Course on Phase Equilibrium Thermodynamics
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Lecture 45
Deviations from Ideal Dilute Solutions

Well, so long we were discussing ideal solutions and deviations from ideality and we found out that that we have introduced a term Gamma and we have tried to express Gamma in terms of the excess properties of the solutions the excess properties arising due to the deviations from ideality, right? The excess properties are the properties of the solution due since it is deviating from ideality and assuming that these excess properties are referred to as the properties of the real solutions minus the properties of the had it, this had the solution been ideal at the conditions of (temp) same temperatures, same pressure and same composition, right?

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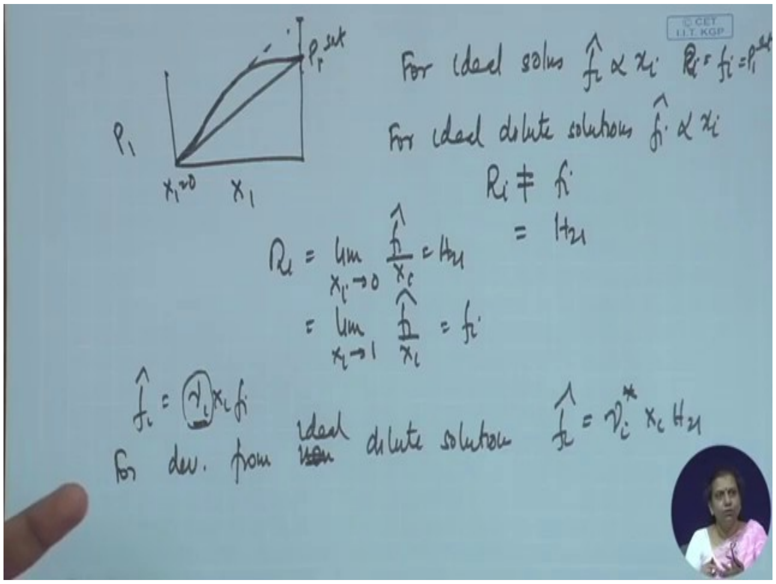

For ideal solns $\hat{f}_i \propto x_i$ $R_i = f_i = P_1^{sat}$

For ideal dilute solutions $\hat{f}_i \propto x_i$

$R_i \neq f_i$

$= H_{21}$

$$R_i = \lim_{x_i \to 0} \frac{\hat{f}_i}{x_i} = H_{21}$$

$$= \lim_{x_i \to 1} \frac{\hat{f}_i}{x_i} = f_i$$

$\hat{f}_i = \boxed{\gamma_i} x_i f_i$

For dev. from ~~non~~ ideal dilute solution $\hat{f}_i = \gamma_i^{*} x_i H_{21}$

Now what about the ideal dilutes solutions? If you remember we had discussed that if we take up say suppose pressure versus X1 plot for an ideal solution I had told you that the plot will be something of this sort, this is the partial pressure P1 versus X1, right? For most of the cases as we had mentioned the plot is something of this, fine. So therefore we find that when the component is in excess then the slope is almost linear and intercept is P1 saturated.

We found that at X1 equals to 0 also the slope is more or less linear but if we extend it then it the intercept here is not at P1 saturated it is at some other point and therefore we said that for both the cases it is linear or in other case we found we proposed that or we found out that for ideal solution your fi bar is proportional to xi, okay. And in the same way we can say that for ideal dilutes solutions also fi bar is proportional to xi, what is the difference?

Suppose in this case we take the proportionality constant as ki so in this particular case your ki or in maybe say Ri or something that is equal to the fugacity of the pure component at this conditions of temperature and pressure of the solution, right? And for low to moderate pressure this becomes equals to Pi saturated for ideal dilute solution in this particular case Ri it is not equal to fi, what is it? It is equal to rather this is equal to H21 which is the Henry's constant of component 2 in component 1; we had already discussed these things.

So that Ri this is equal to limit Xi tends to 0 fi bar by Xi is equals to H21 and limit Xi tends to 1 fi bar by Xi which is equals to fi. Now suppose there is (jus) just as if when there is deviation from ideal solution that in that case what do we write? We write fi bar equals to gamma i Xi fi, similarly for deviations from ideal dilute solutions what should be put up? We should have a some sort of an identical activity coefficient and this identical activity coefficient should incorporate the non the deviations from ideal dilute solution. So in this particular case we should have fi bar equals to say gamma i star Xi H21, agreed?

Now you should remember that when we have an ideal solution then in that case for Xi of every component tending to 1 fi reduces to or fi bar reduces to the saturated vapor pressure of that component for low to moderate pressure or the pure component fugacity of that component at the same temperature and pressure of the solution.

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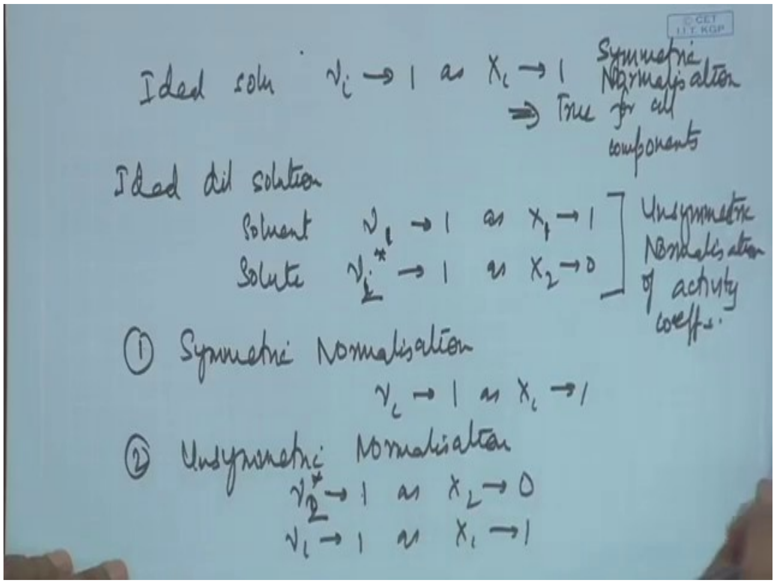

Ideal soln $\gamma_i \to 1$ as $X_i \to 1$ Symmetric Normalisation

⇒ True for all components

Ideal dil solution

Solvent $\gamma_1 \to 1$ as $X_1 \to 1$

Solute $\gamma_2^* \to 1$ as $X_2 \to 0$

] Unsymmetric Normalisation of activity coeffs.

① Symmetric Normalisation

$\gamma_i \to 1$ as $X_i \to 1$

② Unsymmetric Normalisation

$\gamma_2^* \to 1$ as $X_2 \to 0$

$\gamma_1 \to 1$ as $X_1 \to 1$

What I mean to say is when we are talking about an ideal solution then in that case for each and every case for each and every component we can write gamma I tends to 1 as Xi tends to 1 this is true for all components, isn't it?

But when we are dealing with an ideal dilute solution then in that case definitely when it is when it is dilute with respect to one component other component is in much excess. So suppose it's a binary component then for the solvent plot we have gamma i tends to 1 as Xi tends to 1 and for the solute part, what do we have? Gamma i star maybe it's a binary mixture, so this is gamma 1 X1 and gamma 2star tends to 1 as X2 tends to 0.

So what do we find? We find that while the normalization of activity coefficient is symmetric it is same for all the components for the case of ideal solution in this particular case the normalization of gamma is un- symmetric while we find that the solvent if it obeys the Raoult's law the solute it obeys the Henry's law and therefore while for an ideal solution this is known as symmetric normalization of activity coefficients in this particular case we call it as un-symmetric normalization of activity coefficients, right?

And so therefore again I would repeat that symmetric normalization it tells you that Gamma i tends to 1 as Xi tends to 1 and un-symmetric normalization because in this particular case the normalization for the different components are different so therefore this is gamma 1 tends rather gamma 2 tends to 1 as X2 tends to 0 gamma 1 tends to 1 as X1 tends to 1, right? And in the similar way this should be gamma 2 star and therefore we have 2 types of gamma normalization 1 for ideal solution 1 for ideal dilutes solution. And what is the relation between gamma2 and gamma2 star of any particular component.

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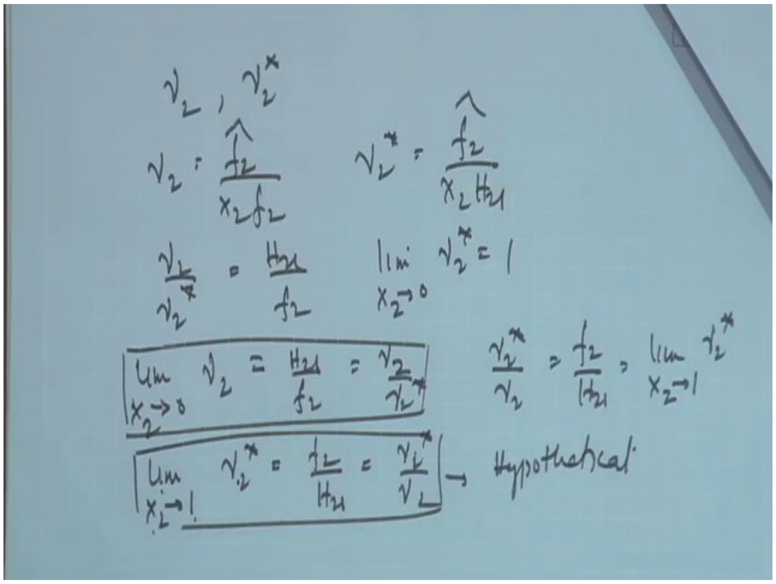

$$\gamma_2, \gamma_2^*$$

$$\gamma_2 = \frac{\hat{f}_2}{x_2 f_2} \qquad \gamma_2^* = \frac{\hat{f}_2}{x_2 H_{21}}$$

$$\frac{\gamma_2}{\gamma_2^*} = \frac{H_{21}}{f_2} \qquad \lim_{x_2 \to 0} \gamma_2^* = 1$$

$$\boxed{\lim_{x_2 \to 0} \gamma_2 = \frac{H_{21}}{f_2} = \frac{\gamma_2}{\gamma_2^*}} \qquad \frac{\gamma_2^*}{\gamma_2} = \frac{f_2}{H_{21}} = \lim_{x_2 \to 1} \gamma_2^*$$

$$\boxed{\lim_{x_2 \to 1} \gamma_2^* = \frac{f_2}{H_{21}} = \frac{\gamma_2^*}{\gamma_2}} \rightarrow \text{Hypothetical}$$

We know gamma2 is f2 by X2 f2 we know gamma2 star this is equals to f2 by X2H21. Now what is gamma2 by gamma2 star? This is equals to H21 by f2. So therefore this limit X2 tends to 0 gamma 2star equals to 1, right? And therefore limit again limit X2 tends to 0 gamma2 this is equal to H21 by f2 this is equals to Gamma2 by gamma2 star or in other words gamma2star by gamma 2 equals to f2 by H21 equals to limit X2 tends to 1 gamma2star, isn’t it?

So therefore what do we find? We find that limit X2 tends to 0 gamma2 this is equal to this and limit X2 tends to 1 gamma2star this is equal to f2 by H21 equals to gamma2star by gamma2 and this we need to remember that limit X2 tends to 1 gamma 2star which is given by this. This is a hypothetical situation because X2 tends to 1 for that particular case the component 2 does not exist in the phase of the solution as a result of which this is a hypothetical state.

So therefore when there is deviation from ideal dilutes solution and in that particular case.

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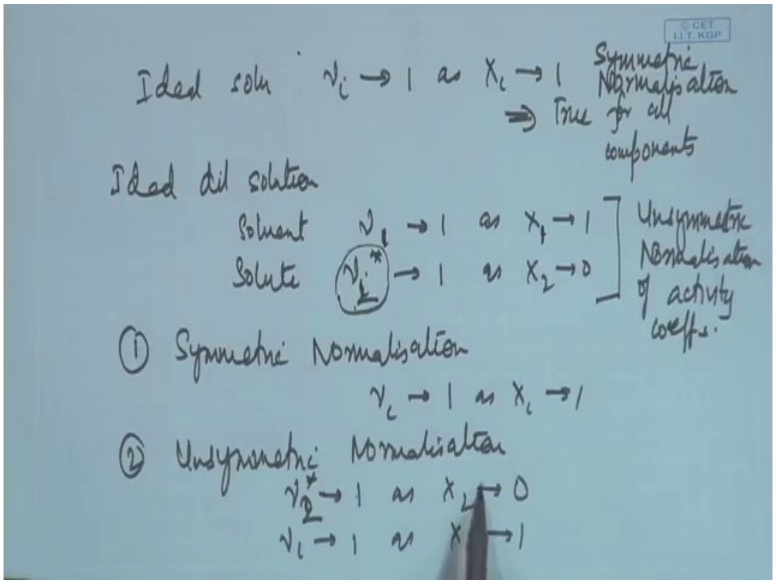

Ideal soln $\gamma_i \to 1$ as $x_i \to 1$ Symmetric Normalisation

$\Rightarrow$ True for all components

Ideal dil solution

Solvent $\gamma_1 \to 1$ as $x_1 \to 1$

Solute $\boxed{\gamma_2^*} \to 1$ as $x_2 \to 0$

] Unsymmetric Normalisation of activity coeffs.

① Symmetric Normalisation

$\gamma_i \to 1$ as $x_i \to 1$

② Unsymmetric Normalisation

$\gamma_2^* \to 1$ as $x_2 \to 0$

$\gamma_1 \to 1$ as $x \to 1$

We can also make the correction considering some form of an activity coefficient just to differentiate it from the activity coefficient we have been using for deviation from ideal solution we have named it as omega, gamma2star you can use any other name if you wish for such cases we have un-symmetric normalization of activity coefficients.

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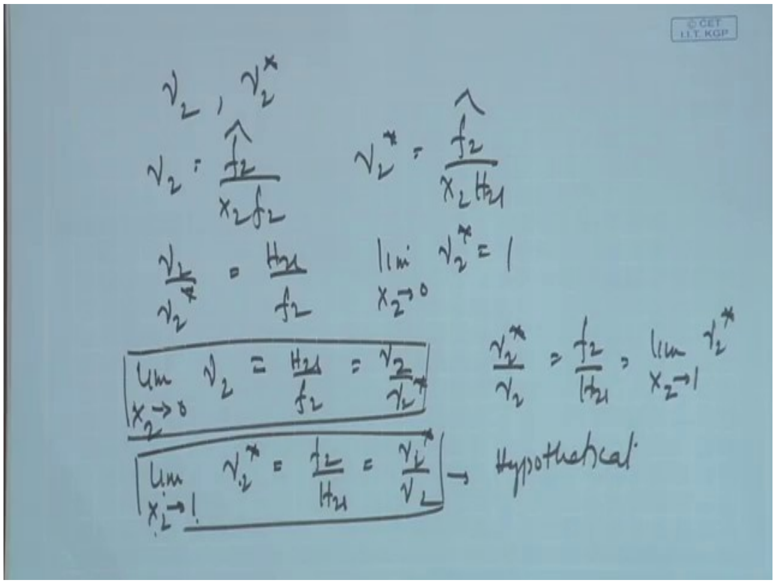

γ_2 , γ_2^*

$\gamma_2 = \frac{\hat{f}_2}{x_2 f_2}$ $\quad \gamma_2^* = \frac{\hat{f}_2}{x_2 H_{21}}$

$\frac{\gamma_2}{\gamma_2^*} = \frac{H_{21}}{f_2}$ $\quad \lim_{x_2 \to 0} \gamma_2^* = 1$

$\boxed{\lim_{x_2 \to 0} \gamma_2 = \frac{H_{21}}{f_2} = \frac{\gamma_2}{\gamma_2^*}}$

$\frac{\gamma_2^*}{\gamma_2} = \frac{f_2}{H_{21}} = \lim_{x_2 \to 1} \gamma_2^*$

$\boxed{\lim_{x_2 \to 1} \gamma_2^* = \frac{f_2}{H_{21}} = \frac{\gamma_2^*}{\gamma_2}}$ → Hypothetical

And if we want to find out gamma2star from gamma2 we can use either of these equations where this particular equation is hypothetical since we know that gamma2star or rather 2 does not remain in the phase of the solution at the conditions of temperature pressure of the solution.

And in the same way like we have tried to relate the activity coefficient gamma2 or gamma in terms of Gibbs free energy and the partial molar volume and the partial molar enthalpy we can do a similar endeavor and relate gamma2star with the partial molar excess Gibbs free energy considering it to be the difference or they excess property to be the difference between the actual property minus the property at in finite dilution for the same temperature and pressure of the composition. So by this we have covered ideal solutions, ideal dilute solutions as well as deviations from ideal solutions, deviations from ideal dilutes solutions.

Next the thing which is left is so far we have been discussing everything assuming that the 2 component are completely miscible over the entire range of composition but there are situations where we find that the 2 components are not miscible over the entire range of composition they can either be completely immiscible over the entire range which is again an extreme state or there can be partial immiscibility which is much more real situation where we find that for very low and very high concentration the 2 components are totally miscible and within the intermediate composition there is the 2 components are immiscible such systems are known is partially miscible systems.

So therefore we are going to deal with situations as partial immiscible systems, completely immiscible systems and why do substances prefer to, prefer not to mix when do substances prefer to mix. We already know that the, for constant temperature and pressure conditions this is governed by Gibbs free energy. So definitely the 2 component would like to separate out when the Gibbs free energy of the 2 particular liquid separated is less as compared to the Gibbs free energy of the solution.

So therefore we are going to deal with those conditions when 2 particular substances or 2 particular components form an immiscible pair when do they form a miscible pair? And the phase diagrams the Pxy, Txy diagrams for completely immiscible and partially miscible substances and since no discussion on thermodynamics can end without having or without discussing thermodynamic consistency of VLE data. We will be spending a short amount of time by discussing how exactly the Gibbs Duhem equation is used to test thermodynamic consistency of VLE data with that more or less the class or the course on thermodynamics will be coming to an end. So we will be discussing these things in the next class, thank you very much.