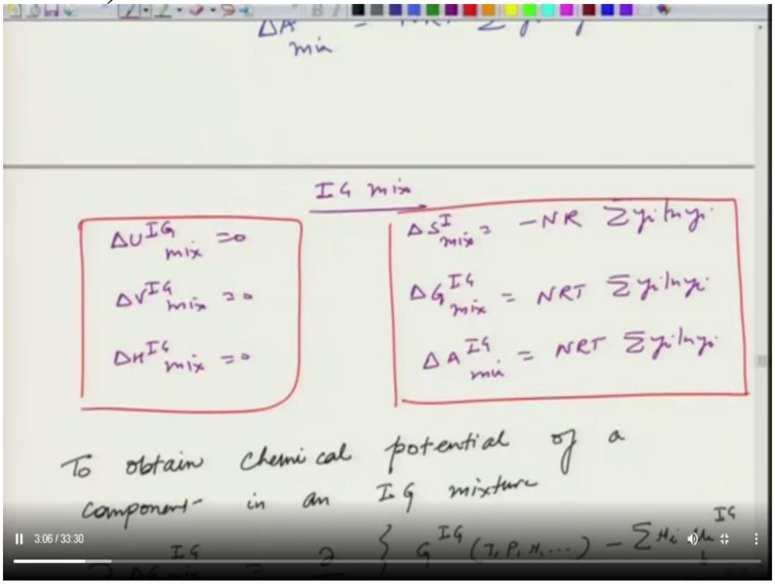

ΔA_{mix}

IG mix

$\Delta U^{IG}_{mix} = 0$

$\Delta V^{IG}_{mix} = 0$

$\Delta H^{IG}_{mix} = 0$

$\Delta S^{IG}_{mix} = -NR \sum y_i \ln y_i$

$\Delta G^{IG}_{mix} = NRT \sum y_i \ln y_i$

$\Delta A^{IG}_{mix} = NRT \sum y_i \ln y_i$

To obtain chemical potential of a component in an IG mixture

$\{ G^{IG}(T, P, N_1, \ldots) - \sum N_i$

So this was the summary of all the ideal gas properties here where essentially we say that well you have this component the change in the thermodynamic properties such as U, V and H for ideal gas mixture is going to be 0 and for the case of entropy Gibbs free energy and Helmholtz free energy the changes are written in this form, which is nothing but summation y i ln y i. For the case of G and A free energies, you will be multiplying that with NRT, for the case of entropy which is multiplying by minus NR.

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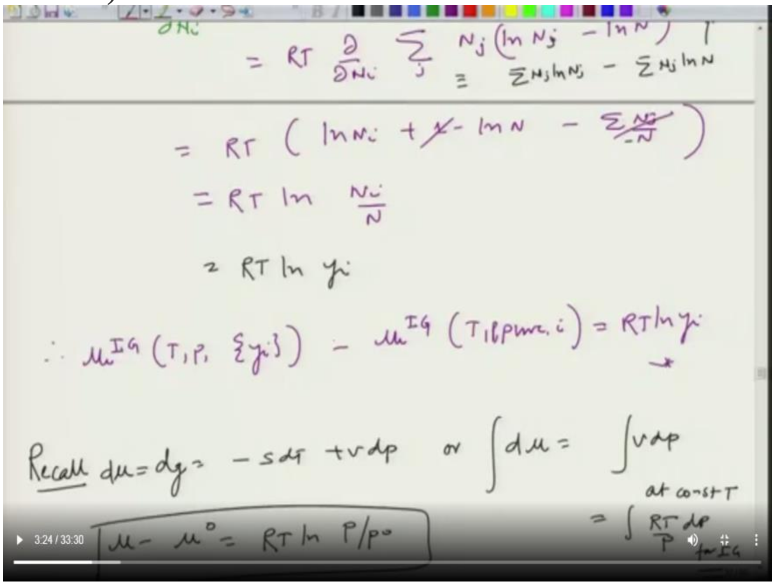


$$= RT \frac{\partial}{\partial N_i} \sum_j N_j (\ln N_j - \ln N) \equiv \sum N_j \ln N_j - \sum N_j \ln N$$

$$= RT \left(\ln N_i + \cancel{1} - \ln N - \cancel{\sum \frac{N_j}{N}} \right)$$

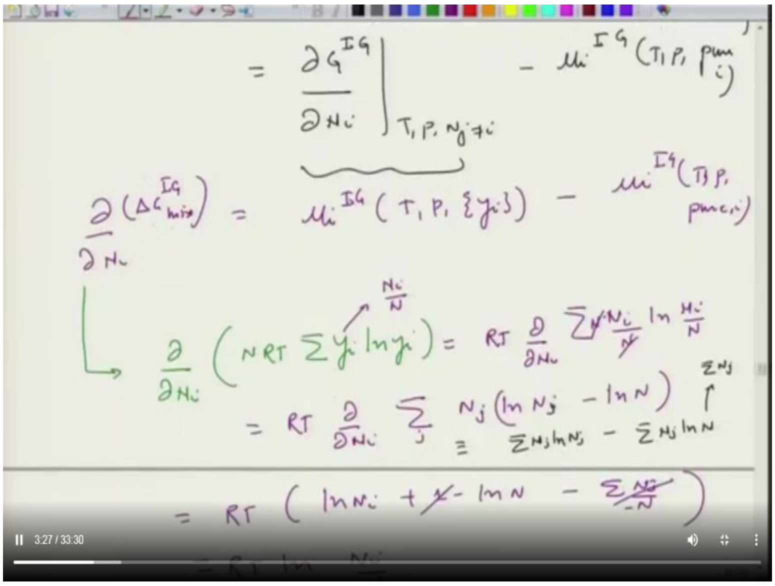
$$= RT \ln \frac{N_i}{N}$$

$$= RT \ln y_i$$

$$\therefore \mu_i^{IG}(T, P, \{y_i\}) - \mu_i^{IG}(T, P, \text{pure } i) = RT \ln y_i$$

Recall $d\mu = dg = -s\,dT + v\,dP$ or $\int d\mu = \int v\,dP$ at const T $= \int \frac{RT\,dP}{P}$ for IG

$$\boxed{\mu - \mu^\circ = RT \ln P/P^\circ}$$



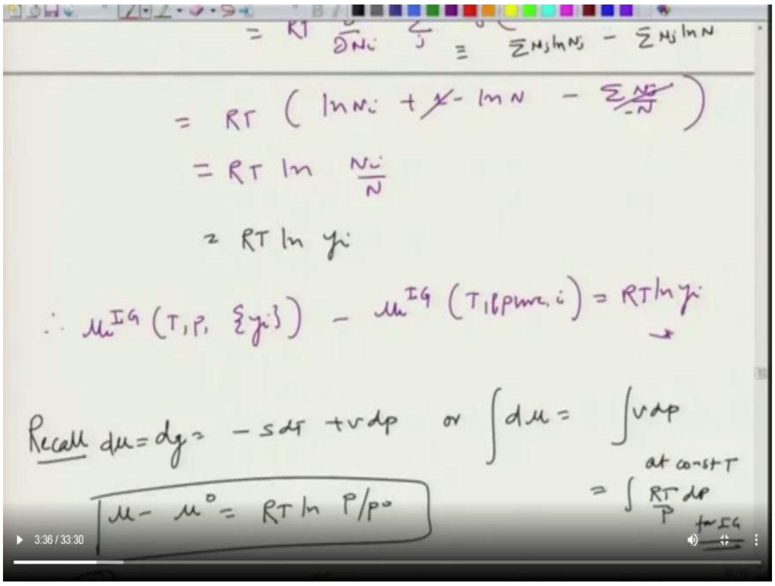
$$= \left.\frac{\partial G^{IG}}{\partial N_i}\right|_{T, P, N_{j \neq i}} - \mu_i^{IG}(T, P, \text{pure } i)$$

$$\frac{\partial (\Delta G^{IG}_{mix})}{\partial N_i} = \underbrace{\mu_i^{IG}(T, P, \{y_i\})} - \mu_i^{IG}(T, P, \text{pure } i)$$

$$\frac{\partial}{\partial N_i}\left(NRT \sum \overset{N_i/N}{y_i} \ln y_i \right) = RT \frac{\partial}{\partial N_i} \sum \cancel{N} \frac{N_i}{\cancel{N}} \ln \frac{N_i}{N}$$

$$= RT \frac{\partial}{\partial N_i} \sum_j N_j (\ln N_j - \ln N) \equiv \sum N_j \ln N_j - \sum N_j \ln N$$

$$= RT \left(\ln N_i + \cancel{1} - \ln N - \cancel{\sum \frac{N_j}{N}} \right)$$



$$= RT \frac{\partial}{\partial N_i} \sum_j \equiv \sum N_j \ln N_j - \sum N_j \ln N$$

$$= RT \left(\ln N_i + \cancel{1} - \ln N - \cancel{\sum \frac{N_j}{N}} \right)$$

$$= RT \ln \frac{N_i}{N}$$

$$= RT \ln y_i$$

$$\therefore \mu_i^{IG}(T, P, \{y_i\}) - \mu_i^{IG}(T, P, \text{pure } i) = RT \ln y_i$$

Recall $d\mu = dg = -s\,dT + v\,dP$ or $\int d\mu = \int v\,dP$ at const T $= \int \frac{RT\,dP}{P}$ for IG

$$\boxed{\mu - \mu^\circ = RT \ln P/P^\circ}$$

And then subsequently what we did is we try to relate the change in the chemical potential of a component i in the mixture with respect to that in the pure component and then the derivation was simply we had to take the partial derivative of this delta G mix with respect to N i and that we could show that is nothing but RT ln y.

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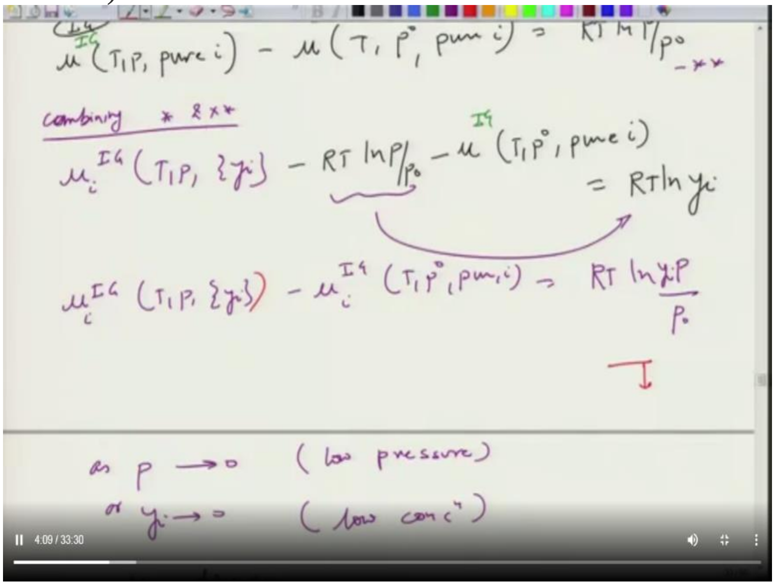

$$\mu^{IG}(T, P, \text{pure } i) - \mu(T, P^{\circ}, \text{pure } i) = RT \ln P/P_0 \quad -**$$

combining * & **

$$\mu_i^{IG}(T, P, \{y_i\}) - \underbrace{RT \ln P/P_0} - \mu^{IG}(T, P^{\circ}, \text{pure } i) = RT \ln y_i$$

$$\mu_i^{IG}(T, P, \{y_i\}) - \mu_i^{IG}(T, P^{\circ}, \text{pure } i) = RT \ln \frac{y_i P}{P_0} \quad \text{I}$$

as $P \to 0$ (low pressure)

or $y_i \to 0$ (low conc^n)

Using the concept of the thermodynamic equations for the pure component we can figure it out that this can be further written in terms of this expression, where mu i ideal gas T P y i minus mu i ideal gas T P is 0, Pure i is nothing but RT ln y i P which is a partial pressure divided by P 0 and P 0 are something which is a reference pressure. So, if pressure goes to 0 that is low pressure, then of course y i concentration will also diverge, also the concentration will tend to 0 and in that case if you plug in there it tells you that the chemical potential diverges. And that is how we introduced the fugacity. That is the definition of the fugacity.

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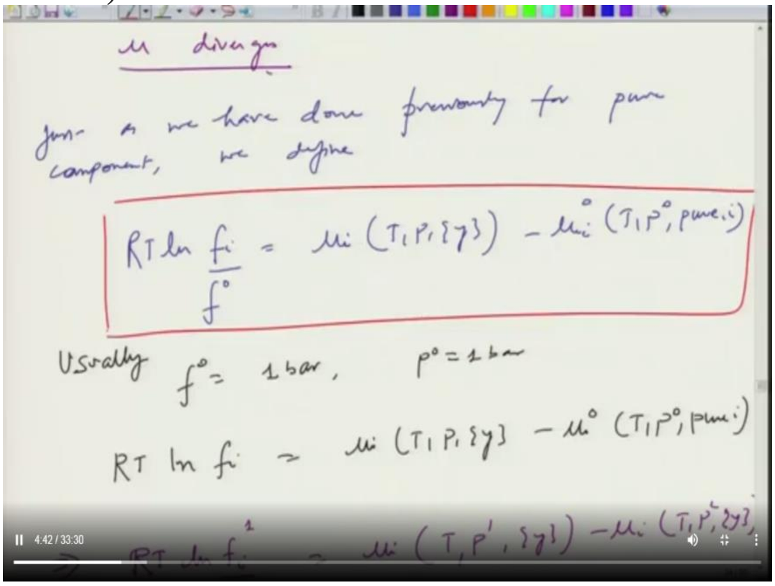

μ diverges

Hence, as we have done previously for pure component, we define

$$\boxed{RT \ln \frac{f_i}{f^0} = \mu_i(T,P,\{y\}) - \mu_i^0(T,P^0,\text{pure } i)}$$

Usually $f^0 = 1$ bar, $P^0 = 1$ bar

$$RT \ln f_i = \mu_i(T,P,\{y\}) - \mu_i^0(T,P^0,\text{pure } i)$$

$$\Rightarrow RT \ln \frac{f_i^1}{f_i^2} = \mu_i(T,P^1,\{y\}) - \mu_i(T,P^2,\{y\})$$

Because to avoid these kind of diversions and we wrote it in this way that RT ln f i f 0 is nothing but the chemical potential of a component i in the mixture minus chemical potential of i for the reference state, which could be a pure state but at a P 0. And f 0 and P zeroes are related; usually these are at 1 bar.

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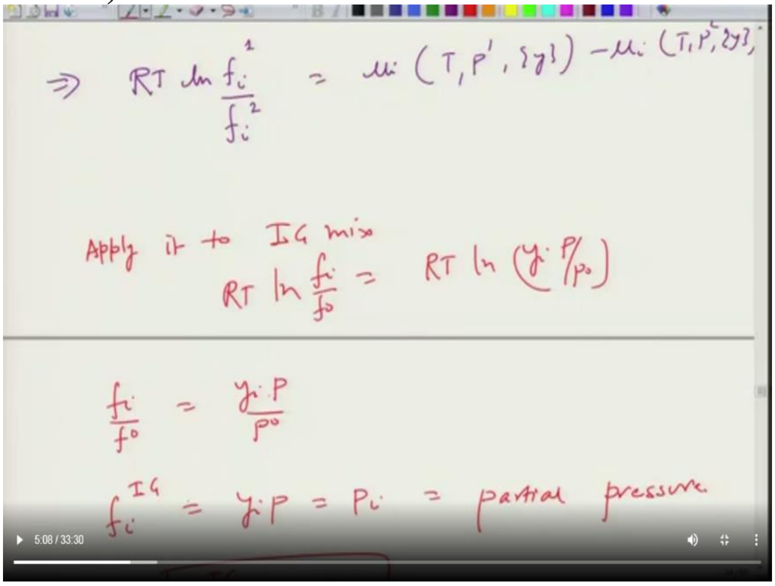

$$\Rightarrow RT \ln \frac{f_i^1}{f_i^2} = \mu_i(T,P^1,\{y\}) - \mu_i(T,P^2,\{y\})$$

Apply it to IG mix

$$RT \ln \frac{f_i}{f^0} = RT \ln \left(y_i P/P^0\right)$$

$$\frac{f_i}{f^0} = \frac{y_i P}{P^0}$$

$$f_i^{IG} = y_i P = P_i = \text{partial pressure}$$

So for the case of ideal gas when we use this expression, because this is a generic expression if we put it at for particular for ideal gas it you can show that for the ideal gas f i need to be equal to y i P. That means f i for ideal gas is nothing but the partial pressure. So this is something which we showed.

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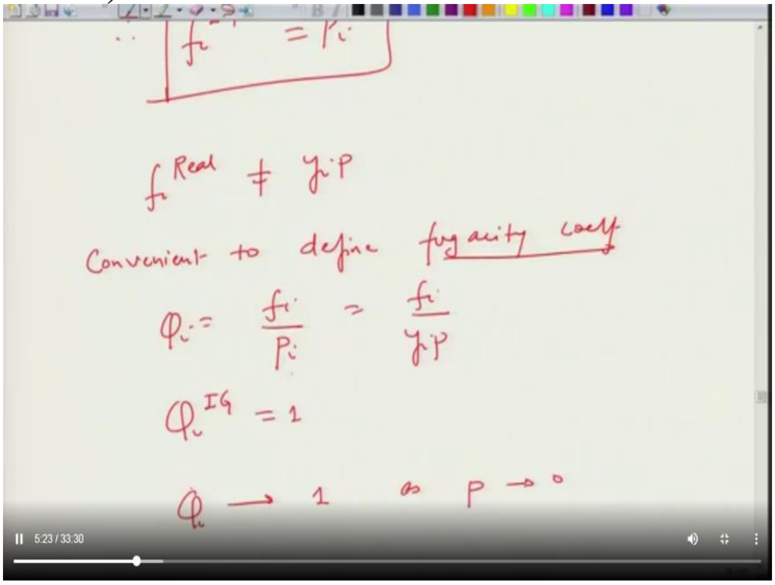

$$\boxed{f_i = p_i}$$

$f_i^{Real} \neq y_i P$

Convenient to define fugacity coeff

$$\phi_i = \frac{f_i}{p_i} = \frac{f_i}{y_i P}$$

$$\phi_i^{IG} = 1$$

$$\phi_i \longrightarrow 1 \quad \text{as} \quad P \to 0$$

And for the case of the real one, of course, this will not be same as partial pressure. So we define the fugacity coefficient which was nothing but the ratio of the fugacity with respect to partial pressure and this will approach 1 as P goes to 0. And then the second question was that how do we relate fugacity coefficient to the measurable quantities?

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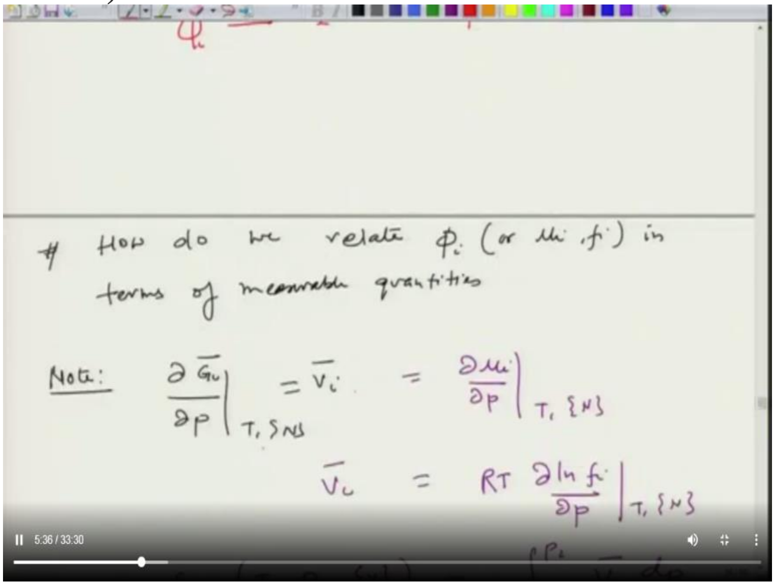

\# How do we relate ϕ_i (or μ_i, f_i) in terms of measurable quantities

Note: $$\left.\frac{\partial \bar{G}_i}{\partial P}\right|_{T,\{N\}} = \bar{V}_i = \left.\frac{\partial \mu_i}{\partial P}\right|_{T,\{N\}}$$

$$\bar{V}_i = RT \left.\frac{\partial \ln f_i}{\partial P}\right|_{T,\{N\}}$$

So you can have a measurable quantity in terms of volumetric data in experiment or something like an equation of state. So we derived two expressions and I will just show you directly there.

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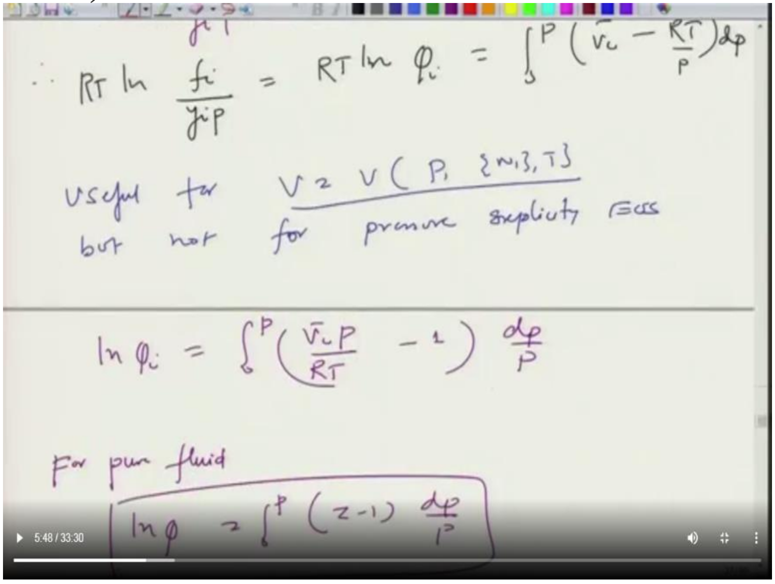

$$\therefore RT \ln \frac{f_i}{y_i P} = RT \ln \phi_i = \int_0^P \left(\bar{V}_i - \frac{RT}{P}\right) dP$$

Useful for $V = V(P, \{N_i\}, T)$

but not for pressure explicitly EOS

$$\ln \phi_i = \int_0^P \left(\frac{\bar{V}_i P}{RT} - 1\right) \frac{dP}{P}$$

For pure fluid

$$\boxed{\ln \phi = \int_0^P (Z-1) \frac{dP}{P}}$$

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Just to recall this, one is of course this. So this is the expression where you need to have volumetric data as a function of P that we need to have the V i's and P's.

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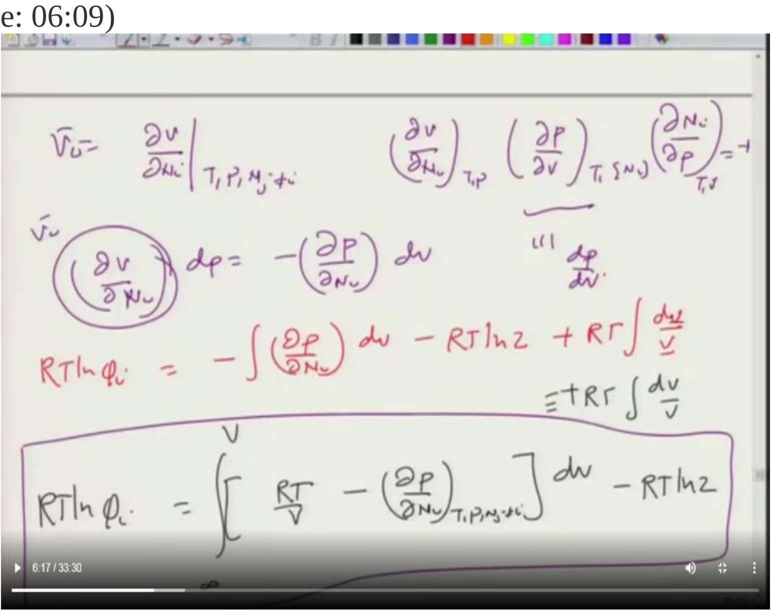

$$\bar{V}_i = \left.\frac{\partial V}{\partial N_i}\right|_{T,P,N_{j\neq i}} \qquad \left(\frac{\partial V}{\partial N_i}\right)_{T,P} \underbrace{\left(\frac{\partial P}{\partial V}\right)_{T,\{N_j\}}}_{\frac{dP}{dV}} \left(\frac{\partial N_i}{\partial P}\right)_{T,V} = -1$$

$$\overset{\bar{V}_i}{\left(\frac{\partial V}{\partial N_i}\right)} dP = -\left(\frac{\partial P}{\partial N_i}\right) dV$$

$$RT \ln \phi_i = -\int \left(\frac{\partial P}{\partial N_i}\right) dV - RT \ln Z + RT \int \frac{dV}{V}$$

$$\equiv + RT \int \frac{dV}{V}$$

$$\boxed{RT \ln \phi_i = \int_\infty^V \left[\frac{RT}{V} - \left(\frac{\partial P}{\partial N_i}\right)_{T,P,N_{j\neq i}}\right] dV - RT \ln Z}$$

6:17 / 33:30

If it is not available if it is only Z information is there or the equation of state is available, then we make use of a different expression which we derived it like this. So let me just further, yeah. So this is the final expression which we came. So here essentially what we require something like in a P as a function of V and T and something you plug in there and you obtain the fugacity coefficient Phi i.

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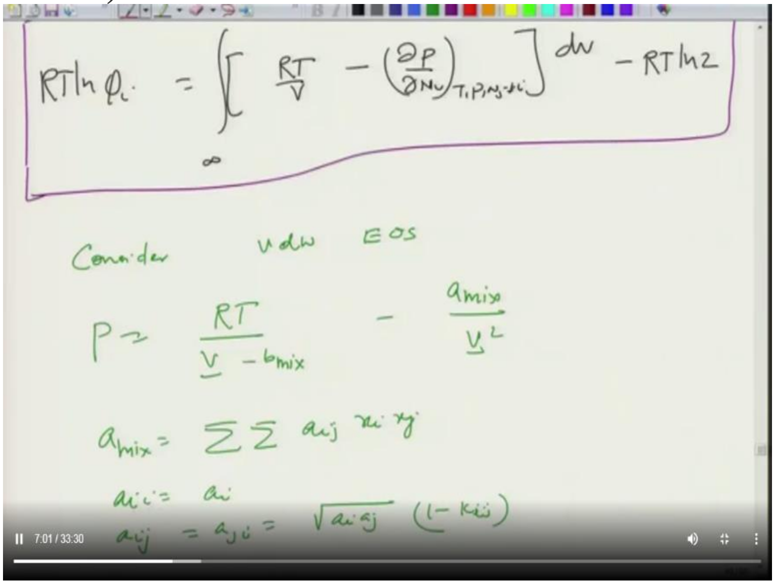


$$RT\ln\phi_i = \int_{\infty} \left[\frac{RT}{V} - \left(\frac{\partial P}{\partial N_i}\right)_{T,P,N_{j\neq i}} \right] dV - RT\ln z$$

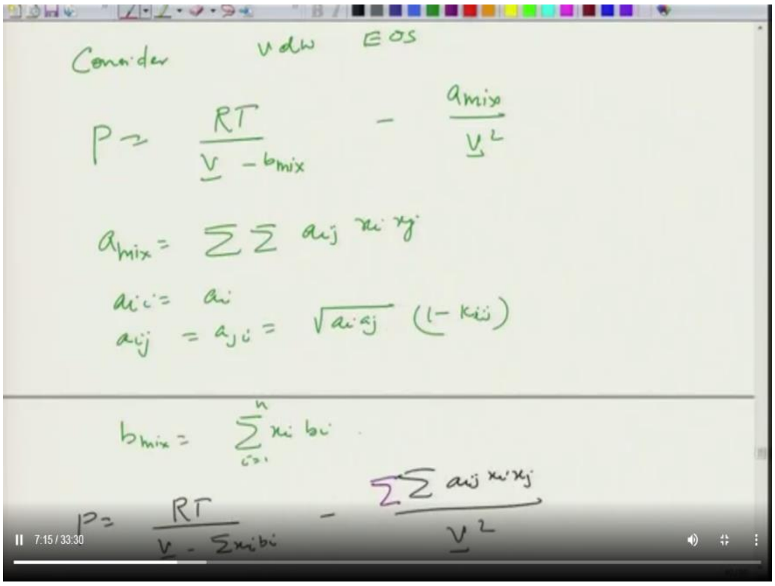
Consider vdw EOS

$$P = \frac{RT}{\underline{V} - b_{mix}} - \frac{a_{mix}}{\underline{V}^2}$$

$$a_{mix} = \sum\sum a_{ij} x_i x_j$$

$$a_{ii} = a_i$$

$$a_{ij} = a_{ji} = \sqrt{a_i a_j}\,(1 - k_{ij})$$



Consider vdw EOS

$$P = \frac{RT}{\underline{V} - b_{mix}} - \frac{a_{mix}}{\underline{V}^2}$$

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$$a_{ii} = a_i$$

$$a_{ij} = a_{ji} = \sqrt{a_i a_j}\,(1 - k_{ij})$$

$$b_{mix} = \sum_{i=1}^{n} x_i b_i$$

$$P = \frac{RT}{\underline{V} - \sum x_i b_i} - \frac{\sum\sum a_{ij} x_i x_j}{\underline{V}^2}$$

So we extended this exercise. We employed our equation of state. We said well, can we just consider let us say Vander Waals equation of state for the mixtures and apply this to obtain the fugacity coefficient.

So we did this exercise where pressure was written in terms of RT molar volume minus b mix, a minus a mix divided by molar volume square and here we use something called mixing rule where a mix is interaction energy or interaction parameter, which is nothing here. It would be a weighted average of a i j where a i i is equal to a i that is for the pure component and a i j is equal to a j i which is nothing but geometric mean of the pure component multiplied by the correction factor. Whereas b is a size effective size, which is nothing but the weighted average of the individual components b's. So we added replace this information here and rearrange that.

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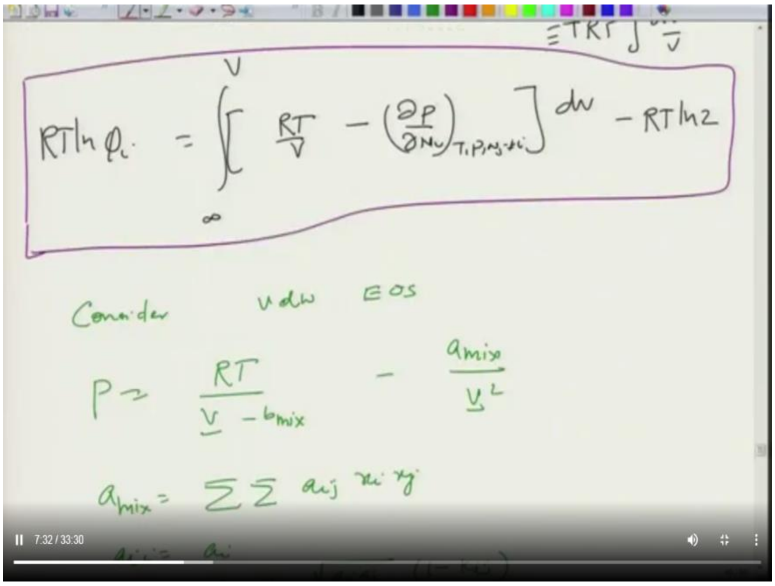

$$\boxed{RT\ln\phi_i = \int_{\infty}^{V}\left[\frac{RT}{V} - \left(\frac{\partial P}{\partial N_i}\right)_{T,P,N_{j\neq i}}\right]dV - RT\ln Z}$$

Consider vdW EOS

$$P = \frac{RT}{\underline{V} - b_{mix}} - \frac{a_{mix}}{\underline{V}^2}$$

$$a_{mix} = \sum\sum a_{ij}\, x_i x_j$$

And essentially if you look at carefully this one, this is equation of state based expression. So what we need is a partial derivative of the pressure with respect to the N i's.

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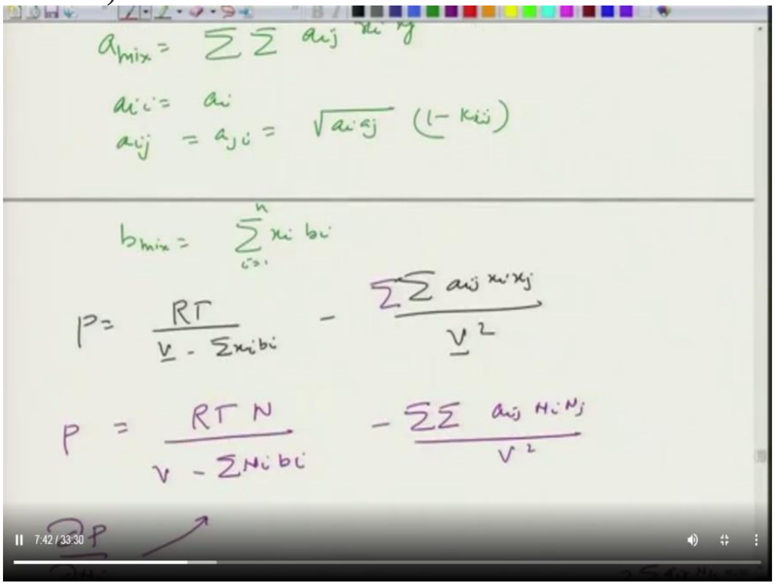


$$a_{mix} = \sum\sum a_{ij}\, x_i x_j$$

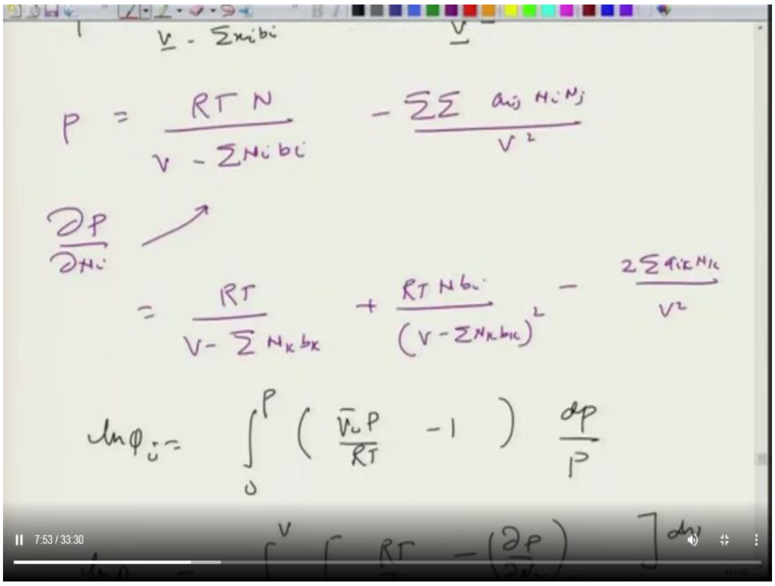
$$a_{ii} = a_i$$

$$a_{ij} = a_{ji} = \sqrt{a_i a_j}\,(1 - k_{ij})$$

$$b_{mix} = \sum_{i=1}^{n} x_i b_i$$

$$P = \frac{RT}{\underline{V} - \sum x_i b_i} - \frac{\sum\sum a_{ij}\, x_i x_j}{\underline{V}^2}$$

$$P = \frac{RTN}{V - \sum N_i b_i} - \frac{\sum\sum a_{ij}\, N_i N_j}{V^2}$$



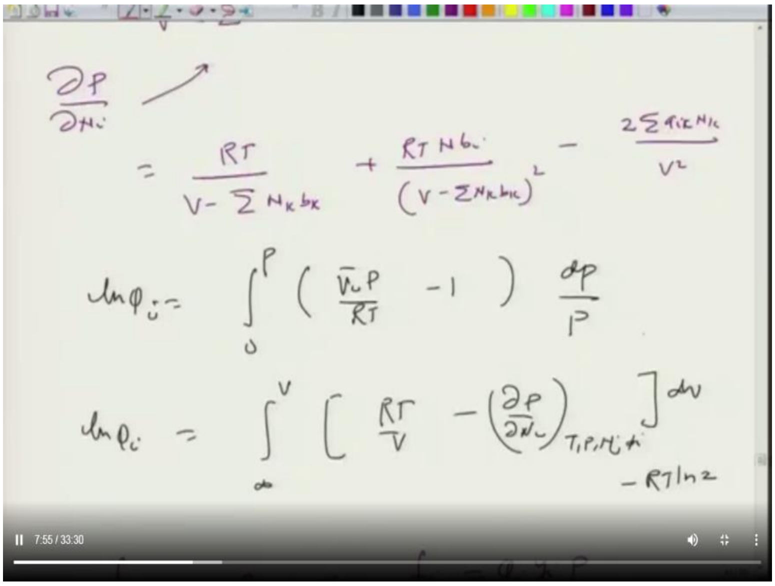
$$\underline{V} - \sum x_i b_i \qquad \underline{V}$$

$$P = \frac{RTN}{V - \sum N_i b_i} - \frac{\sum\sum a_{ij} N_i N_j}{V^2}$$

$$\frac{\partial P}{\partial N_i} \nearrow$$

$$= \frac{RT}{V - \sum N_k b_k} + \frac{RTNb_i}{(V - \sum N_k b_k)^2} - \frac{2\sum a_{ik} N_k}{V^2}$$

$$\ln \phi_i = \int_0^P \left(\frac{\bar{V}_i P}{RT} - 1 \right) \frac{dP}{P}$$



$$\frac{\partial P}{\partial N_i} \nearrow$$

$$= \frac{RT}{V - \sum N_k b_k} + \frac{RTNb_i}{(V - \sum N_k b_k)^2} - \frac{2\sum a_{ik} N_k}{V^2}$$

$$\ln \phi_i = \int_0^P \left(\frac{\bar{V}_i P}{RT} - 1 \right) \frac{dP}{P}$$

$$\ln \phi_i = \int_\infty^V \left[\frac{RT}{V} - \left(\frac{\partial P}{\partial N_i} \right)_{T,P,N_{j \neq i}} \right] dV - RT \ln z$$

And now you have this equation of Vander Waal for the mixtures where you have replaced the coefficients in terms of the compositions which you can convert into mole fraction. And subsequently you can take the partial derivative of this pressure as a function of N i leading to this expression. And then you plug in here and you can obtain more elaborate expression of that. So that is one way to do that.

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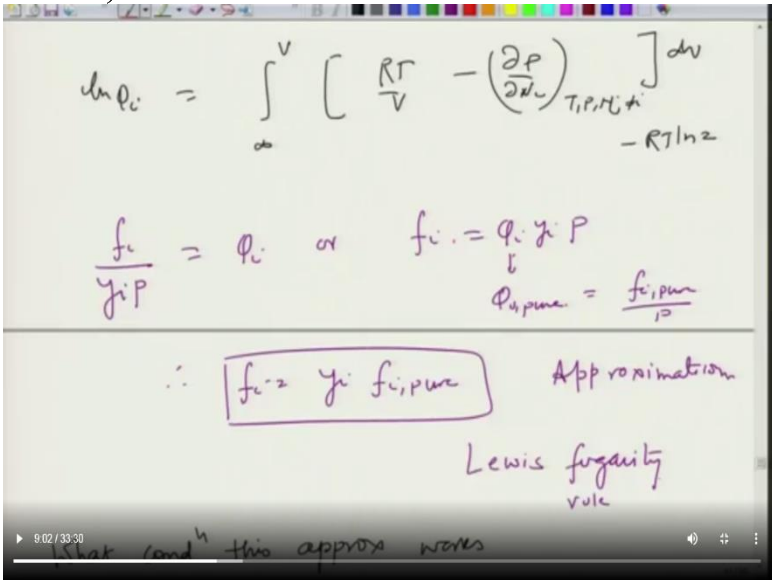

$$\ln \phi_i = \int_{\infty}^{V} \left[\frac{RT}{V} - \left(\frac{\partial P}{\partial N_i}\right)_{T,P,N_j \neq i} \right] dV - RT \ln z$$

$$\frac{f_i}{y_i P} = \phi_i \quad \text{or} \quad f_i = \phi_i y_i P$$

$$\phi_{i,\text{pure}} = \frac{f_{i,\text{pure}}}{P}$$

$$\therefore \boxed{f_i = y_i f_{i,\text{pure}}}$$

Approximation

Lewis fugacity rule

What cond^n this approx works

So this is something which we describe that, then we also mention about one important thing is that well Phi i is nothing but the fugacity ratio of the fugacity with partial pressure or in other word I can write the fugacity of component i in a mixture is nothing but the fugacity coefficient multiplied by y i multiplied by the pressure where I can approximate phi i to phi i pure. And phi i pure that means the fugacity of a component i in a pure state is nothing but fi P o by P.

So if I approximate this, by this then the expression would be simply y i f i pure. So it simply says that the fugacity in a component, in a mixture of a component i is nothing but is proportional to the fugacity of the pure component and the proportionality constant is nothing but the mole fraction and this is something or this approximation is something we call it Lewis fugacity rule. So what condition this approximation works that is something which we talked about.

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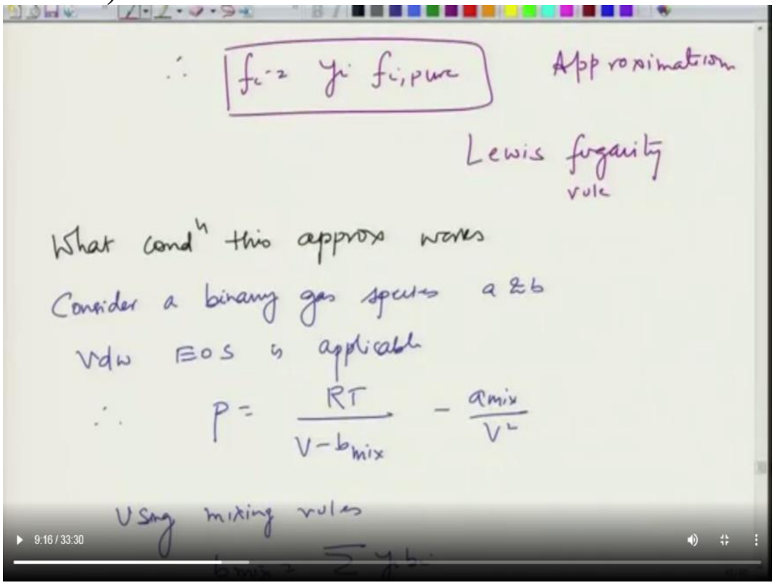


$$\therefore \boxed{f_i = y_i f_{i,pure}}$$ Approximation

Lewis fugacity rule

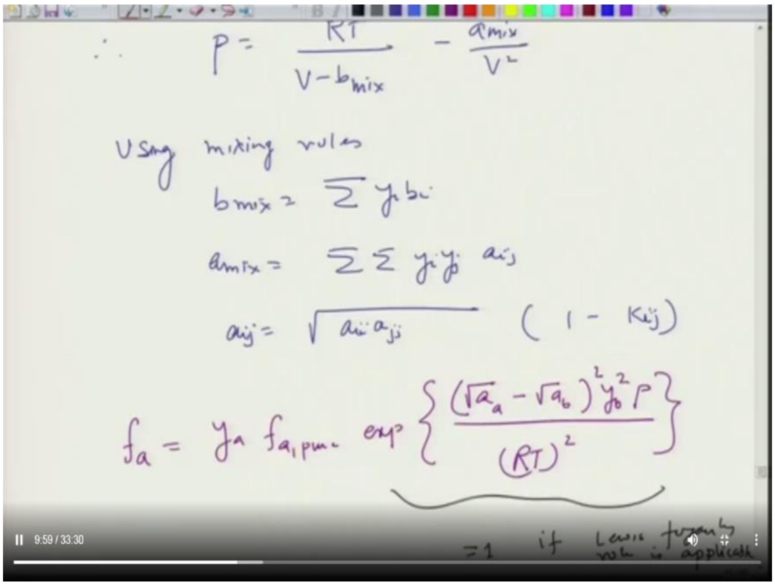
What condn this approx works

Consider a binary gas species a & b

vdw EOS is applicable

$$\therefore \quad P = \frac{RT}{V-b_{mix}} - \frac{a_{mix}}{V^2}$$

Using mixing rules



$$\therefore \quad P = \frac{RT}{V-b_{mix}} - \frac{a_{mix}}{V^2}$$

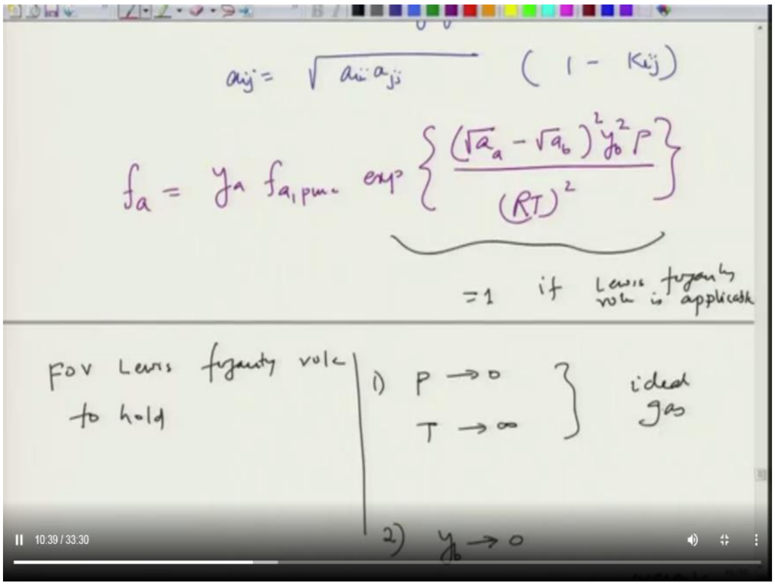
Using mixing rules

$$b_{mix} = \sum y_i b_i$$

$$a_{mix} = \sum \sum y_i y_j a_{ij}$$

$$a_{ij} = \sqrt{a_{ii} a_{jj}} \; (1 - k_{ij})$$

$$f_a = y_a f_{a,pure} \underbrace{\exp\left\{\frac{(\sqrt{a_a} - \sqrt{a_b})^2 y_b^2 P}{(RT)^2}\right\}}_{=1 \text{ if Lewis fugacity rule is applicable}}$$



$$a_{ij} = \sqrt{a_{ii} a_{jj}} \; (1 - k_{ij})$$

$$f_a = y_a f_{a,pure} \underbrace{\exp\left\{\frac{(\sqrt{a_a} - \sqrt{a_b})^2 y_b^2 P}{(RT)^2}\right\}}_{=1 \text{ if Lewis fugacity rule is applicable}}$$

For Lewis fugacity rule to hold

1) $\left.\begin{array}{l} P \to 0 \\ T \to \infty \end{array}\right\}$ ideal gas

2) $y_b \to 0$

So for finding out what particular condition this approximation work we again resort back to the Vander Waal equation of state. Again, we plug in all this information and without going into details, we wrote this expression. This expression was nothing but the fugacity of component a. So we can just consider a binary mixture in this case and then we derive this or we obtain this expression directly where we wrote here f of a is nothing but y a f a pure multiplied by this term which is exponential and the numerator contains this square of the difference of the root of a's which is the interaction parameters of a component a and b, and then you have this y b square multiplied by P divided by RT square.

Now in order to have this Lewis fugacity rule applicable, which means this exponential term should be 1. So we discuss about what condition would lead to this particular expression approaching towards 1. So when we look at these terms here, we saw very clearly that well numerator if the numerator is 0 then essentially the exponential term will be 1 or temperature is infinity, that means there is also that exponential term will be 1. So if P goes to 0 or T goes to infinity that condition would lead to, this term leading to 1.

And this is nothing but ideal gas conditions. Because we can approximate the gas when the pressure is approaching towards 0 or temperature approaches towards infinity.

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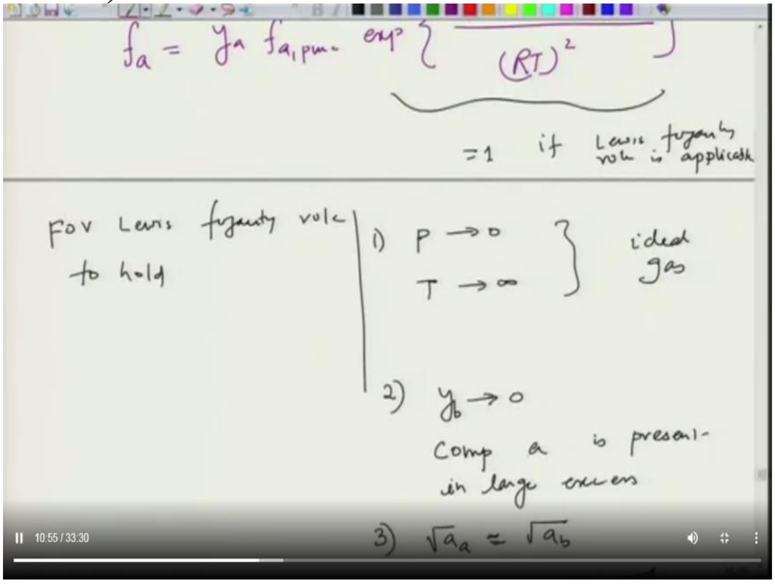

$f_a = y_a f_{a,pure} \exp\left\{ \frac{}{(RT)^2} \right\}$

= 1 if Lewis fugacity rule is applicable

For Lewis fugacity rule to hold

1) $P \to 0$ } ideal gas
$T \to \infty$

2) $y_b \to 0$
Comp a is present in large excess

3) $\sqrt{a_a} \approx \sqrt{a_b}$

The other possibilities were that you know y b is equal to 0 or y b approaches towards 0. That means when the component a is extremely large or b is in dilute condition, then you can consider this to be 0. Or you have this term which is the difference in the root of the a's, square of that. If that goes to 0 that means the root of a is approximated or approximately same as root of a of b, which means essentially the interaction strength or effectively the interaction between of a and b are similar. That means your chemical nature of the species is similar to that of species b. In such case also you can approximate this exponential to 1.

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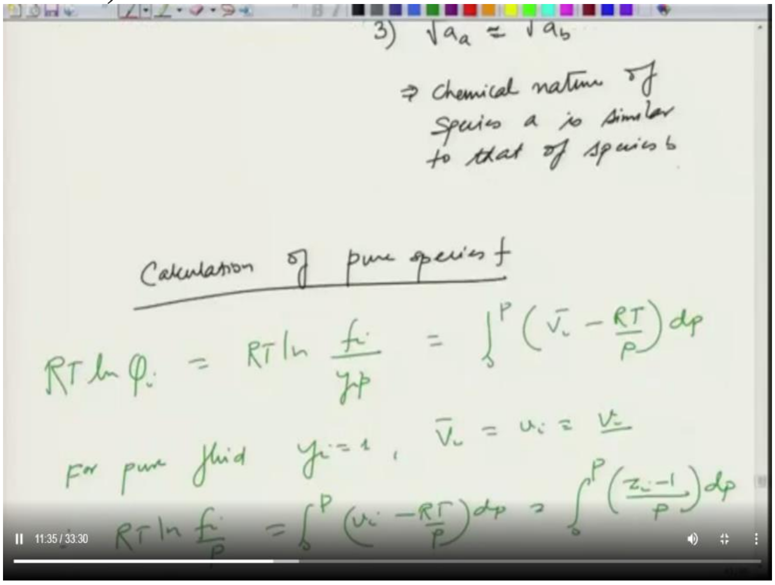


3) $\sqrt{a_a} \approx \sqrt{a_b}$

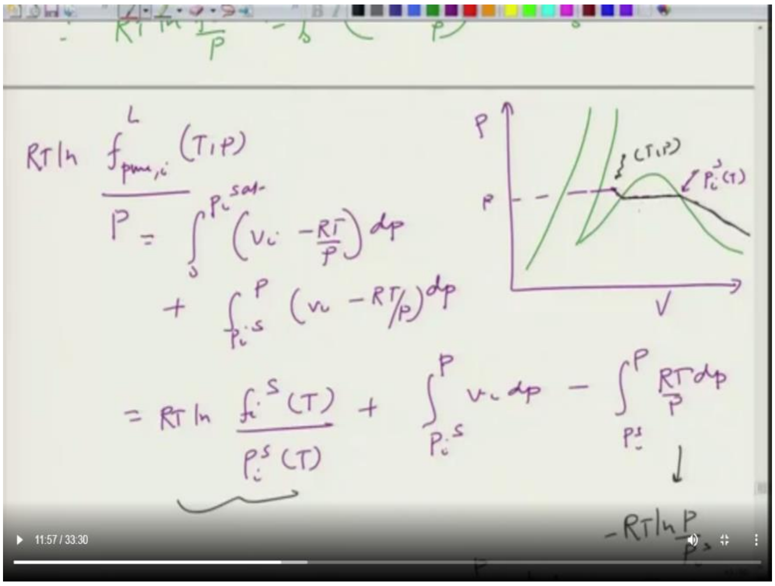
⇒ Chemical nature of species a is similar to that of species b

Calculation of pure species f

$$RT\ln\varphi_i = RT\ln\frac{f_i}{y_i P} = \int_0^P\left(\bar{V}_i - \frac{RT}{P}\right)dp$$

For pure fluid $y_i = 1$, $\bar{V}_i = v_i = V_i$

$$RT\ln\frac{f_i}{P} = \int_0^P\left(v_i - \frac{RT}{P}\right)dp = \int_0^P\left(\frac{z_i - 1}{P}\right)dp$$



$$RT\ln\frac{f^L_{pure,i}(T,P)}{P} = \int_0^{P_i^{sat}}\left(v_i - \frac{RT}{P}\right)dp + \int_{P_i^s}^{P}\left(v_i - RT/P\right)dp$$

$$= RT\ln\underbrace{\frac{f_i^s(T)}{P_i^s(T)}} + \int_{P_i^s}^{P} v_i\,dp - \int_{P_i^s}^{P}\frac{RT\,dp}{P}$$

$$\downarrow$$

$$-RT\ln\frac{P}{P_i^s}$$

So this was the case what we looked at. Then also, we calculate the pure fugacity coefficient particularly fugacity coefficient of liquid and essentially made use of the equality of the fugacity here because the chemical potential equality would lead to fugacity of these two point here to be same.

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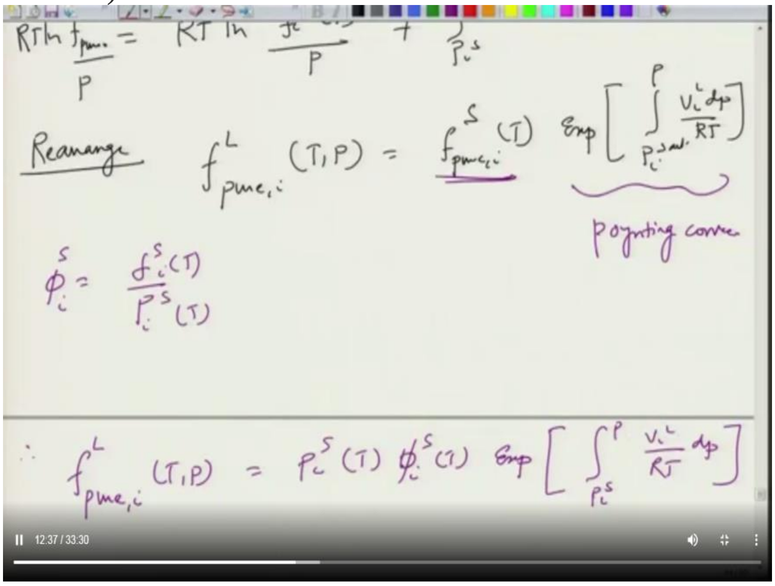


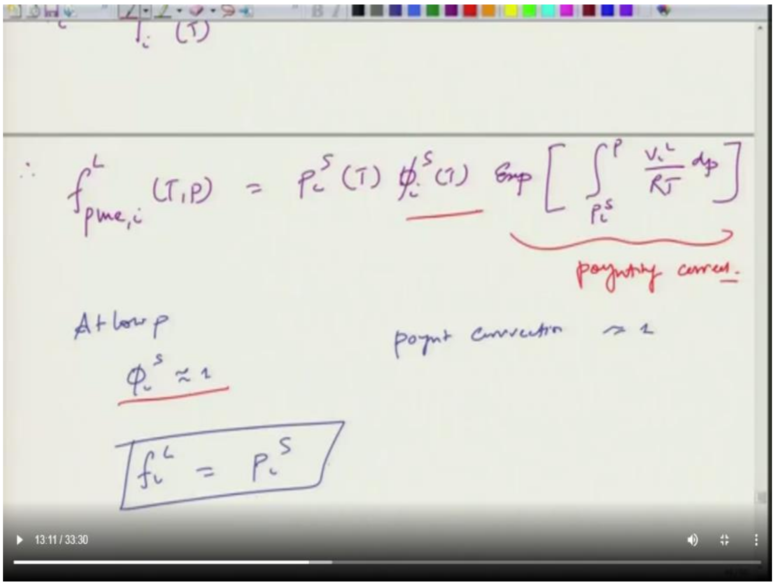
$$RT\ln \frac{f_{pure}}{P} = RT\ln \frac{f_i}{P} + \int_{P_i^s}$$

Rearrange

$$f^L_{pure,i}(T,P) = f^S_{pure,i}(T)\ \mathrm{Exp}\underbrace{\left[\int_{P_i^{sat}}^{P} \frac{V_i^L dp}{RT}\right]}_{\text{Poynting corrn}}$$

$$\phi_i^S = \frac{f_i^S(T)}{P_i^S(T)}$$

$$\therefore\ f^L_{pure,i}(T,P) = P_i^S(T)\,\phi_i^S(T)\ \mathrm{Exp}\left[\int_{P_i^S}^{P} \frac{V_i^L}{RT}dp\right]$$



$$P_i^S(T)$$

$$\therefore\ f^L_{pure,i}(T,P) = P_i^S(T)\,\underline{\phi_i^S(T)}\ \mathrm{Exp}\underbrace{\left[\int_{P_i^S}^{P} \frac{V_i^L}{RT}dp\right]}_{\text{poynting correct.}}$$

At low P

$$\phi_i^S \approx 1 \qquad \text{Poynt correction} \approx 1$$

$$\boxed{f_i^L = P_i^S}$$

And with this we came up with this expression where we said well f of L pure in the liquid phase at a given temperature and pressure is nothing but the saturation pressure at that particular temperature multiplied by the fugacity coefficient at that temperature at saturation and multiplied by this term which we call it a pointing correction, which is basically tells you that this term VL by RT integral from the saturation pressure to the pressure where we desire and exponential of that. That means V i L if it is for example constant then essentially this term is not going to give you much contributions here.

So this is something we call it a pointing correction. At low pressure we can consider Phi i this to be 1. Assuming it to be behave like an ideal gas and pointing correction to be 1 and so at low pressure we can approximate fugacity of the liquid phase as nothing but the saturation pressure at that particular temperature. So this is something which we went through last few lectures, today's lecture I will describe about ideal mixture. For the case of the gas we can take reference of ideal gas mixture. But for the case of a liquid, what would be the relevant or useful reference for us to consider?

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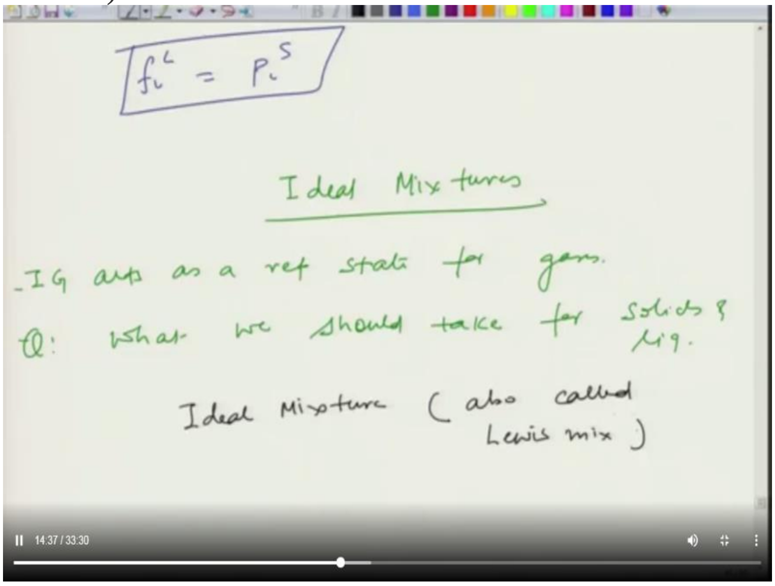


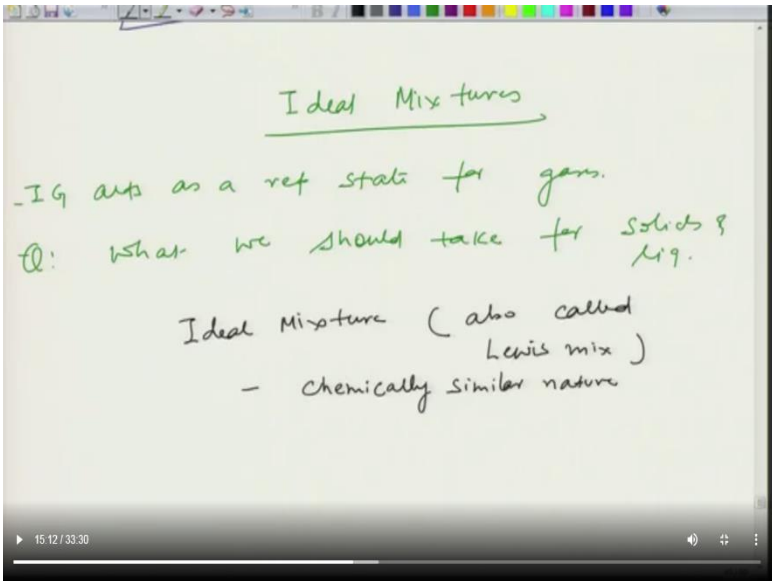
$\boxed{f_i^L = P_i^S}$

Ideal Mixtures

- IG acts as a ref state for gases.

Q: what we should take for solids & liq.

Ideal Mixture (also called Lewis mix)



Ideal Mixtures

- IG acts as a ref state for gases.

Q: what we should take for solids & liq.

Ideal Mixture (also called Lewis mix)

- chemically similar nature

So let me first describe an ideal mixture which can act like a reference for liquid mixtures. So ideal mixtures, as I said ideal gas acts as a reference state for gases. So the question is, what would what we should take? Take reference for solids and liquids. So that is a question here. So for that we defined ideal mixtures. Now, sometimes it is also called Lewis mixture. So in the similar sense as we considered for the ideal gas mixture ideal mixture would be also for those where we would be having some chemical similarity and the nature, so it will be chemically similar nature.

Now, if that is the case that if ideal mixtures almost behaves like, let us say the similar kind of behavior as we have seen for ideal gas mixtures, then we can consider the property of ideal mixtures in a similar line as we have obtained that for ideal gas mixtures. So we can, without going into that we can define ideal mixtures such that the following holds:

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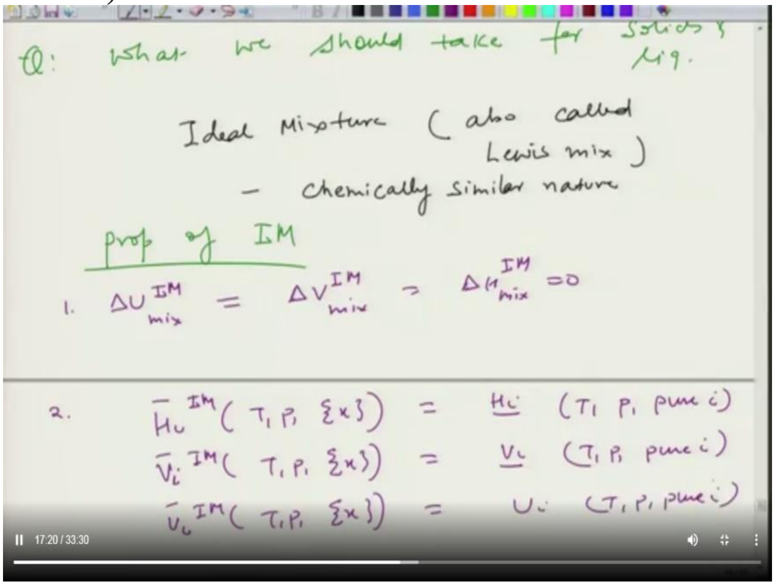

Q: What we should take for Solids & Liq.

Ideal Mixture (also called Lewis mix)

– chemically similar nature

Prop of IM

1. $\Delta U_{mix}^{IM} = \Delta V_{mix}^{IM} = \Delta H_{mix}^{IM} = 0$

2. $\bar{H}_i^{IM}(T, P, \{x\}) = \underline{H_i}(T, P, pure\ i)$

$\bar{V}_i^{IM}(T, P, \{x\}) = \underline{V_i}(T, P, pure\ i)$

$\bar{U}_i^{IM}(T, P, \{x\}) = U_i(T, P, pure\ i)$

So, I can say that well, ideal mixtures are meant for chemically similar nature, but with these following properties. So you have delta U ideal mixture that should be equal to, so what we are saying is delta U of ideal mixture or delta V of ideal mixture or delta H of ideal mixture this must be 0. So that is one of the important properties because this is something which you obtained for ideal gas mixtures also. The other thing which we can also write is that H i bar of ideal mixture.

$$Ideal\ mixture\ (also\ called\ Lewis\ mixture):$$

1. $$\Delta U_{mix}^{IM} = \Delta V_{mix}^{IM} = \Delta H_{mix}^{IM} = 0$$

2. $$\overline{\mathrm{H}_\mathrm{i}}^{IM}(T, P, \{x\}) = \underline{H_i}(T, P, pure\ i) \quad \overline{V_i}(T, P, \{x\}) = \underline{V_i}(T, P, pure\ i)$$

$$\overline{U_i}(T, P, \{x\}) = U_i(T, P, pure\ i)$$

Now here I am putting x here because we are talking about liquids. So it says that the partial molar property of component i is nothing but a molar property of i at the same temperature pressure of the pure component. Similarly, I can do the same thing for V i's. Similarly, for internal energy. So this was two things, which is a part of the properties of the ideal mixtures.

The third is the delta of other property thermodynamic property which we missed, that is for entropy and free energies.

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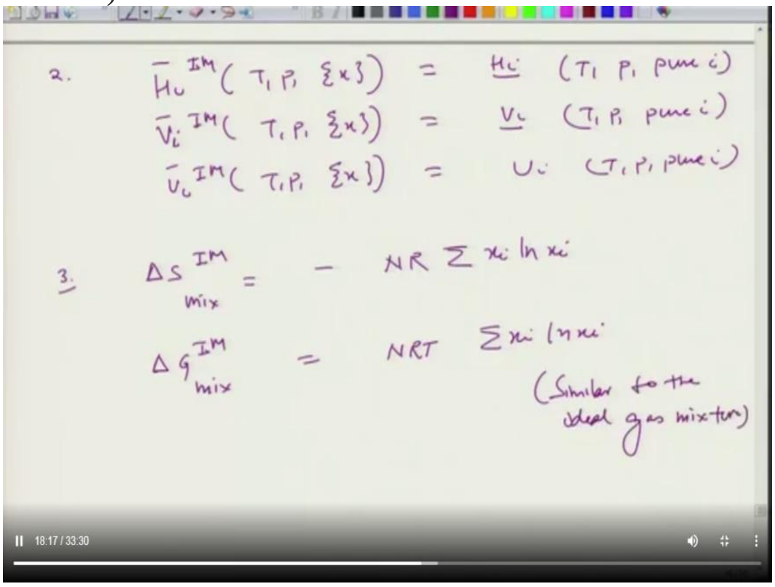


2. $\bar{H}_i^{IM}(T, P, \{x\}) = \underline{H_i}$ (T, P, pure i)

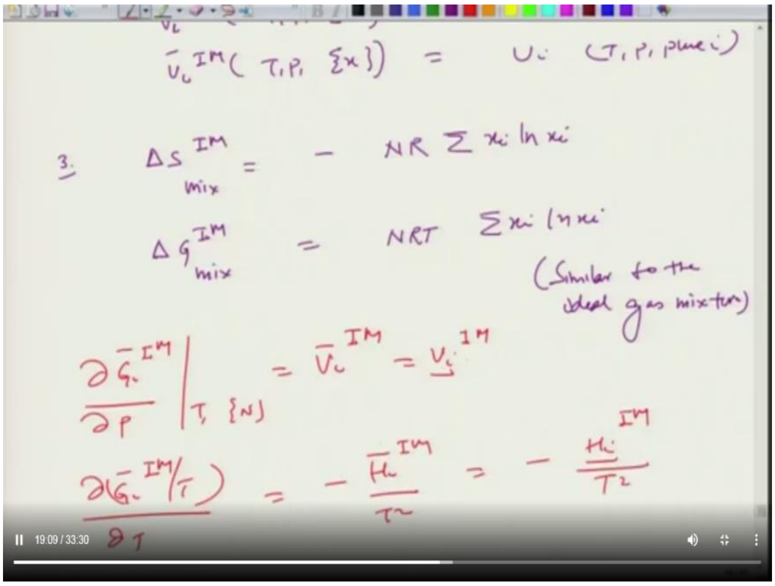
$\bar{V}_i^{IM}(T, P, \{x\}) = \underline{V_i}$ (T, P, pure i)

$\bar{U}_i^{IM}(T, P, \{x\}) = U_i$ (T, P, pure i)

$\underline{3.}$ $\Delta S^{IM}_{mix} = -NR\sum x_i \ln x_i$

$\Delta G^{IM}_{mix} = NRT \sum x_i \ln x_i$

(Similar to the ideal gas mixture)



$\bar{U}_i^{IM}(T, P, \{x\}) = U_i$ (T, P, pure i)

$\underline{3.}$ $\Delta S^{IM}_{mix} = -NR\sum x_i \ln x_i$

$\Delta G^{IM}_{mix} = NRT \sum x_i \ln x_i$

(Similar to the ideal gas mixture)

$$\left.\frac{\partial \bar{G}_i^{IM}}{\partial P}\right|_{T,\{N\}} = \bar{V}_i^{IM} = \underline{V_i}^{IM}$$

$$\frac{\partial(\bar{G}_i^{IM}/T)}{\partial T} = -\frac{\bar{H}_i^{IM}}{T^2} = -\frac{H_i^{IM}}{T^2}$$

So delta S of ideal mixture can be written in a similar sense as we have done for ideal gas, but instead of y's I am going to put x here. And similarly I can write delta G of ideal mixture. This will be NRT summation x i ln i. So remember that this is similar to the ideal gas mixture. I can also extend this exercise and also write here Delta G i ideal mixture as a function with respect to P at T N others constant is nothing but V i ideal mixture. Similarly, d i. So this comes very naturally. If you have done that for ideal gas part, you can simply write it this K easily because of all these properties or thermodynamic relations, y is valid for partial molar also.

$$3.\,\Delta S_{mix}^{IM} = -NRx_i \ln x_i$$
$$\Delta G_{mix}^{IM} = NRTx_i \ln x_i$$

So I can simply write this expression but then we are using the properties of ideal mixtures where H i bar can be written as molar enthalpy or molar volume in this case.

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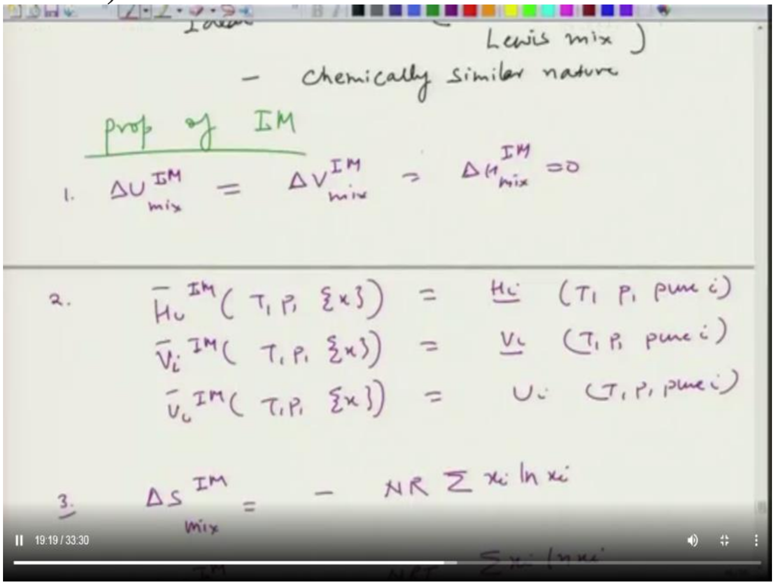

Lewis mix)

– Chemically similar nature

prop of IM

1. $\Delta U^{IM}_{mix} = \Delta V^{IM}_{mix} = \Delta H^{IM}_{mix} = 0$

2. $\bar{H}_i^{IM}(T, P, \{x\}) = \underline{H_i}\,(T, P, \text{pure } i)$

$\bar{V}_i^{IM}(T, P, \{x\}) = \underline{V_i}\,(T, P, \text{pure } i)$

$\bar{U}_i^{IM}(T, P, \{x\}) = U_i\,(T, P, \text{pure } i)$

3. $\Delta S^{IM}_{mix} = -NR\sum x_i \ln x_i$

We have defined the ideal gas mixture, sorry in this case ideal mixtures which is a liquid mixtures. Now what I am interested now is to obtain the change in the chemical potentials with respect to the pure phase.

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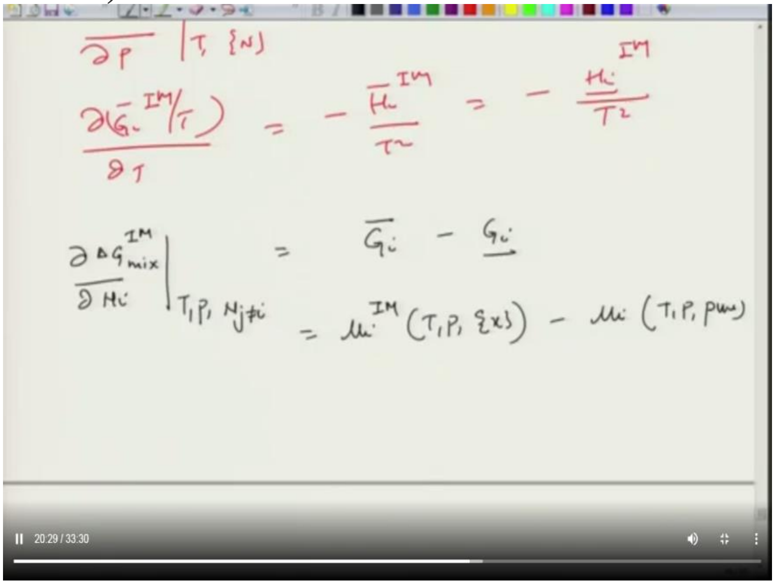

$\partial P \,\big|_{T,\{N\}}$

$$\frac{\partial(\bar{G}_i^{IM}/T)}{\partial T} = -\frac{\bar{H}_i^{IM}}{T^2} = -\frac{\underline{H_i}^{IM}}{T^2}$$

$$\left.\frac{\partial \Delta G^{IM}_{mix}}{\partial N_i}\right|_{T,P,N_{j\neq i}} = \bar{G}_i - \underline{G_i} = \mu_i^{IM}(T,P,\{x\}) - \mu_i(T,P,\text{pure})$$

$$\frac{\partial \bar{G}_i^{IM}}{\partial P}\Big|_{T,\{N\}} = \bar{V}_i^{IM} = \underline{V}_i^{IM}$$

$$\frac{\partial\left(\frac{\bar{G}_i^{IM}}{T}\right)}{\partial T} = -\frac{\bar{H}_i^{IM}}{T^2} = -\frac{\underline{H}_i^{IM}}{T^2}$$

So let me derive it. So if you consider I am also going to do the similar exercise as similar. I will take the similar steps that I am going to take the partial derivative of delta G with respect to N i. And this is going to be G of i minus G i that is by definition of delta G mix, so that is the definition. But this itself can be written because this is a partial molar Gibbs free energy, then it would be mu i for the ideal mixture and this is of course the molar case for the, and here this one is for the pure and hence I am going to write this as T P pure. So this is the right hand side part, but what about the left hand?

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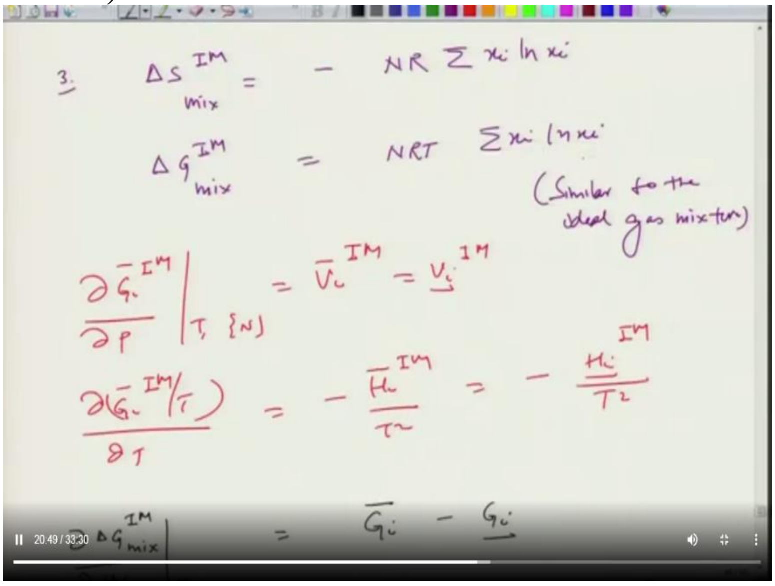

3. $\Delta S^{IM}_{mix} = - NR \sum x_i \ln x_i$

$\Delta G^{IM}_{mix} = NRT \sum x_i \ln x_i$

(Similar to the ideal gas mixture)

$\frac{\partial \bar{G}_i^{IM}}{\partial P}\Big|_{T,\{N\}} = \bar{V}_i^{IM} = \underline{V}_i^{IM}$

$\frac{\partial(\bar{G}_i^{IM}/T)}{\partial T} = -\frac{\bar{H}_i^{IM}}{T^2} = -\frac{\underline{H}_i^{IM}}{T^2}$

$\partial \Delta G^{IM}_{mix}\Big| = \bar{G}_i - \underline{G}_i$

So left hand side is delta G ideal gas mixture is NRT summation x i ln x i. So I can write x i is simply N i by divided by N and ln x i can be written as ln N i divided by N.

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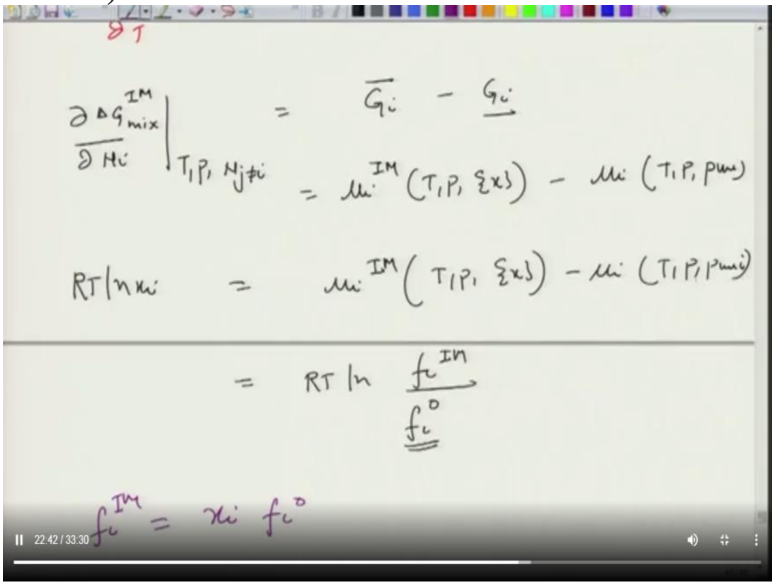

$$\partial T$$

$$\left.\frac{\partial \Delta G^{IM}_{mix}}{\partial N_i}\right|_{T,P,N_{j\neq i}} = \overline{G}_i - \underline{G_i}$$

$$= \mu_i^{IM}(T,P,\{x\}) - \mu_i(T,P,pure)$$

$$RT\ln x_i = \mu_i^{IM}(T,P,\{x\}) - \mu_i(T,P,pure\ i)$$

$$= RT\ln \frac{\underline{f_i^{IM}}}{\underline{\underline{f_i^0}}}$$

$$f_i^{IM} = x_i f_i^0$$

$$\frac{\partial \Delta G^{IM}_{mix}}{\partial H_i}|_{T,P,N_{j\neq i}} = \overline{G_\iota} - \underline{G_i} = \mu_i^{IM}(T,P,\{x\}) - \mu_i(T,P,pure\ i)$$

$$RTln\ x_i = \mu_i^{IM}(T,P,\{x\}) - \mu_i(T,P,pure\ i) = RTln\frac{f_i^{IM}}{f_i^0}$$

$$f_i^{IM} = x_i f_i^0$$

And the similar line as we have done that for gas system, this right-hand side can be shown to be simply RT ln x i. So ln x i RT ln x i is basically the right hand side is this and this right hand side can also be written in terms of the fugacity definition which we have written earlier because that definition does not just applicable to the gas phase, you can apply for generic definition where we say that the chemical potential of a component n in the mixture minus that with respect to pure fluid is nothing but RT ln f i by f 0.

So, in this case f zeros are going to get cancelled. So what I will have is nothing but RT ln f i of ideal mixture divided by f i of a pure fluid. So I am going to say simply for the sake of generality that this could be simply the some reference state f i 0, which could be maybe the ideal part. So this is a pure case. So I am just going to write it like that.

And then I will explain a little bit more that why this has been considered. So if you consider this what you have is your f i ideal mixture is nothing but x i times f i the corresponding to the pure phase or corresponding to some reference state. So the reference state, for example in this case is pew. At this point we are saying that but I am going to generalize it. Actually I can generalize this more later.

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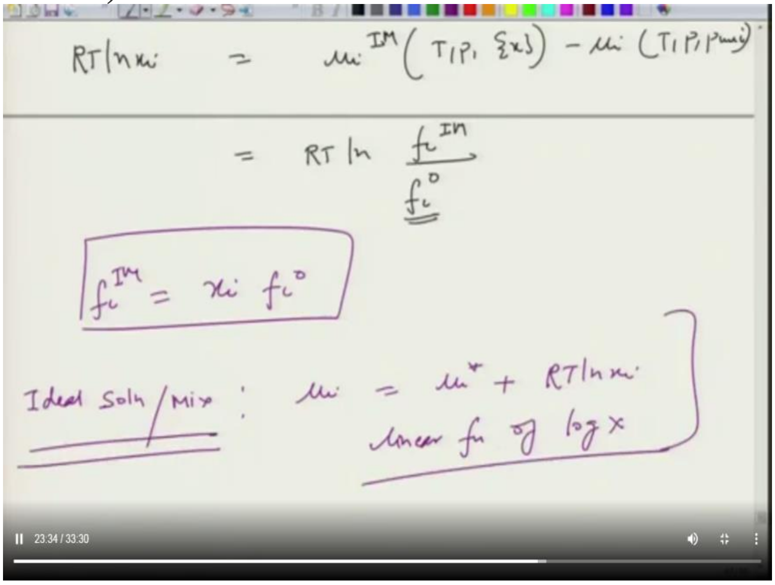


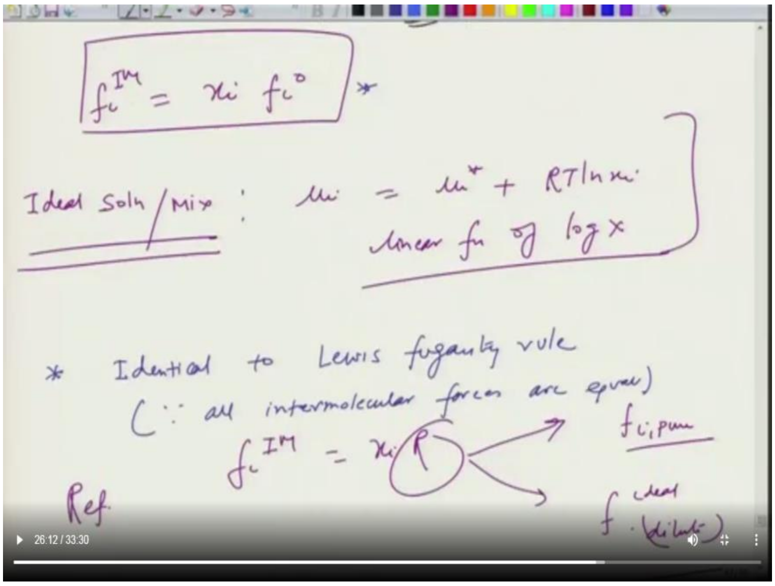
$RT\ln x_i = \mu_i^{IM}(T, P, \{x\}) - \mu_i(T, P, P_{pure})$

$= RT\ln \frac{f_i^{IM}}{f_i^0}$

$\boxed{f_i^{IM} = x_i f_i^0}$

Ideal Soln / Mix : $\mu_i = \mu_i^* + RT\ln x_i$

linear fn of log x



$\boxed{f_i^{IM} = x_i f_i^0}$ *

Ideal Soln / Mix : $\mu_i = \mu_i^* + RT\ln x_i$

linear fn of log x

* Identical to Lewis fugacity rule

(∵ all intermolecular forces are equal)

$f_i^{IM} = x_i \, R$ → $f_{i,pure}$ → f_i^{ideal} (dilute)

Ref.

$$\mu_i = \mu_i^* + RT ln\, x_i$$

So, let me also consider one part, so I will talk about this part little later. But let us also look at one aspect of it is that what we have written for ideal mixture or ideal solution. So, ideal solution or mixture. What you have noticed is very clear that mu of i in such a case is some reference state, which could be this or something else plus RT ln x i. So, it says that for the case of ideal solution mixture the chemical potential is nothing but as a linear function of logarithmic value of x. That is what we are talking about as far as the ideal solution or mixtures are concerned.

So it is nothing but is just a linear function of logarithmic of x. In the later part I am going to make a claim that fugacity as such is not so much useful for the case of liquid. It is truly is meant for gas. And one of the reasons is that since fugacity we can clearly see that it is a some of the, you know, the reference state is usually considered to be an ideal gas which is not feasible for the liquid state. For liquid state you need to have a different kind of reference state which is feasible or practical for the purpose of calculations. So we will define something else.

Now if you look at very carefully this expression is looks like so basically it looks like, is identical basically to Lewis fugacity rule, which says that well the fugacity of component is directly proportional to the fugacity of the pure phase or which is the reference which is considered there. But here let us say f i 0 or reference here. So he says that if fugacity of a component i in a mixture is proportional to the reference fugacity and the proportionality is nothing but the mole fraction.

So, this looks very similar to Lewis fugacity rule. So one of the things in the Lewis fugacity rule which of course we later using Vander Waal equation of state we could figure it out was that all the interaction or intermolecular forces are equal. Now so let us little bit dwell on these aspects that would be the appropriate reference states for this expression.

So what will be the reference? So, essentially, I can actually write this now as more like f i ideal mixture is x i times R. And what is R? So, R could be there are two possible states. First is we can consider it to be some absolutely pure phase or we consider another phase which we say still the ideal. But this is the case where we consider is a dilute phase. So there are two possibilities which we are going to now spend some time to understand it. So let us look at it because eventually what the ideal kind of solution is that the fugacity has to be proportional. That means there is some linear relation which we talking about it.

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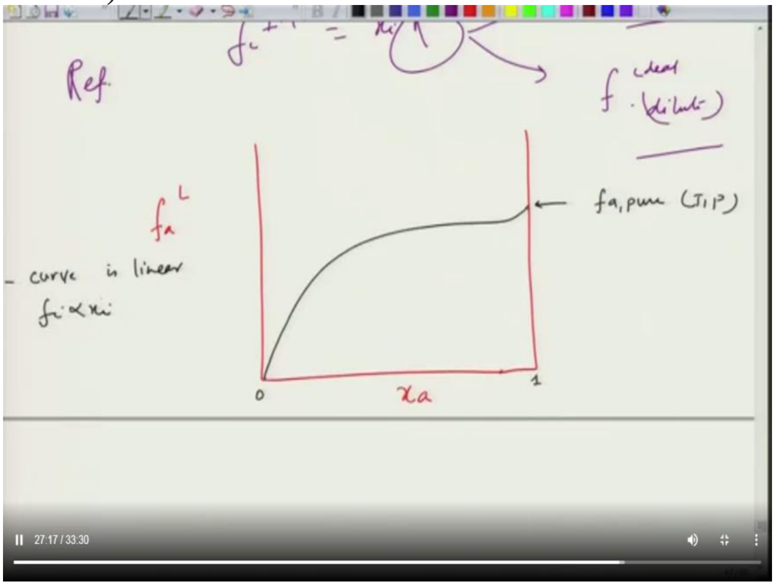

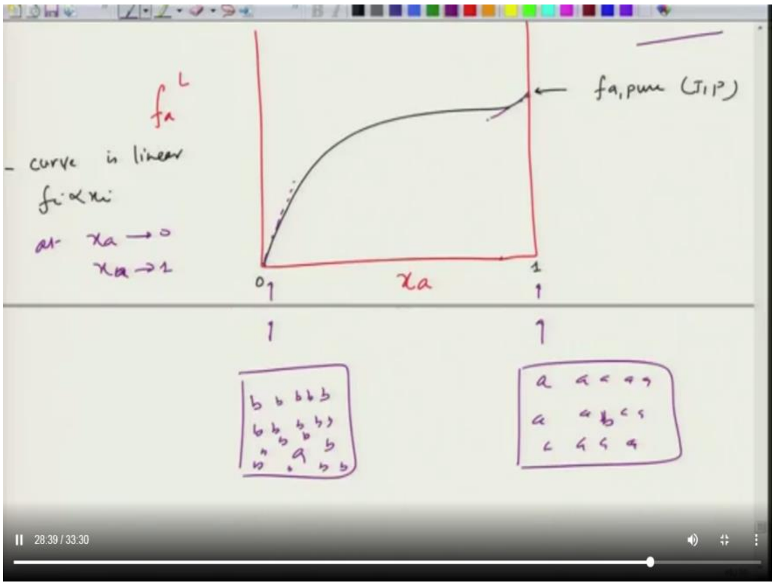

So if we just focus on the typical curve which we get for the fugacity, so consider let us say a fugacity of a in the liquid phase and we are plotting here is x of a. So here we draw something like this. And of course, this is x a. This was 0, this is 1. So this is going to be f a of pure at particular temperature T and P. So what we notice is two things, one is essentially these curves are linear.

Curve is linear at two places which we clearly see which satisfies f i is proportional to x i. So we satisfy f i proportional to x i. In this case because here also so I can say that f i is proportional to R. But of course I can also say that f i is directly proportional to x i where i is proportionality constant. So I see two places, one here, other here. So there are two possible locations where we can clearly see that the fugacity is proportional to x i. So, at x a goes to 0 or x a goes to 1. Now if you look at the typical behavior here, particularly here, you will see that well, in this case x a is equal to 0 which essentially means is purely filled with component b. If it is a binary mixture and is one of the very few a's are present here.

So essentially if you look at the kind of interaction, these are interaction between a, b. And in the other case it will be other way around where essentially it is filled with a and you have only b. A very dilute amount of b is present, almost negligible.

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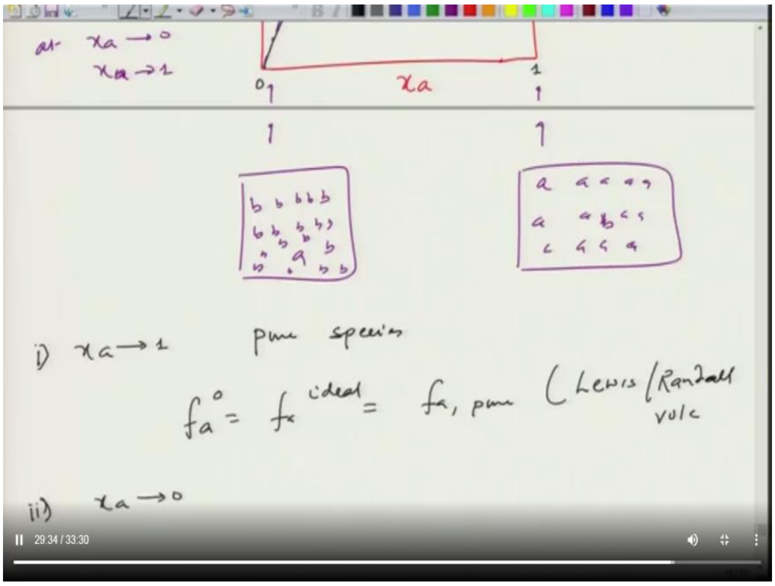

So let us look at this. So essentially you have case 1 where x a goes to 0. Now in such a case all interactions are similar interactions are there, it is a pure species where I am saying that well f a ideal the one which is 0 or ideal is nothing but f a of pure component. So this we call it a Lewis Randall Rule.

And here mainly the interactions are very similar kind of interactions represent. The second possibility is where a is extremely dilute that is x a tends to 0. Here you have only b b interactions are present.

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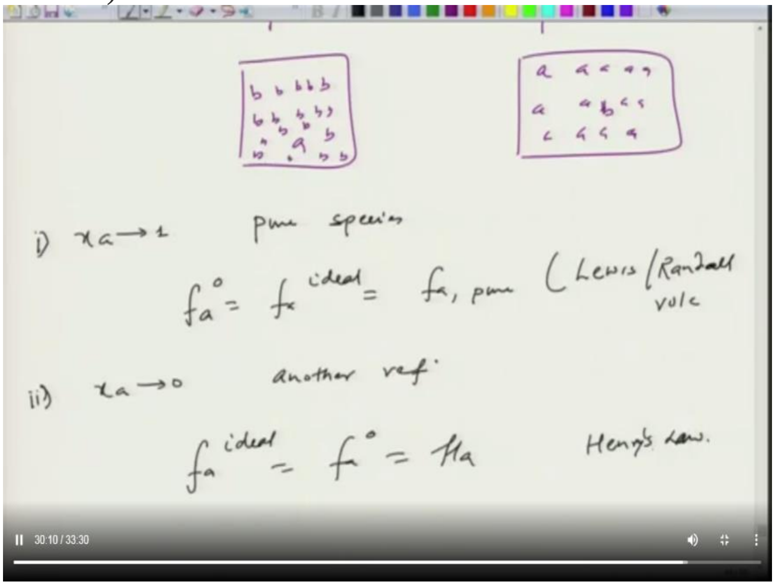

a b interactions are very small but a only sees b and the dominant interactions are only b b. Now this provides a separate or another reference where we are saying f a ideal or f a 0 is nothing but H of a Henry's constant, and this is also called Henry's law. So these are two different references.

$$i)\ x_a \rightarrow 1\ \ Pure\ species \qquad f_a^0 = f_a^{ideal} = f_{a,pure} \quad (Lewis\ Randall\ rule)$$

$$ii)\ x_a \rightarrow 0 \qquad f_a^{ideal} = f_a^0 = H_a \ \ Henry's\ Law$$

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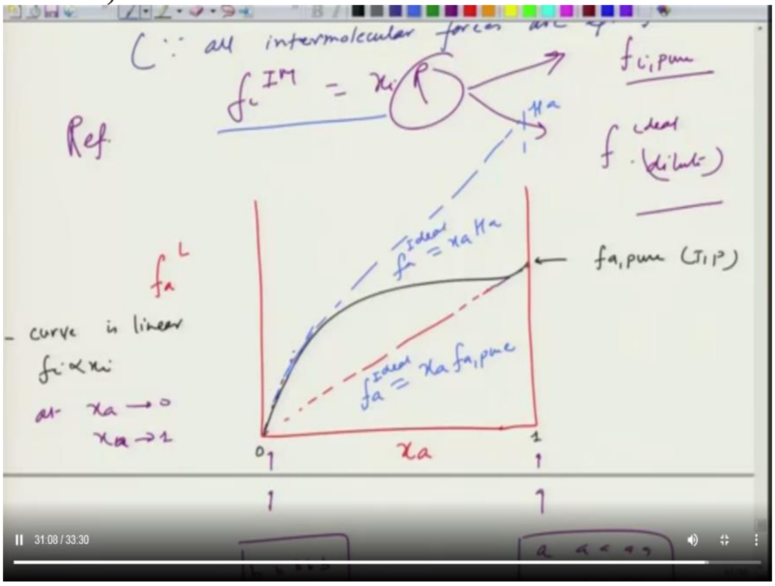

One which is this which is the case where we are saying the following that you have…So this turns out to be the case where we are saying f of a is x a multiplied by f of a pure. So this is the ideal. That is what we say, this is ideal mixture. So we say well this is ideal. So this is the case where we have Lewis Randall rule, which is valid for the range for 0 to a. And the other case is the following where we are saying well, so somewhere here you have H of a and this rule is f of a is x a H a which is valid only in this region which is dilute region. Again, this is an ideal part, because for ideal f is proportional to x a in this case.

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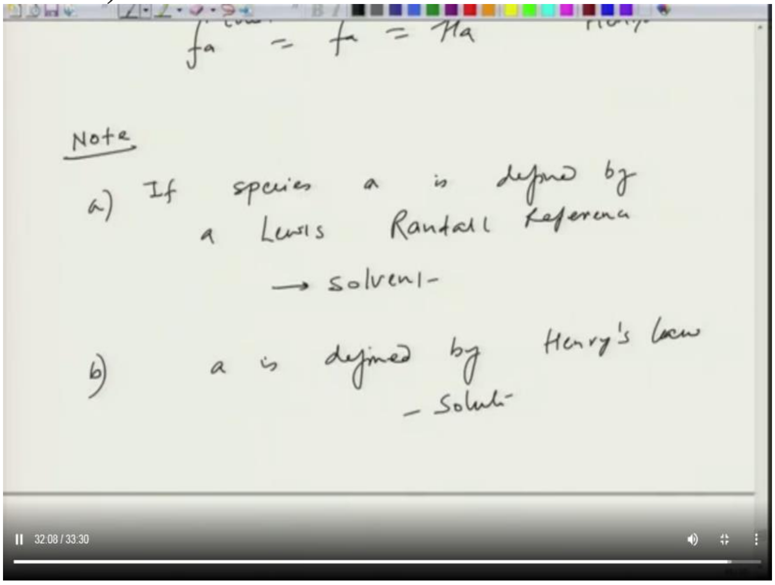

$f_a = f_a = H_a$

Note

a) If species a is defined by a Lewis Randall Reference

→ solvent

b) a is defined by Henry's law

– Solute

So one of the important thing which we note is the following: if species a is defined by a Lewis Randall reference state, then we basically are stating that all the composition from 0 to 1 is feasible and which is the case would be for the case of solvent. So that means we are referring to a solvent. However, if a is defined by Henry's law then most likely what we are talking about is for the solute. So we are mainly referring to solute which is valid only at those regions. So that is usually will be working based on these kind of concept. One is rich in a component which will be acting like a solvent, other is rich in or other is a dilute in the concentration which will be mainly solute.

So I think, now I will stop here in today's lecture and I will take this discussion further probably elaborate more on Henry's and constants, understand a bit of the constraints on that and subsequently we will try to do some examples also and then what we want to do is to come with a better expressions rather than fugacity for the liquid phase and that is why we are going to introduce something called activity or activity coefficient. So, with that I will stop and see you in the next lecture.