Thermodynamics of Fluid Phase Equilibria
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Lecture - 42
Fugacity of Liquid Mixture – 1

Come back in this lecture, I will start a new topic Fugacity in Liquid Mixtures.

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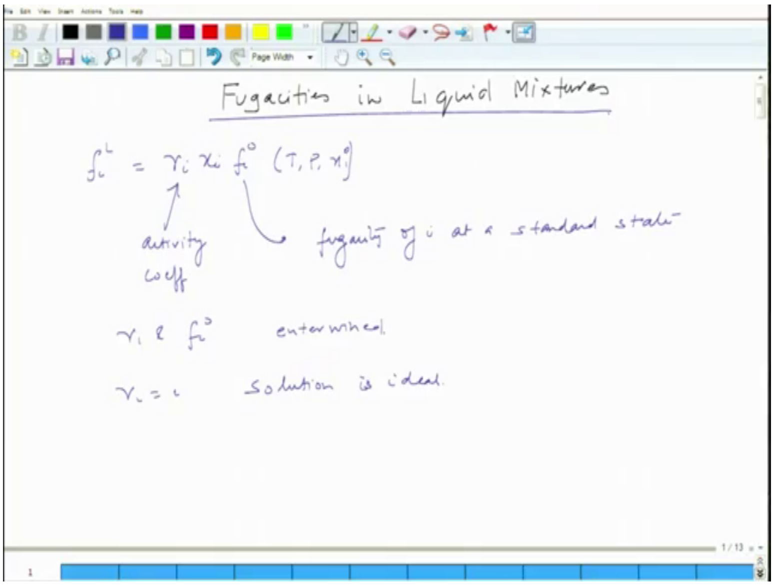

Fugacities in Liquid Mixtures

$f_i^L = \gamma_i x_i f_i^0 (T, P, x_i^0)$

activity coeff

fugacity of i at a standard state

γ_i & f_i^0 enterwined.

$\gamma_i = 1$ solution is ideal.

So, let me just write down first a generic expression of the fugacity and liquid phase is written as gamma i times x i times fi 0 ok. And fi 0 is a function of T P and some concentration or mole fraction. So, gamma i is nothing, but activity coefficient whereas, this fi 0 is the fugacity of i at a standard state ok.

Now, it is important to understand that gamma i and fi 0 are interlinked. So, as we know that gamma is equal to 1 when solution is ideal now; however, gamma equal to 1 can have different interpretation; that means, the ideality depends on the reference state. And thus its it is it is important to understand that whether this reference is with respect to dilute conditions or in general it is in Raoult's law sense; so, something which I am going to elaborate now.

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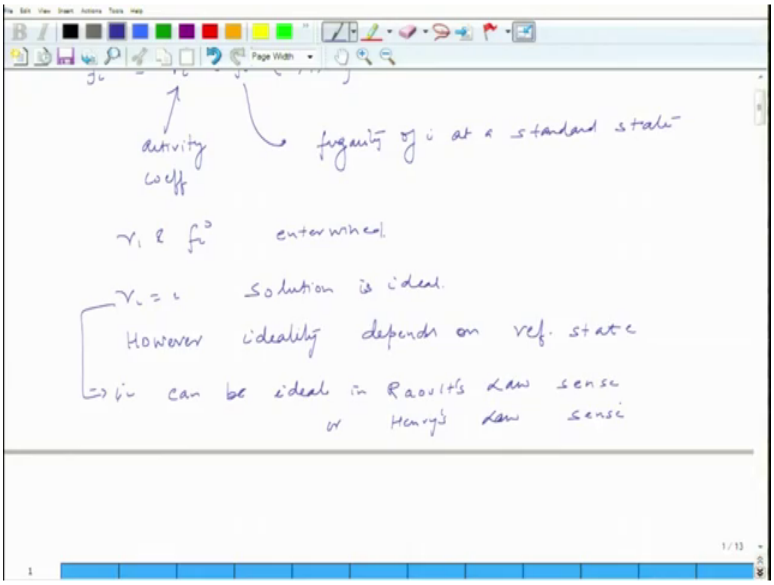

activity coeff

fugacity of i at a standard state

γ_i & f_i^0 enterwined

$\gamma_i = 1$ solution is ideal.

However ideality depends on ref. state

$\Rightarrow$ i.e. can be ideal in Raoult's Law sense or Henry's Law sense

So, that is this can be ideal in the Raoult's law sense or Henry's law sense. So, what I am going to do is I am going to define formally the ideal solution.

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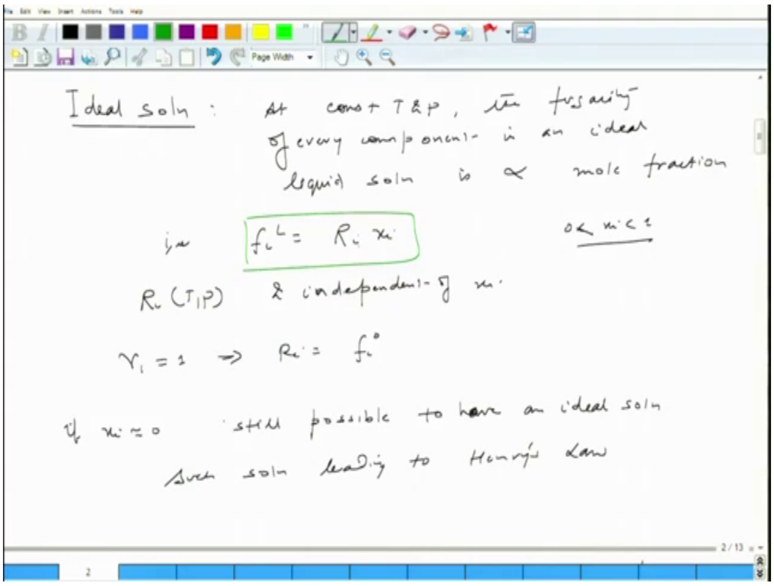

Ideal soln : At const T & P, the fugacity of every component in an ideal liquid soln is $\propto$ mole fraction

i.e. $\boxed{f_i^L = R_i x_i}$ $0 < x_i < 1$

$R_i (T, P)$ & independent of x_i.

$\gamma_i = 1 \Rightarrow R_i = f_i^0$

If $x_i \approx 0$ still possible to have an ideal soln

Such soln leading to Henry's Law

So, at a constant temperature and pressure the fugacity of every component in an ideal solution; in an ideal liquid solution is proportional to the mole fraction; that is what the definition of ideal solution is. So, in other word what we are saying is that f i L is equals to some proportionality constant R i multiplied by x i which holds for x i from 0 to 1 ok.

So, note that R i is just a function of temperature and pressure independent and it should be independent of x i ok. And if gamma i equal to 1 which essentially means R i is nothing, but fi 0 that is what we have written here ok.

Now, for the case of now large range it is; that means, when typically the x i is large then it turns out to be Raoult's law kind of sense, but when x i; that means, the concentration of the solute is extremely small, still you can define ideal solution so; that means, if xi is close to 0; if it is still possible to have an ideal solution.

Now, such solution is with reference to the Henry's law. So, this leads to the Henry's law ok. So, I will come back to this in a bit.

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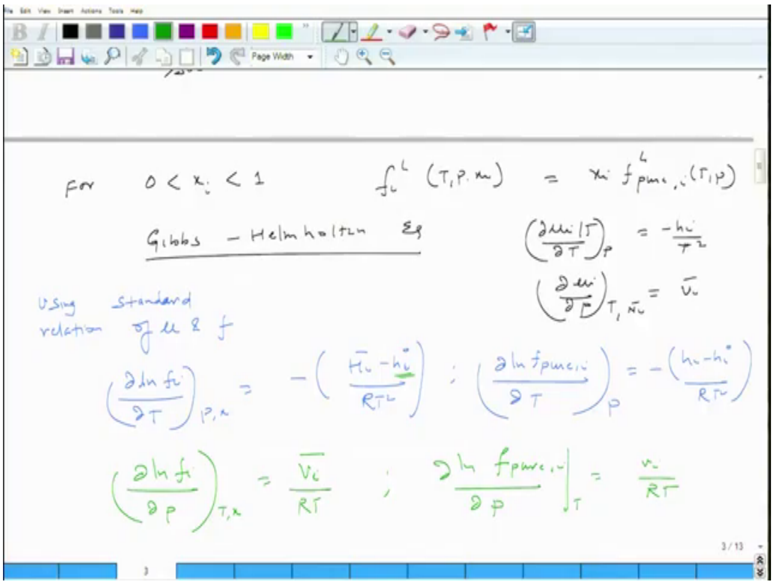

For $0 < x_i < 1$ $\quad f_i^L(T, P, x_i) = x_i f^L_{pure,i}(T, P)$

Gibbs - Helmholtz Eq

$$\left(\frac{\partial \mu_i/T}{\partial T}\right)_P = -\frac{h_i}{T^2}$$

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T, N_i} = \bar{v}_i$$

Using standard relation of μ & f

$$\left(\frac{\partial \ln f_i}{\partial T}\right)_{P,x} = -\left(\frac{\bar{H}_i - h_i^\circ}{RT^2}\right) \;;\; \left(\frac{\partial \ln f_{pure,i}}{\partial T}\right)_P = -\left(\frac{h_i - h_i^\circ}{RT^2}\right)$$

$$\left(\frac{\partial \ln f_i}{\partial P}\right)_{T,x} = \frac{\bar{V}_i}{RT} \;;\; \left.\frac{\partial \ln f_{pure,i}}{\partial P}\right|_T = \frac{v_i}{RT}$$

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But let me now consider the case for 0 x 1 in that case I can write f i L as a function of T P x i as simply x i f L pure i T P ok. So, that would be the case for the Raoult's law point of view.

Now, what I am going to do is; I am going to connect this to for the case. So, I will I will try to use the expression of Gibbs Helmholtz equations and from there I will try to connect the logarithm form of velocity to enthalpy and molar volumes. So, what we have from the Gibbs Helmholtz equations is the following; this is something which we have we have looked into for the pure fluid ok. So, I am just reproducing this; so, for the case of the mixtures this is going to be V i bar and this is something which we can now make use of it for the case of what we are looking at ok.

So, I am going to apply this Gibbs Helmholtz equations; since mu we have defined in terms of the fugacities, mu i minus mu i 0 is equal to your R T l n fi by fi 0. So, if you use this those expression directly and so, you can replace d mu or mu in terms of that and then the derivative would turn out to be with respect to the fugacity ok.

So, using standard relation of mu and f; I can now write I can plug in here and I can show that without going to derivation I can show that del ln fi by del T P x is nothing, but minus of H i say 0 by R T square; now this is something which you can show yourself ok.

Now, for the remember the for the pure fluid we have del ln f pure; i del T P is equal to minus of small h i; H i 0 by R T square here. For the case make sure you have partial molar enthalpy, in case of the pure you have simply molar enthalpy and this is with reference to reference,

So, when you are going to use this mu i there is a reference mu i and that will give us this information ok. So, you can derive this without you know ah; so, you can derive it at home I am not going to go into the details of it. I can also avoid this for the case of this where the partial derivative is raised with respect to the pressure; for the case of the pure fluid this would be simply V i by R T ok.

Now, this is the partial molar enthalpy of i, this is your partial molar enthalpy of the reference state which is basically the ideal gas let us say at T.

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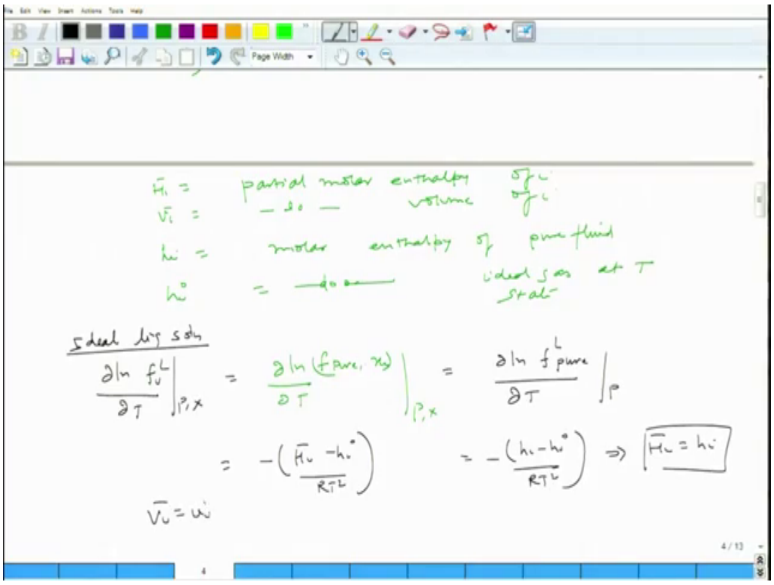

$\bar{H}_i$ = partial molar enthalpy of i

$\bar{V}_i$ = — do — volume of i

h_i = molar enthalpy of pure fluid

h_i^0 = — do — ideal gas at T state

Ideal liq soln

$$\left.\frac{\partial \ln f_i^L}{\partial T}\right|_{P,x} = \left.\frac{\partial \ln (f_{pure,i}\, x_i)}{\partial T}\right|_{P,x} = \left.\frac{\partial \ln f^L_{pure}}{\partial T}\right|_P$$

$$= -\left(\frac{\bar{H}_i - h_i^0}{RT^2}\right) \qquad = -\left(\frac{h_i - h_i^0}{RT^2}\right) \Rightarrow \boxed{\bar{H}_i = h_i}$$

$\bar{V}_i = v_i$

So, H i bar is nothing, but partial enthalpy of i; similarly V i bar is partial volume here of i and small h i is molar enthalpy of pure fluid and h i 0 or V i 0 is basically molar enthalpy of an ideal gas or the reference state at T ideal gas at T ok.

So, this is something which I have written without going through the rigorous derivation, but I believe that you can you can do that; knowing their relation of mu and fugacity you can plug in all these and come up with the derivation. So, the question is why we are doing this? Let us come to that. And now I am going to do is I am going to consider for the idea solution; what would be the del log of i as a function of with respect to or the derivative of log of f L with respect to T at a constant P x.

So, what is this for the case of ideal liquid solution? So, I am going to consider this and here since this is your ideal solution, I can replace f L; i L as f pure multiplied by x i ok. And since this is had derivation is or sorry this differentiation is with respect to T; keeping P and x is equal to constant. So, essentially I can write this as d ln f L pure and del T at P alright.

So, now this if you look at it del f by del T is nothing, but H i bar minus H i small H i 0 divide by R T square. So, this essentially means this should be minus of H i minus hi 0 by R T square. And on other hand this is a pure fluid this should be H i minus hi 0 by R T square; now this must be seen, this implies that H i bar is equal to H i for the case of ideal solution ok. Similarly you can show that for the case of ideal solution V i is equal to V i.

So, earlier we have done this exercise for ideal gas mixtures now we are looking at liquid solution remember that.

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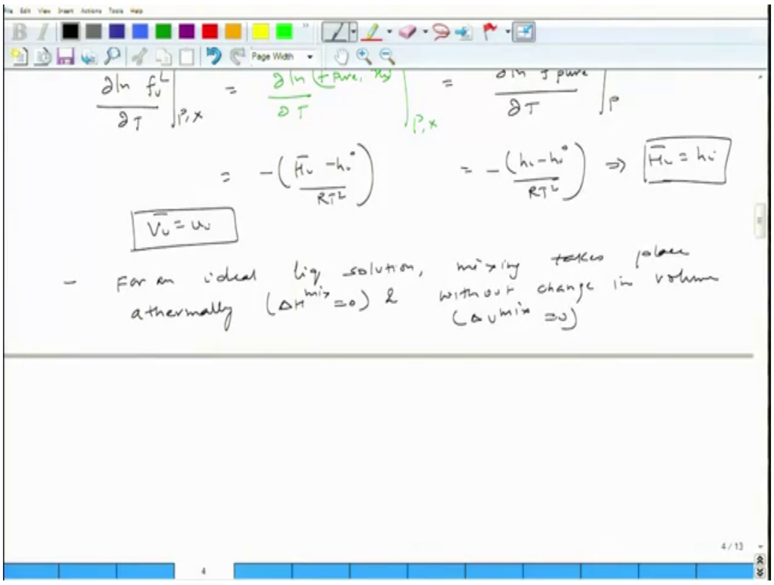

$$\left.\frac{\partial \ln f_i^L}{\partial T}\right|_{P,x} = \left.\frac{\partial \ln (f_{pure,i}\, x_i)}{\partial T}\right|_{P,x} = \left.\frac{\partial \ln f_{pure}}{\partial T}\right|_{P}$$

$$= -\left(\frac{\bar{H}_i - h_i^\circ}{RT^2}\right) \qquad = -\left(\frac{h_i - h_i^\circ}{RT^2}\right) \Rightarrow \boxed{\bar{H}_i = h_i}$$

$$\boxed{\bar{V}_i = v_i}$$

- For an ideal liq solution, mixing takes place athermally ($\Delta H^{mix} = 0$) & without change in volume ($\Delta v^{mix} = 0$)

And liquid solution; you have the this kind of property for the case of ideal conditions ok. So, what does that mean? It by obtaining this, you can conclude that for an ideal solution and a liquid solution mixing takes place a thermally because that H i bar is equal to H i which essentially means delta H mix should be 0 ok.

Similarly, upon mixing for an ideal liquid solution; you should not have or you should not change its volume; that means, the mixing takes place without change in volume which means delta V mix is equal to 0. So, this is the statement directly from this expression.

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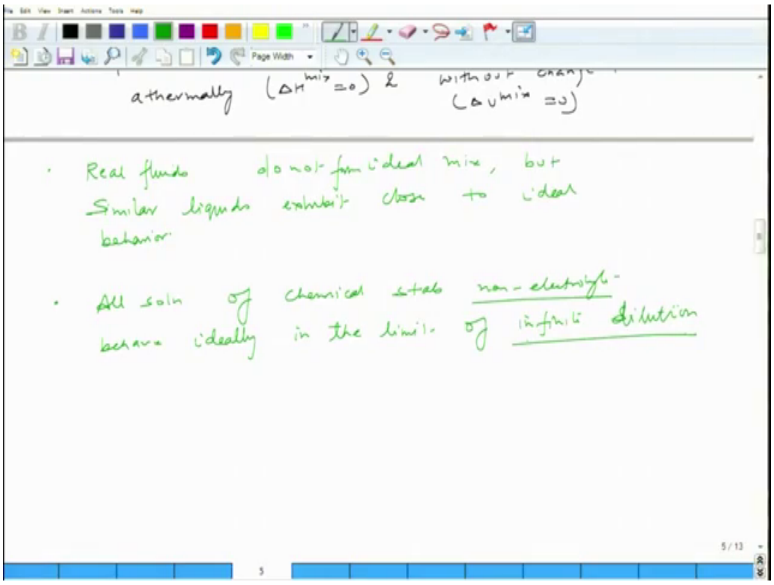

athermally $(\Delta H^{mix} = 0)$ & without change $(\Delta V^{mix} = 0)$

- Real fluids do not form ideal mix, but Similar liquids exhibit close to ideal behavior
- All soln of chemical stable non-electrolyte behave ideally in the limit of infinite dilution

Now, other statement which I am going to make is that the real fluid; of course do not exhibit ideal mixture ok. So, though real fluids do not mix form ideal mixture, but if the similar fluids of similar kind, similar molecule nature they are mixed they behave more like ideal liquid solution ok.

So, but similar liquids exhibit close to ideal behaviour; now other important thing is that all solution of chemically stable non electrolyte; this is important behaves behave ideally in the limit of infinite dilution, which essentially means that if the solution is extremely dilute then they will start behaving like a ideal solution ok.

So, how do you represent deviation from the ideality if the solution real fluid does not behave like a ideal solution; then there is a division from the ideal solution behaviour. So, we make use of excess function; I am could I am going to define that.

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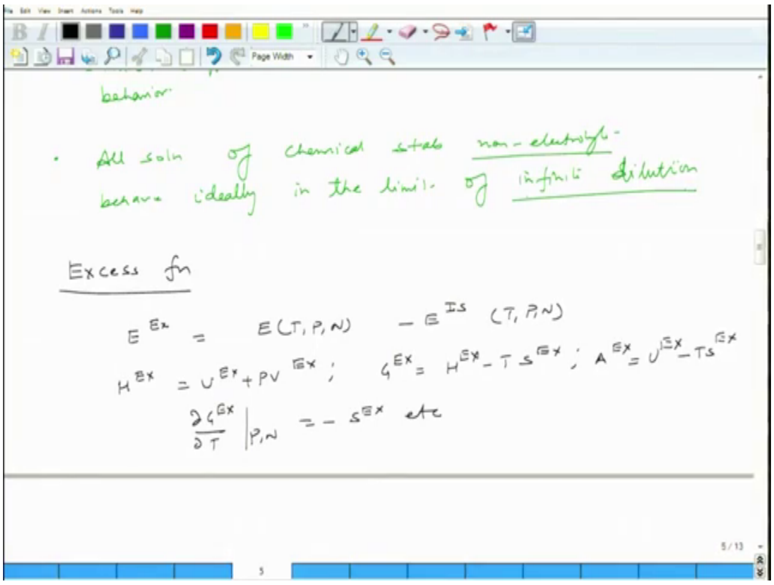

behavior

- All soln of chemical stable non-electrolyte behave ideally in the limit of infinite dilution

Excess fn

$$E^{Ex} = E(T,P,N) - E^{IS}(T,P,N)$$

$$H^{EX} = U^{EX} + PV^{EX}; \quad G^{EX} = H^{EX} - TS^{EX}; \quad A^{EX} = U^{EX} - TS^{EX}$$

$$\left.\frac{\partial G^{EX}}{\partial T}\right|_{P,N} = -S^{EX} \text{ etc}$$

So, the correction term is given in terms of excess function that is for any extensive property; let us say E I am going to define x excess function as E T P N with respect to E I S T P N. In a similar way where we define for the gas mixtures; so, for the solution also I am going to define it.

Now, as we have already discussed earlier therefore, any extensive any excess function you can make use of the standard relation of the enthalpy or in general thermodynamic functions. And the thermodynamic function in terms of excess function will hold such as for example, this ok; so, this holds ok.

Now, usual relation of the derivative also holds for example, this now one of the most important thing in this excess function is basically G excess Gibbs free energy.

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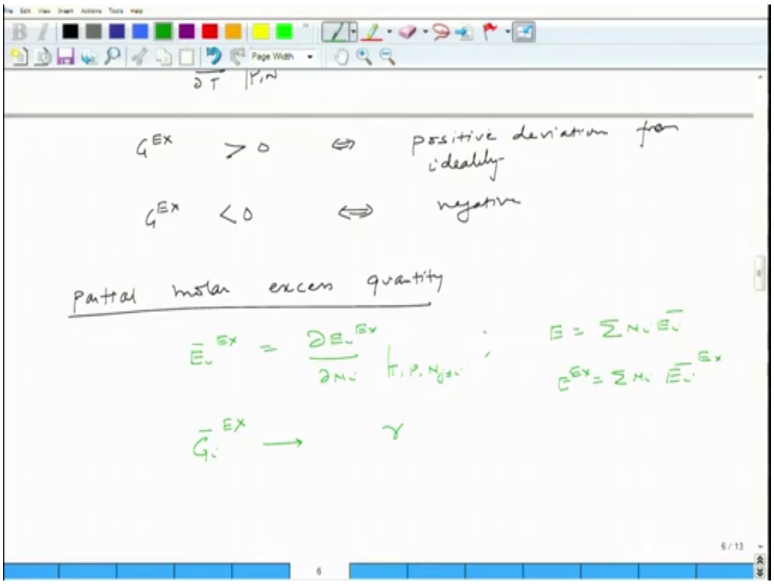

$G^{EX} > 0 \Leftrightarrow$ positive deviation from ideality

$G^{EX} < 0 \Leftrightarrow$ negative

partial molar excess quantity

$\bar{E}_i^{EX} = \frac{\partial E_i^{EX}}{\partial N_i}\Big|_{T,P,N_{j\neq i}}$; $E = \sum N_i \bar{E}_i$

$E^{EX} = \sum N_i \bar{E}_i^{EX}$

$\bar{G}_i^{EX} \longrightarrow \gamma$

Now, this if it is greater than 0; it shows that it is a positive deviation from ideality frizzle less than 0; it shows that negative deviations from ideality ok. So, both ways when you say negative deviation for identity which means basically G excess must be less than 0 ok.

Partial molar excess free energy excess partial molar excess quantity; so, it is E i x and this is nothing, but del E i x divided by del N i; T P all other i constant ok; all other let us say j constant such that j is not equal to i. We know from earlier expression or that earlier lectures that E is nothing, but summation of N i; E i bar. Similarly E x would be summation N i E I excess

So, this is something which we have done this exercise. So, the most useful for our analysis of a liquid mixtures and its property is nothing, but G i partial molar excess Gibbs free energy. So, G i bar excess because this gets reduced to gamma it is connected to gamma which is activity coefficient. So, let me now talk about this activity coefficients and try to connect with this G i excess.

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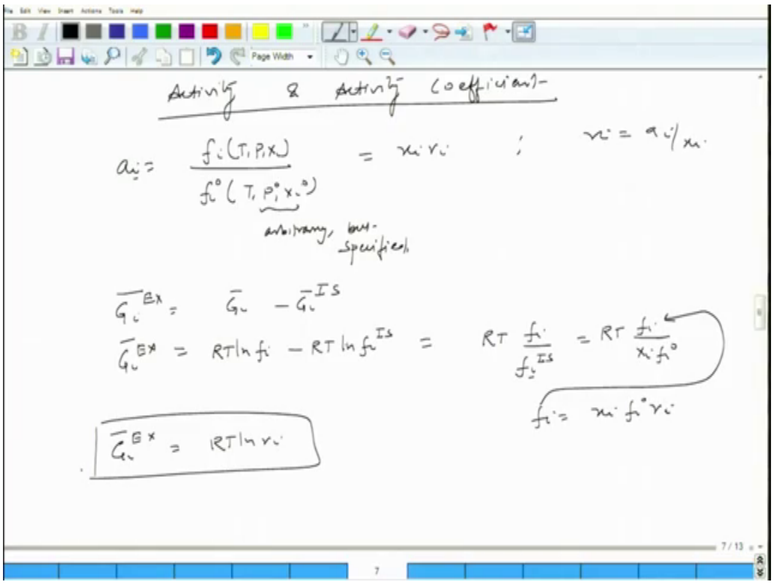

Activity & Activity Coefficient

$$a_i = \frac{f_i(T,P,x)}{f_i^\circ(T,\underbrace{P_i^\circ, x_i^\circ}_{\text{arbitrary, but specified}})} = x_i\gamma_i \quad ; \quad \gamma_i = a_i/x_i$$

$$\bar{G}_i^{EX} = \bar{G}_i - \bar{G}_i^{IS}$$

$$\bar{G}_i^{EX} = RT\ln f_i - RT\ln f_i^{IS} = RT\frac{f_i}{f_i^{IS}} = RT\frac{f_i}{x_i f_i^\circ}$$

$$f_i = x_i f_i^\circ \gamma_i$$

$$\boxed{\bar{G}_i^{EX} = RT\ln\gamma_i}$$

Let me formally define activity and activity coefficient ok. So, activity is defined as ai which is a basically nothing, but the ratio of fi T P x i with respect to fi 0; T P some reference state pressure xi 0. So, this is basically nothing, but arbitrary, but must be specified and ai is nothing, but u x i gamma i ok. So, in other word gamma i is nothing, but ai divided by x i ok. So, this is something which we already know ok.

So, I am defining this here; now let us see how we can connect this gamma i or H to the G i excess ok. So, let me start with G i excess definition which is nothing, but G i bar minus G i with respect to ideal solution ok. So, what is G i? So, G i you can relate this G i to mu i and since mu i is related to R T ln fi, you can show that this is nothing, but R T ln fi ok; minus R T ln fi I S; the reference part which comes here, the second part get cancelled because you are using the same reference here. So, R T ln fi I S remain same which essentially means G i x excess bar is nothing, but R T fi; fi I S ok.

Now, you can relate this to because you know the fi s I S for solution final liquid is nothing, but R T fi x i; fi 0 ok. So, this is for ideal solution; now using the definition of fi is x i fi 0 gamma i that is the definition of f i with respect to gamma i. So, I should be able to now plug this in here and I can write here G i excess as R T ln gamma i ok.

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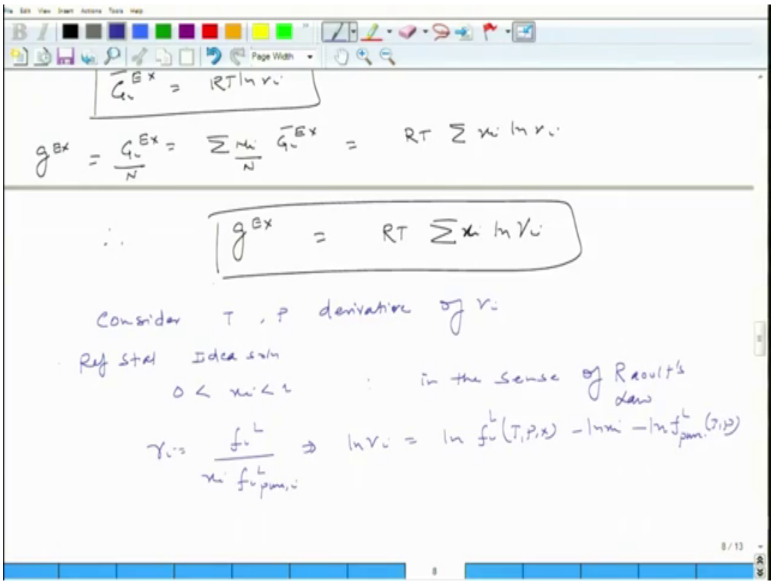

$$\boxed{\bar{G}_i^{Ex} = RT \ln \gamma_i}$$

$$g^{Ex} = \frac{G^{Ex}}{N} = \sum \frac{N_i}{N} \bar{G}_i^{Ex} = RT \sum x_i \ln \gamma_i$$

$$\therefore \quad \boxed{g^{Ex} = RT \sum x_i \ln \gamma_i}$$

Consider T , P derivative of γ_i

Ref state Ideal soln

$0 < x_i < 1$ in the sense of Raoult's law

$$\gamma_i = \frac{f_i^L}{x_i f^L_{pure,i}} \Rightarrow \ln \gamma_i = \ln f_i^L(T,P,x) - \ln x_i - \ln f^L_{pure}(T,P)$$

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Now, the next thing which we would like to do is to make use of the fact that G i excess is summation N i; G i excess this. If we divide by N; i get N here and this is nothing, but small g excess molar x excess Gibbs free energy per particle and this since nothing, but if you if you use G i excess at this then becomes R T summation x i ln gamma i. So, we got an expression of g excess as R T summation x i and ln gamma i alright ok.

So, now what is the next thing which we can do? So, we got an expression of molar Gibbs free Gibbs excess free energy with respect to the activity coefficient. Now let us consider consider T P derivative of gamma i ok. So, consider the ideal you know consider reference state; for ideal solution from the sense of Raoult's law ok. So, this is in the sense of ok; so, I can write gamma i s; f i L x i f I l pure i ok.

So, when you consider this we use this f i 0 is nothing, but f i L pure i. So, essentially means I can write ln gamma i as ln f i L T P x minus ln x i minus ln f L pure T P ok.

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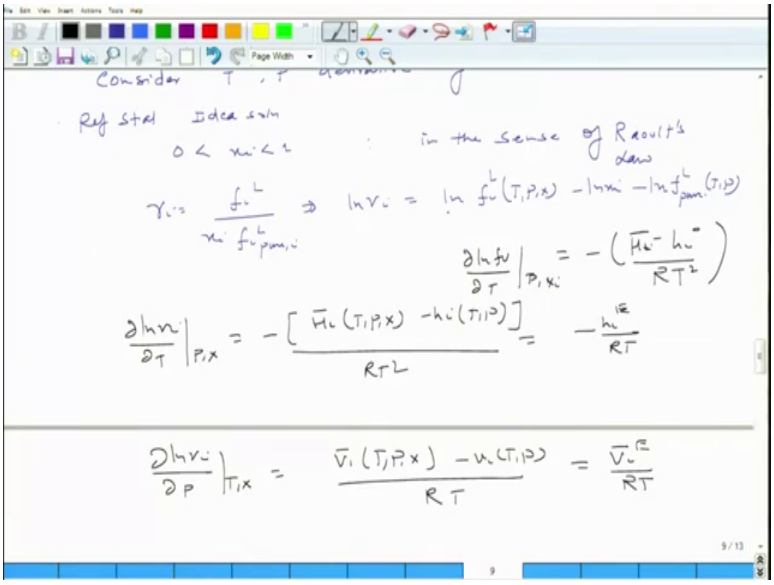

Consider T , P

Ref state Ideal soln in the sense of Raoult's law

$0 < x_i < 1$

$$\gamma_i = \frac{f_i^L}{x_i f^L_{pure,i}} \Rightarrow \ln \gamma_i = \ln f_i^L(T,P,x) - \ln x_i - \ln f^L_{pure}(T,P)$$

$$\left.\frac{\partial \ln f_i}{\partial T}\right|_{P,x_i} = -\left(\frac{\bar{H}_i - h_i^0}{RT^2}\right)$$

$$\left.\frac{\partial \ln \gamma_i}{\partial T}\right|_{P,x} = -\frac{[\bar{H}_i(T,P,x) - h_i(T,P)]}{RT^2} = -\frac{h_i^E}{RT}$$

$$\left.\frac{\partial \ln \gamma_i}{\partial P}\right|_{T,x} = \frac{\bar{V}_i(T,P,x) - v_i(T,P)}{RT} = \frac{\bar{V}_i^E}{RT}$$

Now, we know the expressions of the derivative of fugacity. So, for example, if just rho T then this should P and this is nothing, but minus H i bar minus H i 0 by R T square ok. So, what we can do is we can use this expression; so, you have now expression of ln gamma i ln fi.

So, you can take the derivative of log of gamma i with respect to temperature at a constant pressure and this is the right hand side. So, you can also make use of that and now from here given this expression of Gibbs Helmholtz expressions, you can you can directly connect this the logarithm to the partial molar properties such as enthalpy ok.

So, I will try to show this; so, let us say this is what we want the derivative of log gamma with respect to temperature at put pressure and x. So, this is going to be you can show I am not going to get into details of that. So, you have to take the derivative of this which essentially is as such as 0; this is going to be 0 you have to take the derivative of this also which is nothing, but small hi bar minus H i 0 and says and since is this is at constant temperature.

So, since it is given temperature the H i 0 will cancel out. So, what remains is nothing, but the following only H i will remain ok. So, this will be minus h i add E by R T; so, excess h i.

Similarly, you can show that gamma i by del P by at a constant T i x is nothing, but V i bar T P x minus small v i T P for the pure fluid; R T square here it will be R T here and this will be nothing, but V i excess by R T ok. So, this is by considering the law Raoult's law sense ok.

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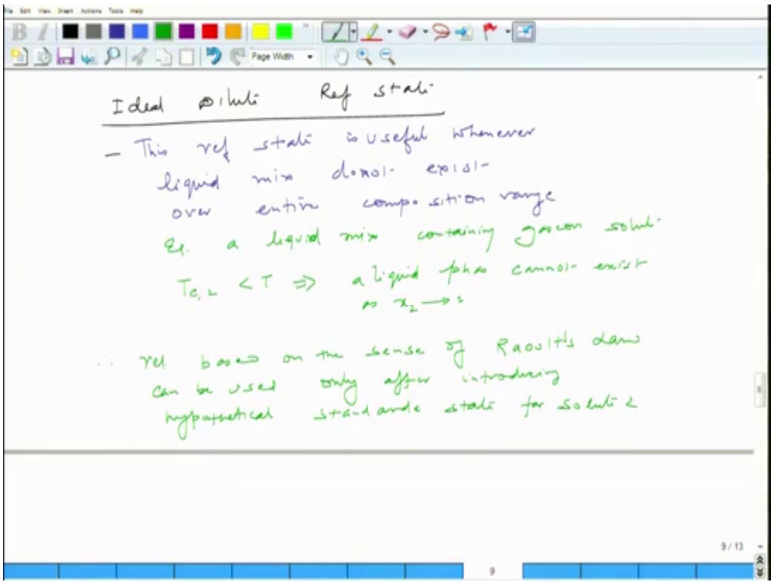

Ideal dilute Ref state

- This ref state is useful whenever liquid mix do not exist over entire composition range

eg. a liquid mix containing gaseous solute

$T_{c,2} < T \Rightarrow$ a liquid phase cannot exist as $x_2 \rightarrow 1$

$\therefore$ ref based on the sense of Raoult's law can be used only after introducing hypothetical standard state for solute 2

Now, for the case of dilute ideal dilute reference rate; if you consider and apply the same expression what we have got here. Then if you apply the same relation which you have got here, for the case of the system where one particular solute is has a has a critical temperature much lower than the temperature of the system. Then we have a serious problem because typical mixtures will not occur in the liquid state at that particular temperature.

So, in that case we have to worry about whether we should use the Raoult's law sense of reference state. So, in such case ideal dilute reference state can be considered. So, this is useful is useful whenever liquid mixture do not exist; over the entire composition range ok.

So, for a given temperature one of the fluid will may remain as a liquid in the pure state, but other one may not it may remain in a supercritical state. So, by considering Raoult's law sense which essentially is valid when the system remains in a liquid phase from 0 to 1 composition; then in that case you have to come up with a kind of fictitious reference state if you want to use a Raoult's law for as a as a different state from the Raoult's law sense.

So, we need to keep we need to change a different reference state that is what the ideal dilute reference state comes into the picture. So, as I was saying that if you consider a liquid mixture containing gaseous solute ok. So, in such case let us say this is the scenario that critical temperature of the solute which is 2 is much less than T of the system, this implies that a liquid phase cannot exist as composition of two approaches towards 1 ok.

Now, if you want to use the Raoult's law based reference system and then the relation which we have developed here for the gamma ok; in order to achieve this we come we must have come up with a hypothetical standard state for state 2 at that particular temperature ok. So, therefore, relation based on the sense of Raoult's law can be used only after introducing a hypothetical reference state or standard state standard state for solute 2 ok.

So, this is why in such a scenario it is more convenient to consider ideal dilute reference state, which avoids this kind of difficulty and that is where the Henry's law comes into the picture ok; so, let me write that.

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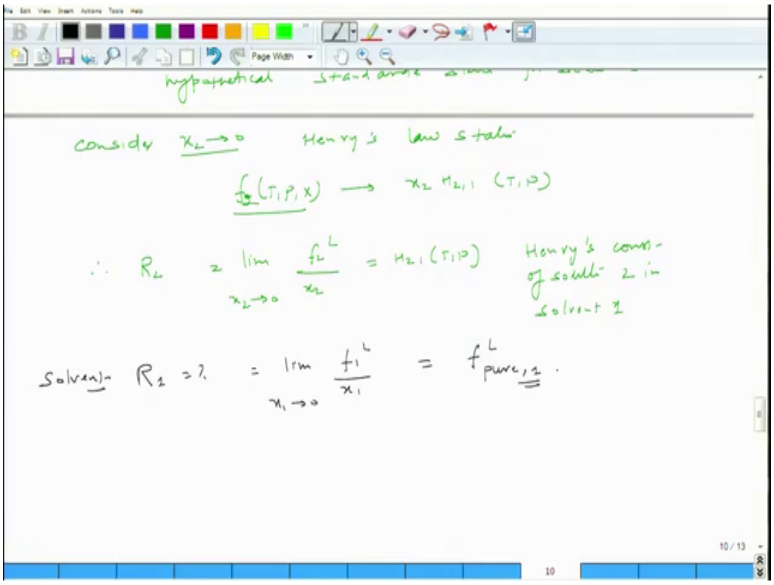

hypothetical standard

consider $\underline{x_2 \to 0}$ Henry's law state

$$\underline{f_2(T,P,x)} \longrightarrow x_2 H_{2,1}(T,P)$$

$$\therefore \mathcal{R}_2 = \lim_{x_2 \to 0} \frac{f_2^L}{x_2} = H_{2,1}(T,P)$$ Henry's const- of solute 2 in solvent 1

$\underline{\text{Solvent}}$: $\mathcal{R}_1 = ?$ $= \lim_{x_1 \to 0} \frac{f_1^L}{x_1} = f^L_{\text{pure},\underline{\underline{1}}}$.

So, consider; in this such case we consider x 2 is very small and in that case we the Henry's laws states that f 2 at T P X this approaches towards 0, this fugacity of 2 approaches towards x 2, H 2 1; T P where H 2 1 is Henry's constant of solute 2 in solvent 1 ok.

So, going back to the original definition of the fugacity which we came up here if you look at this expression ok; so, what would be R 2 in this case R 2 would be f 2 L divided by x 2, where x 2 approaches towards 0. So, therefore, R 2 is equal to limit f 2 L divided by x 2 at x 2 approaches towards 0 ok. And this is nothing, but H 2 1 T P. So, this is a Henry's constant of solute 2 in solvent 1 ok.

In contrast what would be R 1? The R 1 is basically that same R, but for the solvent. So, a solvent will be considering limit f 1 L limit divided by x 1, where x 1 goes to 0 and this will be in the sense of Raoult's law ok. So, this is what is very clear that when you have a system like that, where you may have to consider two different different state; one for different for solvent one for solute. So, I will come back to this in a next lecture and elaborate more on this and particularly other concepts such as normalization ok.

So, I will see you in the next lecture.