Advanced Thermodynamics
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Lecture – 16
Fugacities in Gaseous Mixtures - 3

Welcome to the MOOCs course advanced thermodynamics. The title of this lecture is fugacities in gaseous mixtures part 3. We have been discussing how to obtain the fugacity of a component in a gaseous mixture if the gaseous mixture is obeying some kind of a non-ideality, those things we have been discussing. In the previous lecture, we have discussed fugacities in gaseous mixture at higher densities.

This particular lecture, we will be discussing fugacities in gaseous mixture especially when the case if a condensed phase, a liquid or solid is dissolving in a kind of compressed gas, then if you wanted to know the composition of that particular condensed phase, how much it is dissolved in a compressed gas, so that if you wanted to calculate, the composition if you wanted to calculate, is it possible to use the principles that we have been studying at fugacity or equal fugacity or fugacity of component is equal in all the coexisting in phases which are at equilibrium.

Can we use those principles that is f_i in phase 1 is equal to f_i in phase 2 if phase 1 and phase 2 are co-existing? So, such kind of principles if we use, can we get that information that how much of a condensed phase liquid or solid is dissolved in a kind of a compressed gas. So, those kinds of things is it possible to calculate using the basics that we have been discussing in the last few weeks especially on fugacity of component i in a gaseous mixture.

Those principles we can use and then we try to establish some kind of relations to find out how much composition or how much mole fraction of a condensed liquid or solid phase is dissolved in a compressed gas phase that we are going to see in this particular lecture.

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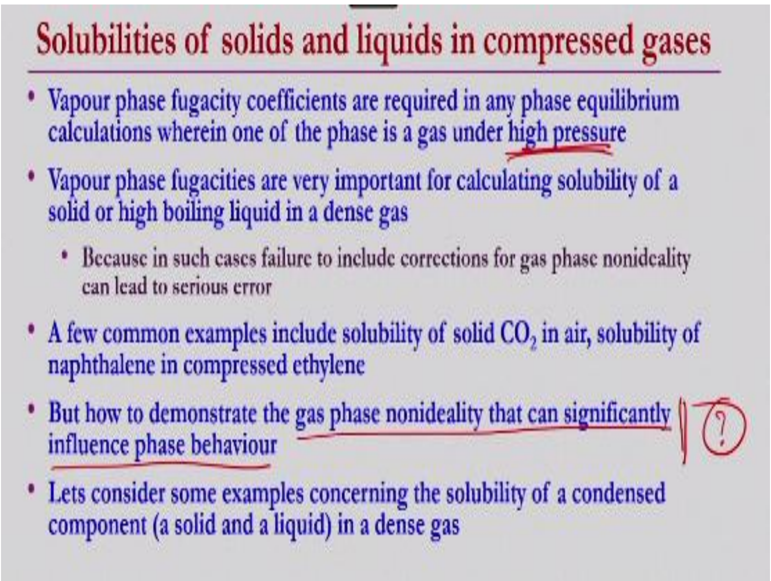

Solubilities of solids and liquids in compressed gases

- Vapour phase fugacity coefficients are required in any phase equilibrium calculations wherein one of the phase is a gas under high pressure
- Vapour phase fugacities are very important for calculating solubility of a solid or high boiling liquid in a dense gas
  - Because in such cases failure to include corrections for gas phase nonideality can lead to serious error
- A few common examples include solubility of solid CO_2 in air, solubility of naphthalene in compressed ethylene
- But how to demonstrate the gas phase nonideality that can significantly influence phase behaviour ?
- Lets consider some examples concerning the solubility of a condensed component (a solid and a liquid) in a dense gas

So, solubilities of solids and liquids in compressed gases is the primary title of this particular lecture and then based on the principles that we will be discussing for the solubilities of either solids or liquids in compressed gases. So, from those principles, we will be solving a few problems as well. This vapor phase fugacity coefficients are required in any phase equilibrium calculations wherein one of the phase is gas under high pressure, okay? So this under high pressure that means compressed gas, that means we are saying that the gas vapor phase is at high pressures, right?

So, that means vapor liquid equilibrium are some other kind of solid-liquid equilibrium, etc., those problems we are going to see. So, if you have a kind of phase equilibrium problems where the vapor phase is involved and then vapor phase is at high pressure, then whatever the principle that we are going to discuss in this particular lecture, they are going to be very much useful because vapor phase fugacity’s are very important for calculating solubility of a solid or high boiling liquid in a dense gas.

Because if you make any kind of mistakes or if there exist a kind of failure to include correction for gas phase non-ideality under such conditions where the gas phase or the vapor phase is at high pressure, then that may lead to serious error and then that may cause serious problems to the phase equilibrium or the phase contacting equipment as well, okay? So, that is the reason one has to be careful and then one has to make a proper adjustment for the non-ideality of the vapor phase which is at the high pressures.

Then in that vapor phase if a solid or a liquid is dissolving, one has to make a kind of proper adjustment very carefully because first of all it is already at the high pressure condition and then any error while incorporating non-ideality in a vapor phase problems for such kind of situations having some kind of errors, then that overall it is going to be dangerous for the operational point of view, okay?

A few common examples include like solubility of solid CO_2 in air, solubility of naphthalene in compressed ethylene, etc., are kind of things that we can take as a kind of examples where solids and liquids are dissolving in a compressed gas phase. But how to demonstrate the gas phase non-ideality that can significantly influence the phase behavior especially liquid or solid is dissolving in a high pressure vapor phase or high pressure gas phase or compressed gas phase, okay? So, that is the question that we are going to do anyway.

For simplicity, what we do? We take a few simple cases where the solubility of a condensed component in a dense gas is taking place.

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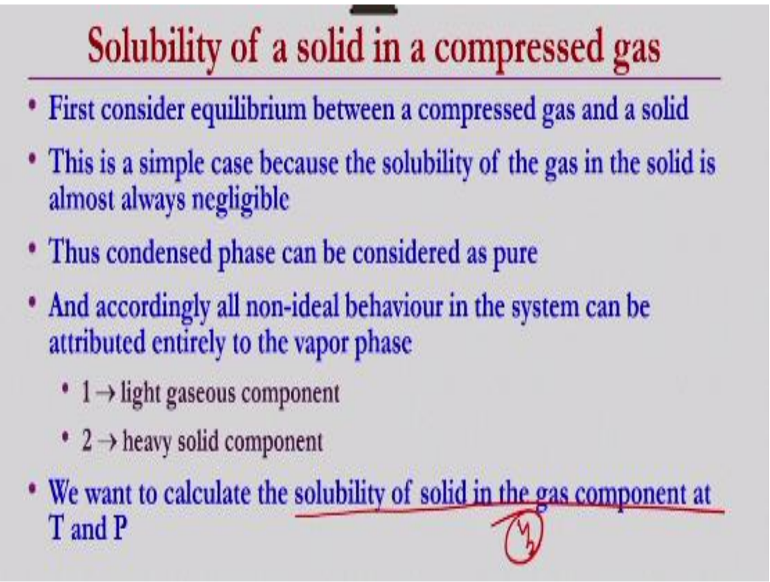

Solubility of a solid in a compressed gas

- First consider equilibrium between a compressed gas and a solid
- This is a simple case because the solubility of the gas in the solid is almost always negligible
- Thus condensed phase can be considered as pure
- And accordingly all non-ideal behaviour in the system can be attributed entirely to the vapor phase
  - 1 → light gaseous component
  - 2 → heavy solid component
- We want to calculate the solubility of solid in the gas component at T and P

y_2

So, for that, we start with solubility of a solid in a compressed gas, okay? First consider equilibrium between a compressed gas and a solid and this is a simple case because in general what happens when there is a compressed gas and there is a solid gas is being dissolved into the solid is a kind of very rare or you very rarely find and in general solubility of gas in a solid phase is in general almost zero whereas the solid may be dissolving in the gas phase, okay? Especially if the gas phase is under high pressure compressed gas conditions, okay?

So, that is the reason if transfer is only one side because what we have, we have a gas, we have a solid. So, solid is being dissolved into the gas phase because of the high pressure compressed gas conditions that is possible, but the other way the gas is being dissolved in solid phase that is you know very rare case. So, that means transfer is in a kind of more or less one directional and though that one directional transfer is taking place that is going to cease at certain points, so there will be a kind of equilibrium, okay?

So, now what happens since the solid is transferring to the gas phase, but gas is not transferring into the solid phase what you can say? The solid phase is almost kind of a pure condensed state and the solid phase can be treated as a kind of a pure condensed phase, okay? And then this if you take the component whatever the gaseous component or lighter component as component 1 and then solid heavier component as 2, so then mole fraction of 2 that is component 2 in gaseous or compressed gas phase that you have to find out.

You are trying to find out how much the solid is dissolved in a compressed gas. So, compressed gas or gas phase is designated by y and then the dissolving of solid that is the heavy component that if you are designating as 2, so then y_2 we have to find out that is what we are going to see now. So, while doing this on, we obviously know what we have f_2^S = f_2^v principles we are having. For f_2^S since the solid phase is almost pure because gas is not dissolving into the solid, whereas the solid is dissolving into the gas.

So, solid phase is almost a pure condensed form. So, then we have already derived this what is this and then f_2^v we already know f_2^v is nothing but y_2 P. So, from here, you can get $\frac{y_2 f_2^S}{\phi_2 P}$, f_2^S is nothing but P_2^s ϕ_2^s $\exp\left[\int_{P_2^S}^{P} \frac{v_2^C}{RT} dP\right]$. This we know and then divided by ϕ_2 P. So, y_2 you can calculate this way. So, basically this is what we are going to derive now. We are going to derive and then see details how to do step by step this calculation, we are going to do now, right?

Now, only the simplicity that we are having here that whatever the solid is there that is a kind of almost a pure condensed phase because, gas is not being dissolved in solid whereas the solid is dissolving in the compressed gas. So, thus condensed phase can be considered as pure and accordingly all nonideal behavior in the system can be attributed entirely to the vapor phase. So, for the notations point of view let us take a light gaseous component as 1, whereas the heavy solid component let us take it as 2. Then we want to calculate the solubility of solid in the gas component at constant temperature and pressure. So, what is this y_2 that we have to find out, right?

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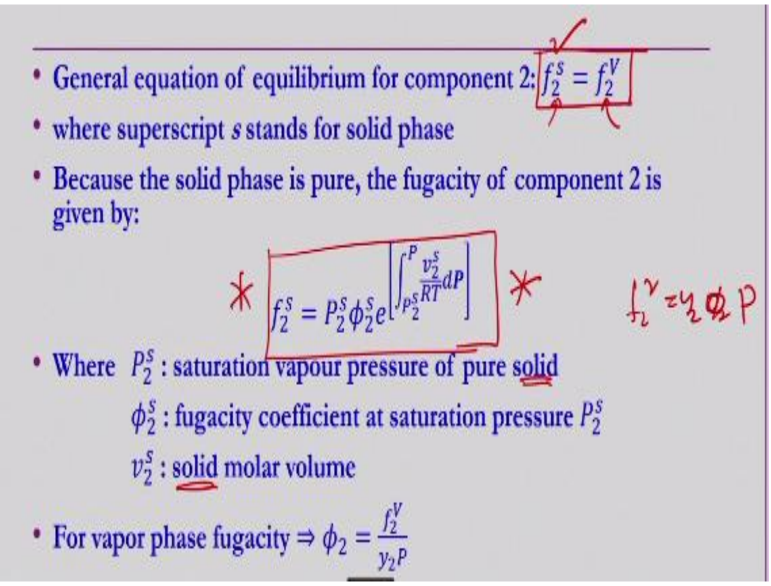

- General equation of equilibrium for component 2: $\boxed{f_2^s = f_2^V}$
- where superscript *s* stands for solid phase
- Because the solid phase is pure, the fugacity of component 2 is given by:

$$* \boxed{f_2^s = P_2^s \phi_2^s e^{\left[\int_{P_2^s}^{P} \frac{v_2^s}{RT} dP\right]}} *$$

$$f_2^v = y_2 \phi_2 P$$

- Where P_2^s : saturation vapour pressure of pure solid
  ϕ_2^s : fugacity coefficient at saturation pressure P_2^s
  v_2^s : solid molar volume
- For vapor phase fugacity $\Rightarrow \phi_2 = \frac{f_2^V}{y_2 P}$

At equilibrium what we know, fugacity of that component should be equal in all the phases which are at equilibrium. So, now here for the component 2, we are trying to find out. So, for the competent 2, whatever the fugacity of component 2 in the condensed phase is there that should be equals to difficulty of the same component 2 in the compressed gas or vapor phase, so that should be the equilibrium relation, right? Where superscript s stands for solid phase or condensed phase.

Because the solid phase is pure, the fugacity of component 2 is given by $f_2^s = P_2^s\ \phi_2^s\ \exp\left[\int_{P_2^s}^{P} \frac{v_2^s}{RT} dP\right]$, this again we have derived in one of the earlier lectures in our week 2, right? That is in lecture number 4, this we have already derived and then several time in between also we have utilized this expressions, so we are not going into the derivation of this expression, okay? So, one is known. Second one is nothing but f_2^v is nothing but $y_2\ \phi_2$ P as I already mentioned.

Here in this expression whatever the P_2^s is nothing but saturation vapor pressure of pure solid and then ϕ_2^s is nothing but fugacity coefficient at saturation pressure P_2^s and then v_2^s is nothing but solid molar volume, specifically we are saying solid because we are taking the condensed phase as a kind of solid phase now. If you take a liquid phase, then it is possible that gas may also dissolve into the liquid phase, that problem we take later case. This problem we are taking in this case was specifically solid, so that is the reason we are writing solid.

Otherwise whether it is solid or liquid, we can generalize as a kind of condensed phase. Previously, we have written the same expression as $f_i^c = P_i^s\ \phi_i^s\ \exp\left[\int_{P_i^s}^{P} \frac{v_i^c}{RT} dP\right]$ that is what we have written, but now here condensed phase is a solid phase. Specifically solid phase we are taking for simplicity because in the solid phase gases will not dissolve in general, okay? So that you can take that solid phase as a kind of a pure component that is a kind of simplification that we can have by explicitly taking the condensed phase as a kind of solid phase, okay? Condensed liquid phase that we are going to take in the subsequent slides anyway.

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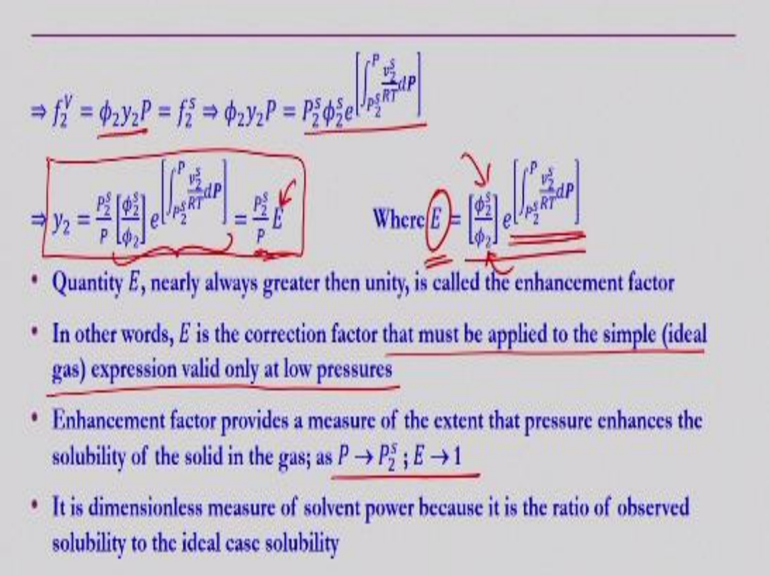

$$\Rightarrow f_2^V = \phi_2 y_2 P = f_2^S \Rightarrow \phi_2 y_2 P = P_2^S \phi_2^S e^{\left[\int_{P_2^S}^{P} \frac{v_2^S}{RT} dP\right]}$$

$$\Rightarrow \boxed{y_2 = \frac{P_2^S}{P}\left[\frac{\phi_2^S}{\phi_2}\right] e^{\left[\int_{P_2^S}^{P} \frac{v_2^S}{RT} dP\right]} = \frac{P_2^S}{P} E} \qquad \text{Where } E = \left[\frac{\phi_2^S}{\phi_2}\right] e^{\left[\int_{P_2^S}^{P} \frac{v_2^S}{RT} dP\right]}$$

- Quantity E, nearly always greater then unity, is called the enhancement factor
- In other words, E is the correction factor that must be applied to the simple (ideal gas) expression valid only at low pressures
- Enhancement factor provides a measure of the extent that pressure enhances the solubility of the solid in the gas; as $P \rightarrow P_2^S$; $E \rightarrow 1$
- It is dimensionless measure of solvent power because it is the ratio of observed solubility to the ideal case solubility

Then f_2^v already we know that it is $y_2\ \phi_2$ P. So, $f_2^v = y_2\ \phi_2\ P = f_2^s$ and then f_2^s is nothing but this particular thing we have derived. So, from here what we can have, $y_2 = \frac{P_2^s}{P}\left[\frac{\phi_2^s}{\phi_2}\right] \exp\left[\int_{P_2^s}^{P} \frac{v_2^s}{RT} dP\right]$, whereas here we write such a that $\frac{P_2^s}{P}$ we write as one term and then remaining everything we write it as E that is $\left[\frac{\phi_2^s}{\phi_2}\right] \exp\left[\int_{P_2^s}^{P} \frac{v_2^s}{RT} dP\right]$. This is known as the enhancement factor, this E we call it as enhancement factor, right?

So, this is nearly always greater than unity and is known as the enhancement factor. In other words E is that correction that must be applied to this simple ideal gas expression, which is valid only at low pressure. At low pressures only ideal gas behavior is valid, but now the pressure is the compressed gas is there because of that one whatever the correction factor that must be brought in that is there because of this enhancement factor. So, that enhancement factor brings in all those correction factors because of taking the conditions away from the ideal gas behavior.

Because of that one, whatever the non-ideality is there all those terms are being taken care or clubbed together including ϕ_2^s. ϕ_2^s indicates what, whatever the non-ideality there in the saturated vapor phase and then ϕ_2 is there whatever the non-ideality is there in vapor phase itself is not under the saturation condition but vapor phase that we take and then this is what, this is nothing but Poynting correction. So, it is having 3 corrections.

So, all those corrections that all these Poynting correction, ϕ_2^s, ϕ_2 all these disclose some amount of non-ideality that has been brought into the system because of pressure is away from the small pressure low pressure conditions. All those non-idealities are clubbed together and then called as a kind of enhancement factor for these kind of problems, okay? Enhancement factor provides a measure of the extent that pressure enhances the solubility of solid in the gas as P → P_2^s and then E → 1, right?

It is a dimensionless measure of solvent power because it is the ratio of observed solubility to the ideal case solubility because P is nothing but that is indicates that ideal case solubility the pressure at which we are finding out and all that.

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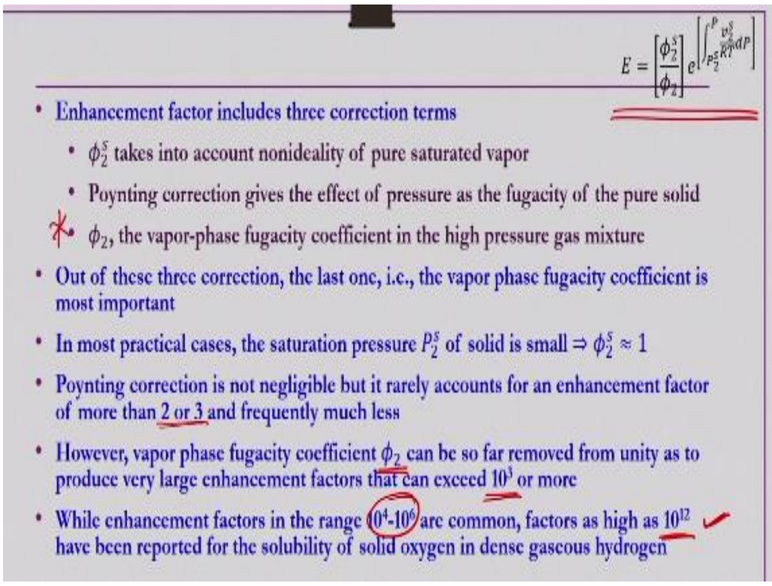

$$E = \left[\frac{\phi_2^s}{\phi_2}\right] e^{\left[\int_{P_2^s}^{P} \frac{v_2^s}{RT} dP\right]}$$

- Enhancement factor includes three correction terms
  - ϕ_2^s takes into account nonideality of pure saturated vapor
  - Poynting correction gives the effect of pressure as the fugacity of the pure solid
  - ϕ_2, the vapor-phase fugacity coefficient in the high pressure gas mixture
- Out of these three correction, the last one, i.e., the vapor phase fugacity coefficient is most important
- In most practical cases, the saturation pressure P_2^s of solid is small ⇒ $\phi_2^s \approx 1$
- Poynting correction is not negligible but it rarely accounts for an enhancement factor of more than 2 or 3 and frequently much less
- However, vapor phase fugacity coefficient ϕ_2 can be so far removed from unity as to produce very large enhancement factors that can exceed 10^3 or more
- While enhancement factors in the range 10^4-10^6 are common, factors as high as 10^{12} have been reported for the solubility of solid oxygen in dense gaseous hydrogen

So, now we see this enhancement factor it is having 3 correction factors as I mentioned. One is the ϕ_2^s that takes into account non-ideality of pure saturated vapor and then Poynting correction that gives the effect of pressure on the fugacity of the pure solid, pure condensed phase that is pure solid, and then ϕ_2 the vapor phase fugacity coefficient in the high pressure gas mixture. So, the 2 non-idealities, whatever the non-ideality is there because of these 3 conditions, so all of them are clubbed together and then written as a kind of enhancement factor E, right?

Then we know ϕ_2^s in general very small because in general for pure substance in general what happens the saturation pressures are in general very small compared to the critical condition. So, then what we can say that ϕ_2^s is almost close to 1 in general. Then Poynting correction also we have seen that it depends on the delta P and then the delta P is far away from the remote from the critical condition, then also we have seen that the Poynting correction is very small in one of our previous lectures.

If delta P is less than or equal to 10 bars and then when v is approximately 100 cc per mole, then we have seen that Poynting correction is coming less than 4% or something like that that can be negligible, okay? So, whatever the effect that primarily is there, most of the effect is coming from this part that is ϕ_2, okay? So, one has to be careful in calculating ϕ_2 but if you make error in calculating ϕ_2, then obviously that is going to show picture that is going to show influence on the composition of the solid in the compressed gas phase.

So, any such kind of errors may lead to dangerous errors, both operational as well as the design of this phase equilibrium contacting equipments because these systems are at high pressures, okay? So, out of these 3 corrections, the last one that is the vapor phase fugacity coefficient is most important, in most practical cases the saturation pressure P_2^s of solid is in general very small. So, then ϕ_2^s can be taken as approximately close to 1, so that is also small.

Then Poynting correction is not negligible in general, but it is nearly constant or nearly accounts for an enhancement factor more than 2 or 3 times only and frequently it is much less, whereas whatever the enhancement factor is there due to the fugacity that is as large as order of 10 power 3 or more. So, that is the reason you know the effect of ϕ_2 in enhancement factor is much higher. It can improve the enhancement factor in order of 10 power 3 or more.

Whereas the Poynting correction may increase the enhancement factor only by 2 or 3 times or even less many a times, whereas the ϕ_2^s is even smaller. So, ϕ_2^s and then Poynting corrections are having small effect on the enhancement factor, whereas the ϕ_2 that is the vapor phase non-ideality whatever is there that is having a kind of large influence and then that may enhance the enhancement factor up to the order of 10^3 or more. Enhancement factors of the order of 10^4 to 10^6 are also very common in general, okay?

So, enhancement factors in the range of 10^4 to 10^6 are common, but factors as high as 10^{12} have been reported for the solubility of solid oxygen and dense gaseous hydrogen. So, order of 10 power 12 is also possible whereas 10^4 to 10^6 is very common, okay?

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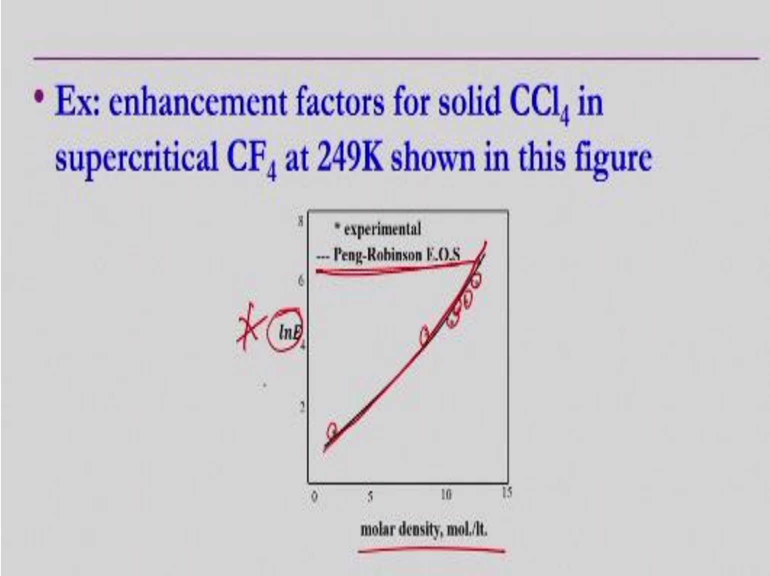

- Ex: enhancement factors for solid CCl_4 in supercritical CF_4 at 249K shown in this figure

So, in order to have a kind of feel about how large is this enhancement factor especially with increasing the molar density that we can see from this picture where It shows the enhancement factors for solid CCl_4 in supercritical CF_4 at 249 Kelvin. You can see as molar density is increasing the, the ln of E, it is not just simple E, ln of E is how it is drastically increasing. Experimentally whatever the results are there they are indicated by the stars, whereas the same behavior if we try to reproduce by Peng-Robinson equation, then we can see this E is increasing drastically with increasing the molar density.

The ln E drastically increasing with the molar density, okay? This is to give a feel how important it is, okay? So, that is about the case where only condensed the solid phase is dissolving in a compressed the gas phase, but now if the condensed phase is a kind of liquid, high boiling liquid or something like that, right? Then it is possible that gas may also dissolve in the liquid because the solubility of gases may be there in the liquid, right? As liquid solubility may be there in the gases. So, now here in this case whatever the next topic we are going to take, we are taking solubility of liquid in a compressed gas.

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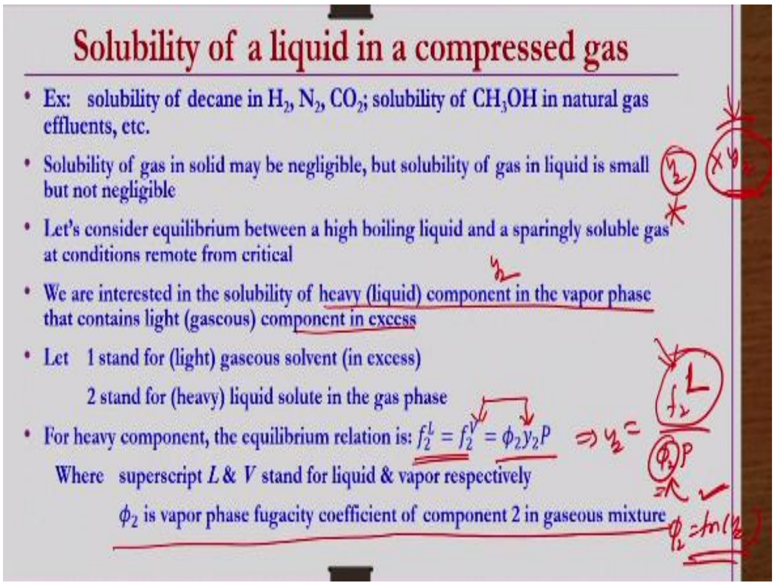

Solubility of a liquid in a compressed gas

- Ex: solubility of decane in H_2, N_2, CO_2; solubility of CH_3OH in natural gas effluents, etc.
- Solubility of gas in solid may be negligible, but solubility of gas in liquid is small but not negligible
- Let's consider equilibrium between a high boiling liquid and a sparingly soluble gas at conditions remote from critical
- We are interested in the solubility of heavy (liquid) component in the vapor phase that contains light (gaseous) component in excess
- Let 1 stand for (light) gaseous solvent (in excess)
  2 stand for (heavy) liquid solute in the gas phase
- For heavy component, the equilibrium relation is: $f_2^L = f_2^V = \phi_2 y_2 P$

  Where superscript L & V stand for liquid & vapor respectively

  ϕ_2 is vapor phase fugacity coefficient of component 2 in gaseous mixture

y_2

x_1 y_2

$\Rightarrow y_2 = \frac{f_2^L}{\phi_2 P}$

$\phi_2 = fn(y_2)$

So, here the component may be transferring both sides, right? So, from the gas to liquid the transfer is possible in this case, where we are discussing about solubility of a liquid in a compressed gas and then liquid to gas is also possible, so that either side the gas to liquid, the transfer is either side, okay? So, in the previous case what happens the solid is being dissolved into the gas phase, so then that is the reason we were only obtaining y_2 in the previous case, okay, where solid is dissolving in the compressed gas.

Now, in this case gas is dissolving in the liquid and then liquid is also dissolving in the gas. If the gaseous component if you designate as 1 and then heavy liquid component if you designate as 2, then you have to find out y_2 how much liquid has gone into the vapor phase that can be given by the y_2 and then how much gaseous component is gone into the liquid phase by dissolving that is nothing but x_1, so both x_1 and y_2 you have to find out. So, that means whatever this equal fugacity $f_1 = f_1$ for both the phases, the vapor phase and the liquid phase that relation you have to make use.

Similarly, f_2 in vapor phase = f_2 in the liquid phase that relation also you should make use, right? Then you have 2 relations. So, then you may be having some kind of expression for x_1 and then y_2. While deriving these equations, you may realize that while finding these x_1 and y_2, you need to do several kind of trial and error solutions as we are going to discuss. So, now, how this problem is different from the previous case, in the previous case only solid was dissolving in the compressed gas, right?

So, solid was almost kind of a pure state, but in this case, now in the present case we are discussing the solubility of a liquid in a compressed gas. So, liquid can obviously will dissolve into the compressed gas but compressed the gas can also be dissolved in the liquid. So, the transfer of this species is taking place either side. So, for both the component and that equal fugacity rule we have to utilize and then find out what is this y_2 and x_1.

The y_2 is nothing but how much liquid is dissolved in gaseous phase, okay? Or in gas phase how much liquid is present because of the solubility of the liquid in gas and then x_1 is nothing but how much gas is present in the liquid, x stands for the liquid. So, how much gas has been dissolved or transferred to the liquid phase that you can obtain by x_1 because 1 we are designating for the light gaseous components, 2 we are designating for the heavy liquid components. So, that we are going to do now.

So, example where a liquid is dissolving in a compressed gas, we can have the solubility of decane in hydrogen, nitrogen, or carbon dioxide. Then solubility of methanol in natural gas effluents, etc., kind of some examples where we can see solubility of a liquid in a compressed gas. Solubility of gas in solid may be negligible but solubility of gas in liquid is small but not negligible, so that is x_1 also we have to find out in addition to y_2 that we have done in the previous case. In the previous case, we have done y_2, now we have to establish relation in addition to y_2, what is x_1.

Be careful now this y_2 relation whatever we are going to derive in this case, it is different from y_2 of the previous case, this is different and this problem y_2 is different. The previous case y_2 takes account only if the transfer is in one directional from the solid to liquid or from the solid to gas, but now herein y_2 it takes account the transfer in either side that is solid to liquid, liquid to solid. So, this expression is going to be different and then it has to be obtained by trial and error solution whereas the previous one is straightforward substitution and getting this y_2 kind of thing if you know whatever this ϕ_2, ϕ_2^s, etc., okay?

So, let us consider equilibrium between a high boiling liquid and sparingly soluble gas at conditions remote from critical. Then we are interested in the solubility of heavy liquid component in the vapor phase that is y_2 that contains light gaseous component in excess, okay? So, now let us take 1 stand for light gaseous solvent in excess and then 2 stand for heavy liquid solute in the gas phase, okay? Then for heavy component, the equilibrium relation is nothing but $f_2^L = f_2^V$ and then f_2^V we know that it is nothing but simply ϕ_2 y_2 P.

Φ_2 if you know and f_2^L you know, so then you can calculate $y_2 = \frac{f_2^L}{\phi_2 P}$. ϕ_2 how you calculate? You calculate based on the equation of state. Let us say vapor phase is described by Van der Waal's equation, so then ϕ_2 expression we have derived. Let us say if the vapor phase is described or the compressed gas phase is described by Van der Waal's equation of state, then we have the ϕ_2 relation. Similarly, if it is described by virial equation of state, then also we have this ϕ_2 relation, right?

But all these ϕ_2 is function of y_2 as well in addition to the temperature, pressure, and then the parameters associated with the equation of state that we are using. So, it is going to be trial and error, you cannot substitute directly. Further, in addition to this ϕ_2, we need to know ϕ_2^L also. What is this ϕ_2^L right? In the previous case ϕ_2^S that we have taken straightforward for the pure condensed phase because in the solid the gas was not dissolving, but now in this condensed liquid phase, gas is also dissolving.

So this relation is going to be different from the previous one. The ϕ_2 is vapor phase fugacity coefficient of component 2 in gaseous mixture.

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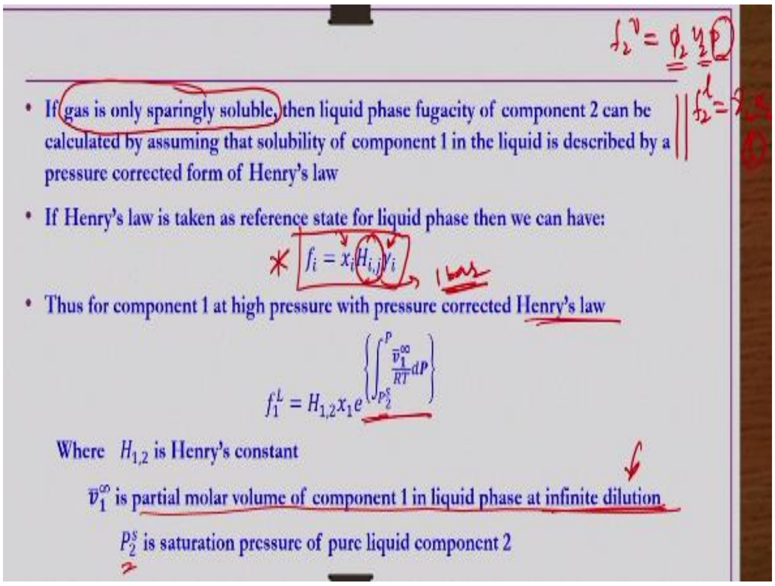

- If gas is only sparingly soluble, then liquid phase fugacity of component 2 can be calculated by assuming that solubility of component 1 in the liquid is described by a pressure corrected form of Henry's law
- If Henry's law is taken as reference state for liquid phase then we can have:

$$f_i = x_i H_{i,j} \gamma_i$$

- Thus for component 1 at high pressure with pressure corrected Henry's law

$$f_1^L = H_{1,2} x_1 e^{\left\{\int_{P_2^S}^{P} \frac{\bar{v}_1^{\infty}}{RT} dP\right\}}$$

Where $H_{1,2}$ is Henry's constant

$\bar{v}_1^{\infty}$ is partial molar volume of component 1 in liquid phase at infinite dilution

P_2^S is saturation pressure of pure liquid component 2

So, now what we do? We have to worry about f_2^L, right? That is if the gases is sparingly soluble, then liquid phase fugacity of component 2 can be calculated by assuming that the solubility of component 1 in the liquid is described by a pressure corrected form of Henry's law, okay? So, basically what we are saying for vapor phase like we have this relation, we are trying to have a similar relation for the liquid phase also. So, here if it is vapor phase ϕ_2 has come, but now if it is liquid phase here Γ_2 has to come into the picture, okay?

Then here if y_2 has come, so here x_2 has to come into the picture and then here P is coming into the picture because we have taken in this derivation ideal gas as a kind of a reference state. So, here in addition to this Γ_2 x_2 you need to have some correction reference state, okay? So, that reference state what is this, okay? This we are going to see in the next module where we are going to start the non-ideality in liquid mixtures. Basically non-ideality in the liquid mixture is coming because of mixing the unlike interactions, unlike interaction in the sense in the gas phase we have to see.

We have to start with the gas phase, in the gas phase ideality is there because all the molecules are of same component and they are far away from each other, there is no interaction. But if you want to define the ideality for liquid phase, you cannot say there is no interaction because in the condensed liquid phase all the molecules are touching each other, there is interaction. So, you cannot say there is no interaction at under whatever the condition, whatever is the lowest pressure or highest temperature whatever the case if it is on the liquid phase, right? There is interaction.

So, that is the reason in the liquid phase, ideality is defined by like-like interaction. Let us say all the molecules are i, so then if all ii interactions are there then in that i liquid if you add something j component, so then there will be in addition to ii interaction, there will be jj interaction, there will be ij interactions also. So, now this ij interaction, right? So one i one j interactions, how it is different from ii or jj interactions. If it is too different, then the system is going to have a kind of some amount of non-ideality, okay?

So, like that non-ideality has brought into the picture. So, when you talk about the unlike interactions, the different reference states are possible like Lewis-Randall reference state, Henry’s law as a kind of reference states, etc., are possible, right? If the gas is only sparingly soluble under such conditions what we can do, we can take Henry’s law as a kind of reference state and then under such conditions, the f_i^L can be written as a Γ_i x_i H_{ij}, H_{ij} is nothing but what does it mean?

H_{ij} indicates solubility of j in i, j stands for solute, i stands for the solvent that is H_{ij} that is Henry's constant that is solubility of j in i, okay? And this x_i is mole fraction of that particular component in the liquid mixture and this Γ_i is nothing but non-ideality of the system because of non-ideality in the liquid mixture, okay? Because now the liquid mixture is having some non-ideality that is what we are taking, okay? So now, this is what we take.

Now thus for component at high pressure with pressure corrected Henry's law. Actually Henry's law, this Henry's constant whatever are there they are derived at 1 bar pressure actually or the information is available at 1 bar pressure, whatever the Henry's constants are there they are all provided at 1 bar pressure. So, as the pressure increases, the solubility also increases, so there will be a kind of a pressure corrected form of Henry's law should be there. So, this pressure corrected Henry's law applied for a component 1 at high pressure.

Then we can have $f_1^L = x_1 H_{1,2} \exp\left[\int_{P_2^s}^{P} \frac{\bar{v}_1^\infty}{RT} dP\right]$ and then this integration from P_2^s to P. This is what you can have, right? So, this is the generalized one if you take Henry's law as a kind of reference state. So, this we are going to come back again in the subsequent lecture, right? So, at 1 bar pressure if you have the Henry's law as a kind of reference state, then this is what we have, but the pressure is away 40 bar, 50 bar, or 1000 bar something like that, there should be correction because of the increased pressure in the Henry's law constant.

So that correction is given by this one, okay? So, now $H_{1,2}$ is nothing but Henry's law constant, $\bar{v}_1^\infty$ is nothing but partial molar volume of component 1 in liquid phase at infinite dilution because we started with the case where the gas is sparingly soluble, it is not very largely soluble. The gas is only sparingly soluble that is the case we are taking, so then we can say that infinite dilution condition valid, so $\bar{v}_1$, rather writing $\bar{v}_1$ we can write $\bar{v}_1^\infty$, okay? And then P_2^s is nothing but saturation pressure of pure liquid component 2, okay?

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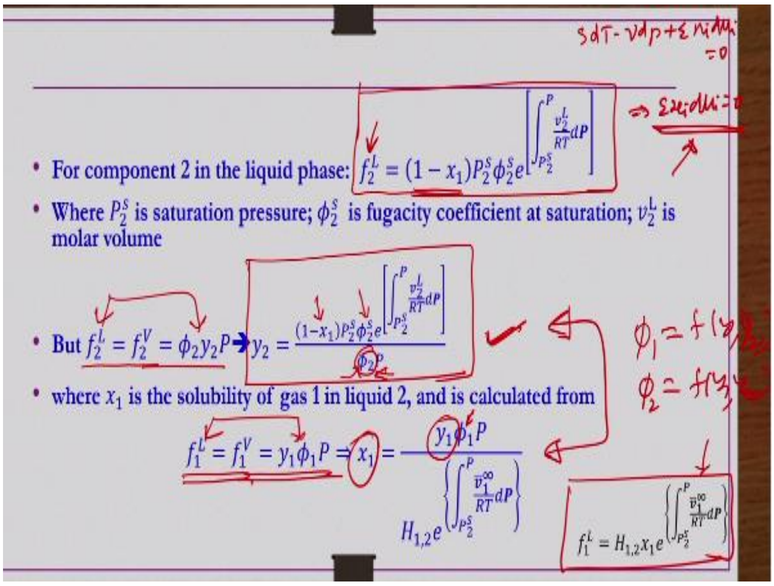

$SdT - Vdp + \sum n_i d\mu_i = 0$

$\Rightarrow \sum x_i d\mu_i = 0$

- For component 2 in the liquid phase: $\boxed{f_2^L = (1 - x_1)P_2^S\phi_2^S e^{\left[\int_{P_2^S}^{P} \frac{v_2^L}{RT} dP\right]}}$
- Where P_2^S is saturation pressure; ϕ_2^S is fugacity coefficient at saturation; v_2^L is molar volume
- But $f_2^L = f_2^V = \phi_2 y_2 P \rightarrow y_2 = \boxed{\frac{(1-x_1)P_2^S\phi_2^S e^{\left[\int_{P_2^S}^{P} \frac{v_2^L}{RT} dP\right]}}{\phi_2 P}}$
- where x_1 is the solubility of gas 1 in liquid 2, and is calculated from

$$f_1^L = f_1^V = y_1\phi_1 P \Rightarrow x_1 = \frac{y_1\phi_1 P}{H_{1,2}e^{\left\{\int_{P_2^S}^{P} \frac{\bar{v}_1^{\infty}}{RT} dP\right\}}}$$

$\phi_1 = f(y$

$\phi_2 = f(y_2$

$$\boxed{f_1^L = H_{1,2}x_1 e^{\left\{\int_{P_2^S}^{P} \frac{\bar{v}_1^{\infty}}{RT} dP\right\}}}$$

So, now for component 2 also, we can write it because we know SdT − Vdp + $\sum n_i d\mu_i$ = 0 from the Gibbs-Duhem equation. From here what we can write $\sum x_i d\mu_i$= 0 if you wanted to write in terms of mole fractions. So, that means following these conditions for both the components if you write, for the first component whatever we have written that one if you make use with this relation and then do some kind of simplification. So then for the second component you will get it as $f_2^L$is nothing but x$_2$ $P_2^S\phi_2^S$ exp$\left[\int_{P_2^S}^{P} \frac{v_2^L}{RT} dP\right]$.

But now, x$_2$ is very small because you know whatever the liquid phase is there in that one the solubility of gas is very small that is what we are taking. So, then that is the reason we are taking 1 minus x$_1$ here. So, that is f_2^L is equal to, so that following this relation $\sum x_i d\mu_i$= 0, then in this relation if you make use of f_i^L information and then obtain f_2^L then we will have this expression f_2^L = (1 − x$_1$) P_2^S ϕ_2^S exp$\left[\int_{P_2^S}^{P} \frac{v_2^L}{RT} dP\right]$, right? So, now only unknown things were you know f_1^L, f_2^L.

So those information we got by taking Henry's law as a kind of reference state. Then remaining calculations should be straightforward. Here in this equation P_2^S is nothing but the saturation pressure, ϕ_2^S is nothing but fugacity coefficient at saturation pressure, v_2^L is nothing but molar volume of component 2. Then we have f_2^L = f_2^v and then f_2^v is nothing but ϕ_2 y$_2$ P. So, from here if you equate these two, then you get y$_2$ =$\frac{f_2^L}{\phi_2 P}$ as I mentioned already.

So then this f_2^L is nothing but $(1 - x_1)$ P_2^S ϕ_2^S $\exp\left[\int_{P_2^S}^{P} \frac{v_2^L}{RT} dP\right]$, this way anyway just now we derived. So, y_2 is known. If you know what is ϕ_2^S, if you know what is ϕ_2, if you know v_2^L and then P_2^S and then x_1, so what you can say that how much liquid is dissolved in compressed gas or the mole fraction of heavier liquid solute component in gaseous phase that you can find out from this expression. But what is x_1, x_1 is nothing but how much this lighter gaseous component that is present in the liquid phase.

Because now gas is also dissolving in the liquid phase, not only liquid is dissolving in gas, gas is also dissolving in the liquid phase, okay? So that x_1 is nothing but how much that lighter gaseous component that is present in the liquid phase that we do not know even if you know ϕ_2, ϕ_2^S. So, that if you wanted to know you have to do this one $f_1^L = f_1^v$ and then f_1^v is nothing but y_1 ϕ_1 P. So, now from these 2 relations, you can write because f_1^L you have already written as H_{12} x_1 exponential of integral $\bar{v}_1$ infinity by RT dP, this you have already derived in the previous slide.

So, $x_1 = \frac{y_1 \phi_1 P}{H_{1,2} \exp\left[\int_{P_2^S}^{P} \frac{\bar{v}_1^{\infty}}{RT} dP\right]}$, right? So, now this equation if you wanted to find out y_2, you need to know what is x_1, right? In order to know x_1, you need to know y_1 that means y_2 you need to know. So, these are interrelated. So, these equations we cannot solve without having a kind of trial and error approach. Because of this reason in addition, we may not know this ϕ_2 also, ϕ_1, ϕ_2, etc. This ϕ_1 here and then this ϕ_2 here, this may also we may not know.

It may be stated simply Van der Waal's equation of state is applicable or virial equation of state is applicable, right? Then again we have to find out, use appropriate ϕ_1, ϕ_2 as per the equation of state and then we know this ϕ_1, ϕ_2 are also a function of composition y_1, y_2. So, again interconnection is there. So, that is the reason because of these so many interconnections, you cannot solve these two values which are required explicitly, x_1 and y_2 we wanted to find out.

The y_2 is nothing but how much liquid is dissolved into the gas phase or otherwise what is the mole fraction of the heavier liquid component in the gaseous phase is y_2 that we wanted to know and then x_1 because the lighter gaseous phase is also dissolving into the heavier liquid phase. So that how much a lighter gaseous component present in the liquid phase that is x_1 that also we wanted to know. So, these are interrelated because of these things, right? So, because of these things we have to do a trial and error approach, how to start with?

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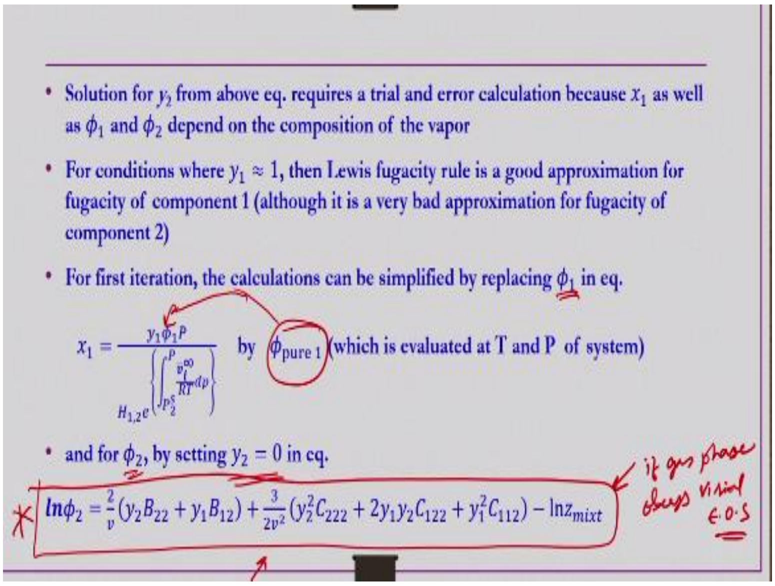

- Solution for y_2 from above eq. requires a trial and error calculation because x_1 as well as ϕ_1 and ϕ_2 depend on the composition of the vapor
- For conditions where $y_1 \approx 1$, then Lewis fugacity rule is a good approximation for fugacity of component 1 (although it is a very bad approximation for fugacity of component 2)
- For first iteration, the calculations can be simplified by replacing ϕ_1 in eq.

$$x_1 = \frac{y_1 \phi_1 P}{H_{1,2} e^{\left\{\int_{P_2^s}^{P} \frac{\bar{v}_1^\infty}{RT} dp\right\}}}$$ by $\phi_{\text{pure 1}}$ (which is evaluated at T and P of system)

- and for ϕ_2, by setting $y_2 = 0$ in eq.

$$\ln\phi_2 = \frac{2}{v}(y_2 B_{22} + y_1 B_{12}) + \frac{3}{2v^2}(y_2^2 C_{222} + 2y_1 y_2 C_{122} + y_1^2 C_{112}) - \ln z_{mixt}$$

if gas phase obeys virial E.O.S

Solution for y2 from above equation requires a trial and error calculation because x_1 as well as ϕ_1, ϕ_2 depend on the composition of the vapor that is y_2, ϕ_1, ϕ_2 as well as x_1 also depends on this y_2 as we have seen in the previous slide, okay? x_1 is nothing but y_1 ϕ_1 P and then y_1 is nothing but $1 - y_2$. So, y_2 is required for all these 3 calculations. So, how to start? We can take like y_1 is approximately 1 then Lewis fugacity rule is a good approximation for fugacity component 1 but for component 2 it is not going to be kind of appropriate approximation.

So, you how to do kind of trial and error iterations, how to start? For the first iteration, what you do? In the calculation where we are finding out this way y_2 what you do you? You replace in the calculation where you have to find out x_1 you replace this $\frac{\phi_1}{\phi_{pure\ 1}}$, right? Because $\phi_{\text{pure 1}}$ you can easily calculate, there is no difficulty. It is not dependent on the composition, it is only dependent on the constants of the equations of state and then temperature and pressure.

So, that you can find out and then you can use as a kind of first assumption here and then find out what is x_1, right? Then for finding ϕ_2 what you have to do? You substitute $y_2 = 0$ and then let us say vapor phase is obeyed by the virial equation of state. Then ϕ_2, you have this expression. This if gas phase or the compressed vapor phase obeys virial equation of state, then only you can use this expression for the ln ϕ_2, right? Otherwise if the gas phase obeys the Van der Waal's equation of state, then you have to use the appropriate ln ϕ_2 expression that we have previously derived.

So, let us start with this. Let us take this one as a kind of exercise and then we take virial equation of state, so in this equation if you need to know ϕ_2 also. If you wanted to know ϕ_2 you do not know, unless you do not know ϕ_2 you cannot know y_2 and then unless you do not know y_2 you cannot calculate ϕ_2 because ϕ_2 is dependent on the composition. So, as a first trial what you do? You take $y_2 = 0$ in this expression and then $y_1 = 1$. So, whatever the ϕ_2 that comes out that you take as a kind of first approximation or the first iteration value and then like that you have to continue, okay?

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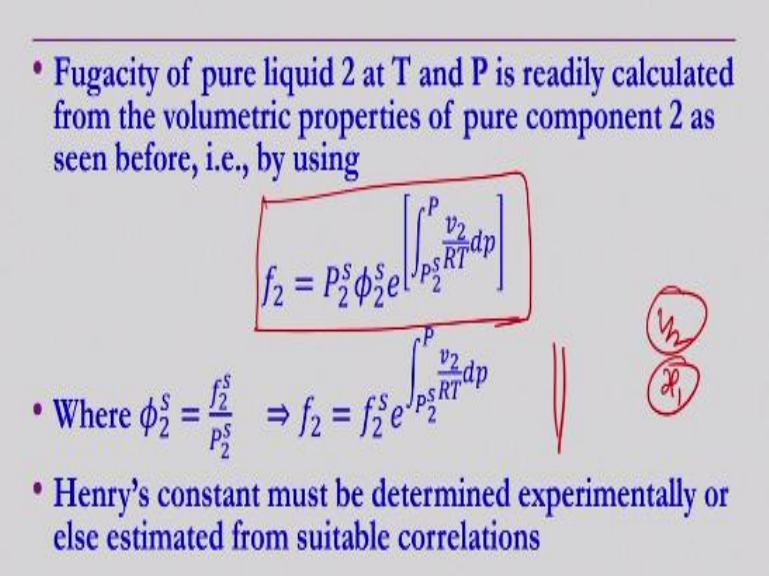

- Fugacity of pure liquid 2 at T and P is readily calculated from the volumetric properties of pure component 2 as seen before, i.e., by using

$$\boxed{f_2 = P_2^S \phi_2^S e^{\left[\int_{P_2^S}^{P} \frac{v_2}{RT} dp\right]}}$$

y_2

x_1

- Where $\phi_2^S = \frac{f_2^S}{P_2^S}$ $\Rightarrow f_2 = f_2^S e^{\int_{P_2^S}^{P} \frac{v_2}{RT} dp}$
- Henry's constant must be determined experimentally or else estimated from suitable correlations

Then fugacity of pure liquid 2 at T and P is readily calculated from volumetric properties of pure component 2 as seen before that is by using this $f_2 = P_2^S\ \phi_2^S \exp\left[\int_{P_2^S}^{P} \frac{v_2}{RT} dP\right]$, this is already we know. ϕ_2^S here in this equation is nothing but $\frac{f_2^S}{P_2^S}$. So, $f_2 = f_2^S \exp\left[\int_{P_2^S}^{P} \frac{v_2}{RT} dP\right]$, okay? These are the kind of suggestive kind of steps to start with which should be a kind of first iteration value, rather starting blindly this will give you what should be a kind of appropriate first iteration value that is the only purpose of these two slides.

Otherwise, those previous equations whatever the y_2 and then x_2 equations that we have derived if you are numerically solving, so then you can solve with any initial guesses and then you can get the solutions, but under such conditions computational iterations may also increase. Henry's constant must be determined experimentally or else estimated from a suitable correlation for a given system obviously because that is also one of the parameter. Without that one, you cannot solve the problems.

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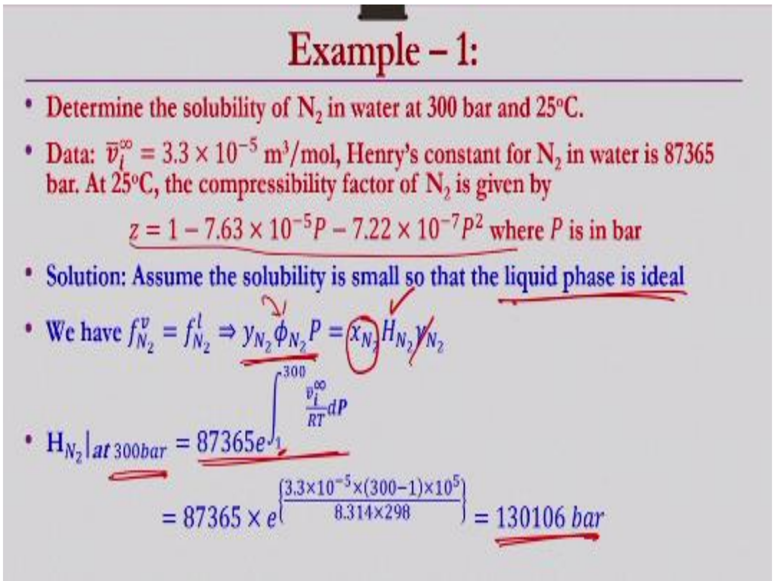

Example – 1:

- Determine the solubility of N_2 in water at 300 bar and 25°C.
- Data: $\bar{v}_i^{\infty} = 3.3 \times 10^{-5}$ m³/mol, Henry's constant for N_2 in water is 87365 bar. At 25°C, the compressibility factor of N_2 is given by

$$z = 1 - 7.63 \times 10^{-5} P - 7.22 \times 10^{-7} P^2 \text{ where } P \text{ is in bar}$$

- Solution: Assume the solubility is small so that the liquid phase is ideal
- We have $f_{N_2}^{v} = f_{N_2}^{l} \Rightarrow y_{N_2} \phi_{N_2} P = \boxed{x_N} H_{N_2} \cancel{\gamma_{N_2}}$
- $H_{N_2}|_{at\,300bar} = 87365 e^{\int_1^{300} \frac{\bar{v}_i^{\infty}}{RT} dP}$

$$= 87365 \times e^{\left\{\frac{3.3 \times 10^{-5} \times (300-1) \times 10^5}{8.314 \times 298}\right\}} = 130106 \; bar$$

So, now we see a few example problems, start with a simple example problem. Determine the solubility of N_2 in water at 300 bar and 25 °C, okay? So, data is given that $\bar{v}_i^{\infty}$ is given, Henry's constant for N_2 in water is given that is 87365 bar at 25 °C the compressibility factor of N_2 is also given. So, here the solubility of N_2 in water we have to find out. It is not mentioned that water is also dissolving in N_2. So, that means transfer is only in one directional transfer, okay?

So, the compressibility factor for N is also given by z = $1 - 7.63 \times 10^{-5} P - 7.22 \times 10^{-7} P^2$, fine. So, now assume the solubility is small so that the liquid phase is ideal, it is not given but you can assume it is an ideal behavior. It is kind of ideal, actually liquid phase can have a non-ideality when there is a kind of foreign element is mixed with the pure liquid then only whatever the possible non-ideality is there that will come into the picture, right? If the liquid is pure phase, then there will not be any kind of non-ideality.

Pure liquid will always be a kind of ideal liquid because all of the interactions are ii interaction, same interactions. In the ideal gas we say no interactions, in the ideal liquid we say semi interactions, equal interactions, both magnitude wise, qualitative, quantitative wise also. So, we have this equal fugacity f_{N_2} in vapor phase should be equals to f_{N_2} in the liquid phase. The f_{N_2} in the vapor or gas phase is nothing but y_{N_2} ϕ_{N_2}P and then f_{N_2} in the liquid phase if you take the Henry's law as a kind of reference state that should be x_{N_2} H_{N_2} Γ_{N_2}.

The liquid phase we are taking ideal phase, so Γ_{N_2} = 1. What we need to find out, solubility of N_2 in water that means x_{N_2} we have to find out. Water is liquid phase, in the liquid phase what is the N_2 is there, that x_{N_2} we have to find out. So, for this purpose H_{N_2} it is given at 1 bar atmospheric pressure it is given but at 300 bar, we have to have a kind of correction, that correction is nothing but H_{12} or $H_{N_2}\exp\left[\int_1^{300}\frac{\bar{v}_i^{\infty}}{RT}dP\right]$.

When you do it, you will get H_{N_2} at 300 bar is nothing but 130106 bar, so H_{N_2} is known, right? ϕ_{N_2} you can know if z is known because ln ϕ_i is nothing but $\int_0^P\frac{z-1}{P}$ dP that we have derived previously, okay?

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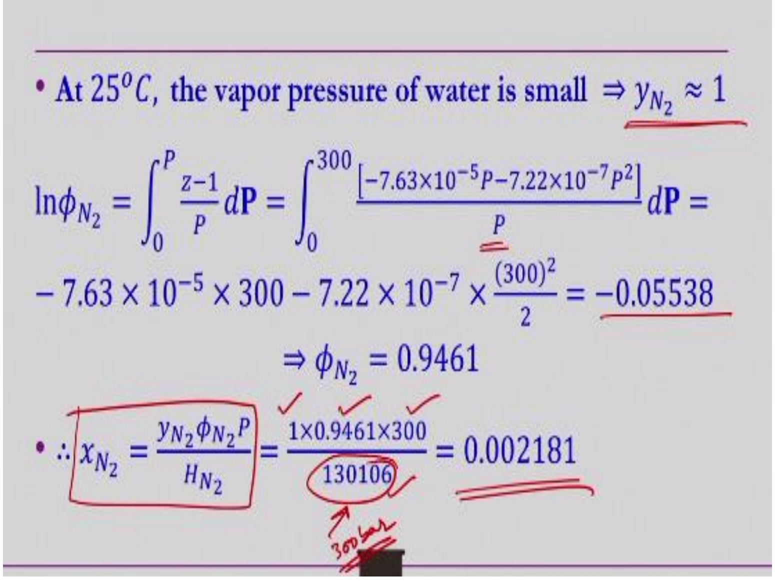

- At 25^oC, the vapor pressure of water is small $\Rightarrow \underline{y_{N_2} \approx 1}$

$$\ln\phi_{N_2} = \int_0^P \frac{z-1}{P}dP = \int_0^{300}\frac{[-7.63\times10^{-5}P - 7.22\times10^{-7}P^2]}{\underline{P}}dP =$$

$$-7.63\times10^{-5}\times300 - 7.22\times10^{-7}\times\frac{(300)^2}{2} = \underline{-0.05538}$$

$$\Rightarrow \phi_{N_2} = 0.9461$$

- $\therefore \boxed{x_{N_2} = \frac{y_{N_2}\phi_{N_2}P}{H_{N_2}}} = \frac{1\times0.9461\times300}{130106} = \underline{\underline{0.002181}}$

300 bar

So the vapor pressure of water is small at 25 °C, so then we can take that y_{N_2} is almost pure, by the problem also we are taking that N_2 is dissolving in water, but water is not dissolving in N_2, so then N_2 is going to be remaining pure. So, then a small fraction is going to be 1 closely, okay? Then from compressibility factor ln ϕ_{N_2} we can write $\int_0^P\frac{z-1}{P}$ dP, P is given, z is given, so $\frac{z-1}{P}$ we are doing and then after integration we are substituting limits 0 to 300.

Then ln ϕ_{N_2} we get 0.0553 that means ϕ_{N_2} is going to be 0.9461. So, ϕ_{N_2} is also known, y_{N_2} is also known and then H_{N_2} is also obtained, so then x_{N_2} you can find it out as $\frac{y_{N_2}\phi_{N_2}\text{P}}{H_{N_2}}$, y_{N_2} is 1, ϕ_{N_2} is 0.9461, P is at 300 bars and the H_{N_2} at 300 bars is 130106, it should not be at 1, it is at the conditions at which we are measuring solubility. We are measuring solubility of N_2 in water at 300 bar, so the adjustment correction because pressure corrected Henry's law constant we have to use here that is this one.

So, x_{N_2} comes out to be 0.002181. So a small amount of N_2 is dissolving in water even though the pressure is 300 bars, okay?

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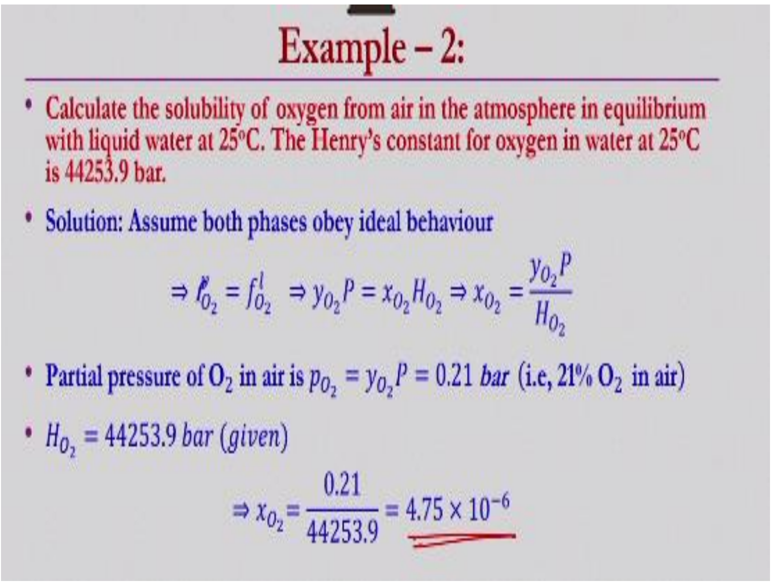

Example – 2:

- Calculate the solubility of oxygen from air in the atmosphere in equilibrium with liquid water at 25°C. The Henry's constant for oxygen in water at 25°C is 44253.9 bar.
- Solution: Assume both phases obey ideal behaviour

$$\Rightarrow f^{v}_{O_2} = f^{l}_{O_2} \Rightarrow y_{O_2}P = x_{O_2}H_{O_2} \Rightarrow x_{O_2} = \frac{y_{O_2}P}{H_{O_2}}$$

- Partial pressure of O_2 in air is $p_{O_2} = y_{O_2}P = 0.21\ bar$ (i.e, 21% O_2 in air)
- $H_{O_2} = 44253.9\ bar\ (given)$

$$\Rightarrow x_{O_2} = \frac{0.21}{44253.9} = 4.75 \times 10^{-6}$$

Now we take another example problem, much simpler one. Calculate the solubility of oxygen from air in the atmosphere in equilibrium with the liquid water at 25 °C. They Henry’s constant for oxygen and water at 25 °C is given. So, assume that both phases ideal behavior because non-ideal behavior equation of state, etc., are not given and especially for the liquid phase non-ideality we have not started working it, okay? So, we are assuming both phases obey ideal behavior.

So, then $f^{v}_{O_2}$should be equals to $f^{l}_{O_2}$and $f^{v}_{O_2}$ is nothing y_{O_2} P and then ϕ_{O_2} is 1 ideal behavior and then $f^{l}_{O_2}$ is nothing but $x_{O_2}H_{O_2}\ \Gamma_{O_2}$, Γ_{O_2} is 1 because idea liquid. So, here what we have to find out? Solubility of oxygen from air in the atmosphere in equilibrium with the liquid water. So, in the liquid water what is the oxygen that is present at these conditions? So, liquid phase, so x we should be using, so x_{O_2} we have to find out. So, x_{O_2} should be $\frac{y_{O_2}\mathrm{P}}{H_{O_2}}$.

$H_{O_2}$is given but $y_{O_2}$is nothing but partial pressure of O_2 and then partial pressure of O_2 in air is nothing but 0.21 bars because 21 % of O_2 is present in the air that is known to everyone. So, we simply substitute, x_{O_2} is nothing but 0.21 divided by the Henry's law constant that is 44253.9. So, x_{O_2} is comes out to be 4.75 * 10^{-6} such small value, okay?

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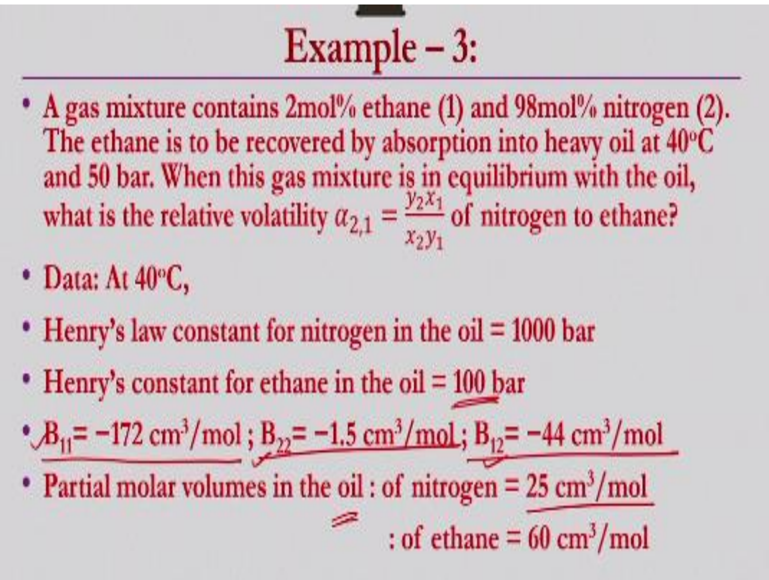

Example – 3:

- A gas mixture contains 2mol% ethane (1) and 98mol% nitrogen (2). The ethane is to be recovered by absorption into heavy oil at 40°C and 50 bar. When this gas mixture is in equilibrium with the oil, what is the relative volatility $\alpha_{2,1} = \frac{y_2 x_1}{x_2 y_1}$ of nitrogen to ethane?
- Data: At 40°C,
- Henry's law constant for nitrogen in the oil = 1000 bar
- Henry's constant for ethane in the oil = 100 bar
- B_{11}= −172 cm^3/mol ; B_{22}= −1.5 cm^3/mol; B_{12}= −44 cm^3/mol
- Partial molar volumes in the oil : of nitrogen = 25 cm^3/mol

  : of ethane = 60 cm^3/mol

Now, we take another example, we take some engineering application problem now. A gas mixture contains 2 mole % of ethane designated as component 1 and 98 mole % of nitrogen designated as component 2. The ethane is to be recovered by absorption into heavy oil at 40 °C and 50 bar. This makes ethane you wanted to extract or separate out, though it is 2 % it is not good, so you wanted to remove it. So, what you are trying to do? You are trying to absorb it into a heavy oil at 40 °C and 50 bar.

So, it is absorption. You have a gaseous mixture, out of that gaseous mixture, one particular gas you are absorbing in a heavy liquid, okay? When this gas mixture is in equilibrium with the oil, what is the relative volatility of nitrogen to ethane? So, because absorption, etc., these kind of problems, we can understand how much would be this performance or how good it is going to be separation that you can find out by relative volatility. If the relative volatility is large, so then you can say qualitatively the separation is going to be effective.

So, the fugacity calculation whatever we have been doing till now using that information, can we get this information of relative volatility or not? That is the purpose of this problem, okay? So, data, a lot of data is required to solve this problem. So, at 40 °C, Henry's law constant for nitrogen in the oil is there. So, because out of this nitrogen-ethane, we are trying to absorb ethane, but nitrogen may also be soluble. So, then solubility of that nitrogen in oil is described by the Henry's law.

Then Henry's law constant for nitrogen the solubility in the oil is 1000 bar, so very difficult to dissolve. Henry's constant for ethane in the oil is only 100 bar, so that means ethane can be relatively easily dissolved in oil compared to the nitrogen because the Henry’s constant is here only just 100 bars, okay? It is not mentioned in the problem but this vapor phase whatever are there gas phase that is obeyed by the virial equation of state.

So, second video coefficient for the pure component 1, pure component 2, and then cross virial coefficient B_{12} are provided here. Also partial molar volumes of this component nitrogen and ethane in oil also given, for the nitrogen it is 25 cc per mole, for the ethane it is 60 cc per mole.

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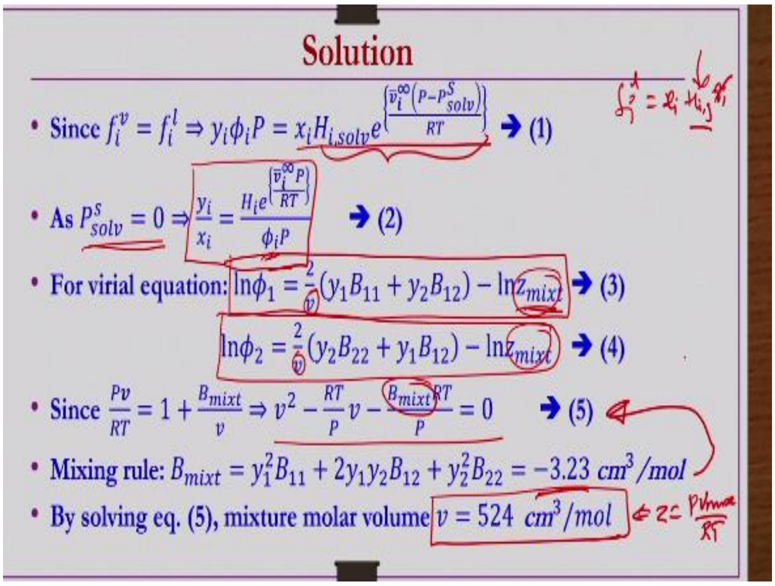

Solution

- Since $f_i^v = f_i^l \Rightarrow y_i\phi_i P = \underbrace{x_i H_{i,solv} e^{\left\{\frac{\bar{v}_i^\infty (P-P_{solv}^S)}{RT}\right\}}}$ → (1) $f_i^l = x_i H_{i,j} \gamma_i$
- As $P_{solv}^S = 0 \Rightarrow \boxed{\frac{y_i}{x_i} = \frac{H_i e^{\left\{\frac{\bar{v}_i^\infty P}{RT}\right\}}}{\phi_i P}}$ → (2)
- For virial equation: $\boxed{\ln\phi_1 = \frac{2}{v}(y_1 B_{11} + y_2 B_{12}) - \ln z_{mixt}}$ → (3)

  $\boxed{\ln\phi_2 = \frac{2}{v}(y_2 B_{22} + y_1 B_{12}) - \ln z_{mixt}}$ → (4)
- Since $\frac{Pv}{RT} = 1 + \frac{B_{mixt}}{v} \Rightarrow v^2 - \frac{RT}{P}v - \frac{B_{mixt}RT}{P} = 0$ → (5)
- Mixing rule: $B_{mixt} = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} = -3.23\ cm^3/mol$
- By solving eq. (5), mixture molar volume $\boxed{v = 524\ cm^3/mol}$ $\leftarrow z = \frac{Pv_{mix}}{RT}$

So, what we have to find out? We have to find out α_{21} that is $\alpha = \frac{y_2/x_2}{y_1/x_1}$. So, you have to find out what is y_2/x_2, you have to find out what is y_1/x_1, right? Now, this problem can be taken as a kind of first case where you know only solid is dissolving in gas, okay? That way we can read because now here it is not mentioned that though the condensed phase is here the liquid it is not mentioned that liquid is dissolving into the gas and then no additional information is given even if it is dissolving.

So in order to calculate how much is dissolved that one, that information is not given. So, that way we are a bit safe that transfer is one direction. So, $f_i^v = f_i^l$. So, f_i^v is nothing but y_i ϕ_i P_i^S equal to and then f_i^l is nothing but x_i $H_{i,solv}$, e or the exp $\left[\frac{\bar{v}_i^\infty (P-P_{solvent}^S)}{RT}\right]$, this is what we have.

This we are having because f_i^l we are using f_i^l = x_i H_i^l or H_{ij} Γ_i, this is what we are using, right? So, now here whatever the non-ideality, etc., in the liquid phase is there that we are not taking and then H_{ij} we are taking.

Then H_{ij} we are taking at the high pressure, so the pressure corrected Henry's constant should be there that is H exp $\left[\frac{\overline{v}_i^{\infty}}{RT}\right]$ dP under integration. So,exp$\int \left[\frac{\overline{v}_i^{\infty}}{RT}\right]$ dP, this is nothing but this one, okay? So, this is how this second part for the liquid part is coming in Γ_i^l we are taking as 1, we are not taking any non-ideality in the liquid phase because we have not done anything about the non-ideality of the liquid phase till now that we are going to start from the next lecture anyway, okay?

So, but these problems are more suitable related to the fugacity of gaseous phase or fugacity of gaseous phase in high pressure conditions etc., right? So, now $P_{solvent}$ is in general very small, okay? So, then what we have from this expression if you take $P_{solvent}$ is also as a kind of 0, right? It is not given, even if it is given in general compared to the P that is we are operating at high pressure compared to that one, saturation pressure of pure solvents in general are very small, so that way also $P_{solvent}$ can be neglected.

Under such conditions, we can write this equation as $\frac{y_i}{x_i}$ = $\frac{H_i e^{\left\{\frac{\overline{v}_i^{\infty} P}{RT}\right\}}}{\phi_i P}$, right? So, now $\frac{y_1}{x_1}$ if you wanted to do, then you have to get $H_{12} e^{\left\{\frac{\overline{v}_1^{\infty} P}{RT}\right\}}$ and then ϕ_1 P. So, ϕ_1 P you have to find out because H_1 is anyway given. So H_1 in oil, H_2 in oil is anyway given, so that you can find out, only thing that you are to find out ϕ_1, ϕ_2, right? Then virial equation of state is mentioned that for the vapor phase, virial equation of status applicable that is indirectly mentioned by giving this virial coefficient.

So, then ln ϕ_1 for virial equation of state we can say that $\frac{2}{v}(y_1 B_{11} + y_2 B_{12}) -$ ln z_{mixt}. So, B_{11} is given, B_{12} is given, right? So, but z_{mixt} also you have to find out. Similarly, ln ϕ_2 also, this also we have derived, ln ϕ_2 = $\frac{2}{v}(y_2 B_{22} + y_1 B_{12}) -$ ln z_{mixt}, right? So, but we know $\frac{Pv}{RT}$ = 1 +$\frac{B_{mixt}}{v}$ that is virial equation of state. So, if you expand this equation, then you have $\frac{v^2}{RT} - \frac{RT}{P} v - \frac{B_{mixt} RT}{P}$. So, if you wanted to calculate ϕ_1, ϕ_2, you also need to know v and then z_{mixt}.

So, here now from this equation number 5, if you know B_{mixt}, then roots of this equation you can find out and then you can find out v because R, T, P also known. So, B_{mixt} you can find out by the mixing rule. $B_{mixt} = y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{22}$. So, then we get minus 3.23 cc per mole. So, now this you substitute here in equation 5, then solve this equation 5, then you get reliable root v as 524 cc per mole. So, once v is known, so then you can find out $\frac{Pv_{mixt}}{RT}$ as a kind of z, so z_{mixt} is also known.

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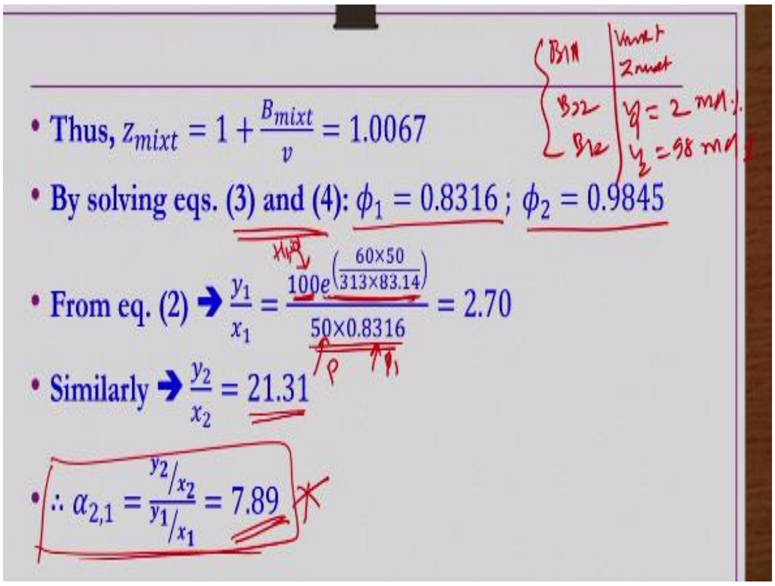

B_{11}, B_{22}, B_{12} | v_{mixt}, z_{mixt}, $y_1 = 2$ mol%, $y_2 = 98$ mol%

- Thus, $z_{mixt} = 1 + \frac{B_{mixt}}{v} = 1.0067$
- By solving eqs. (3) and (4): $\phi_1 = 0.8316$; $\phi_2 = 0.9845$
- From eq. (2) ➔ $\frac{y_1}{x_1} = \frac{100e^{\left(\frac{60\times50}{313\times83.14}\right)}}{50\times0.8316} = 2.70$ (P, ϕ_1)
- Similarly ➔ $\frac{y_2}{x_2} = 21.31$
- $\therefore \alpha_{2,1} = \frac{y_2/x_2}{y_1/x_1} = 7.89$

So, this equation 3 and 4 you can solve. You can solve equation 3 and 4, so then ϕ_1 you will get 0.8316, ϕ_2 you get 0.9849 because y_1 is given as 2 mole % that is 0.02, y_2 is given us 98 mole % that is 0.98 is given and then this v_{mixt} we have already found and then z_{mixt} we have already found and then B_{11}, B_{22}, B_{12} are given. So, equation number 3 and 4 where ln ϕ_1, ln ϕ_2 relations are given. Right hand side everything is known from here.

So, all those things if you substitute and simplify, you will get ϕ_1 and ϕ_2 as 0.8316 and 0.9845 respectively. So, then $\frac{y_1}{x_1}$ you will get 100, H_1 in oil, okay, at normal 1 bar condition. So that is 100 bar is given and then but the pressure for conditions are solubility or absorption of this component in oil we are doing at high pressures. So then that corresponding high pressure correction should be coming into the picture that is $\exp\int \frac{\bar{v}_i^{\infty}}{RT}$ dP, so that is this part and then divided by this one is you know the ϕ_1 P, this is nothing but ϕ_1, this is nothing but P and this is nothing but H_1 in oil, okay?

This is coming from this equation number 2, this equation we are solving, okay? That is what, okay? Similarly, if you do $\frac{y_2}{x_2}$, then you get $\frac{y_2}{x_2}$ as 21.31. So, α_{21} is nothing but $\frac{y_2/x_2}{y_1/x_1}$ will come as 7.89. So, relative volatility is signal significantly large, so then we can say the ethane can be easily absorbed into heavy oil compared to the nitrogen, okay? Indeed, that is also qualitatively clear from the Henry's law constant. Henry’s law constant for ethane in oil is only 100 bar, but Henry's law constant for nitrogen in heavy oil is 1000 bar.

So, so nitrogen is going to be dissolved very difficult in heavy oil compared to the ethane. So that means ethane can be easily absorbed into the oil by taking out from the mixture of ethane and nitrogen, okay? So, now we see this fugacity rule, these thermodynamic principles whatever the non-ideality of the system, etc., in terms of fugacity activity coefficient that we are studying. They are also good enough to solve few mass transfer problems also without any difficulty, such are the importance of this particular course Advanced Thermodynamics, right? This is one of the examples, we can have a number of problems like that.

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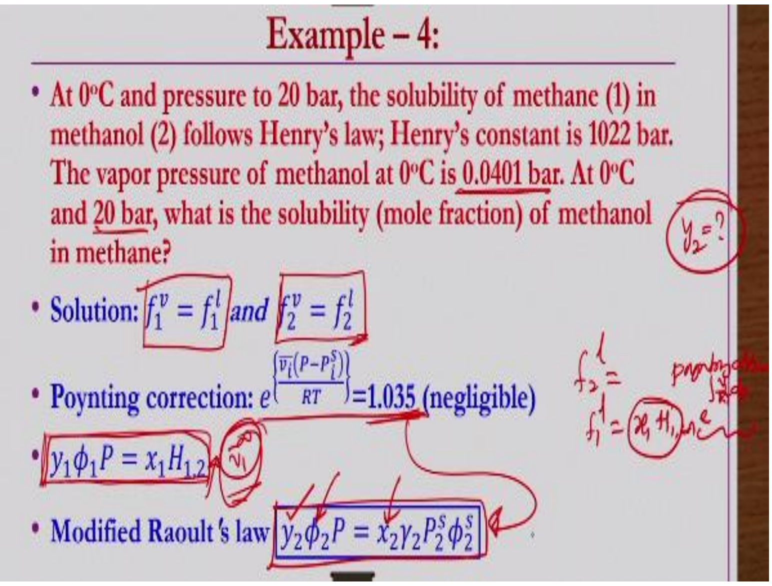

Example – 4:

- At 0°C and pressure to 20 bar, the solubility of methane (1) in methanol (2) follows Henry’s law; Henry’s constant is 1022 bar. The vapor pressure of methanol at 0°C is 0.0401 bar. At 0°C and 20 bar, what is the solubility (mole fraction) of methanol in methane?
- Solution: $\boxed{f_1^v = f_1^l}$ and $\boxed{f_2^v = f_2^l}$
- Poynting correction: $e^{\left\{\frac{\overline{v_i}(P-P_i^S)}{RT}\right\}}$=1.035 (negligible)
- $\boxed{y_1\phi_1 P = x_1 H_{1,2}}$
- Modified Raoult 's law $\boxed{y_2\phi_2 P = x_2\gamma_2 P_2^S \phi_2^S}$

$y_2 = ?$

$f_2^l =$

$f_1^l = x_1 H_1$

Now, last example problem we take. Here at 0 ℃ and pressure up to 20 bar, the solubility of methane in methanol follows Henry's law and Henry’s constant is given as 1022 bar. The vapor pressure of methanol at 0 ℃ is only 0.0401 bar. At 0 ℃ and 20 bar, what is the solubility, mole fraction methanol in methane, so that is y_2, right? Methane, that is now this problem is something related to what we have seen with solubility of a liquid in compressed gas.

So, there the gas and liquid both are transferring into each other that case we are solving and then it has to be done by trial and error approach as we are discussing because in order to find out y_2 you need to know x_1, ϕ_1, ϕ_2 and then ϕ_1 and ϕ_2 are again functions of y_2 and then x_1 is again function of composition y_1, so this is a trial and error approach. So, the purpose is here to find out y_2, okay? So we have $f_1^v = f_1^l$ and $f_2^v = f_2^l$. So, now here we have to solve this equation, we have to expand this equation and solve, and then we have to expand this equation and then solve this one as well, okay?

So, for the liquid phase you know here f_2^l in this term when we are doing if you remember, we have a Poynting correction also into the picture, but now this Poynting correction it is very small that is what we are finding it here, okay, right? So, that is for that purpose this Poynting correction we have separately written. So, for the first component this f_1^l is nothing but x_1 $H_{1,\text{solvent}}$ exp $\int \frac{\bar{v}_1^{\infty}}{RT} dP$. So, this part is also going to be very small because this is we are doing not very high pressures.

Then we found that this exponential is also going to be very small, so we can take only up to x_1 and H_1, this part only we can take for f_1^l and then f_1^v is nothing but y_1 ϕ_1 P and then f_1 is nothing but x_1 $H_{1,2}$. The pressure correction is not required, it is very small because otherwise this molar this whatever the $\bar{v}_1$ infinity is also not given that way also we cannot take that correction factor, either of two reasons we can consider and then neglect that one.

Then for the component here, the right hand side we have here another correction $exp \int_{P_2^s}^{P} \frac{\bar{v}_2}{RT}$ dP. This term is there Poynting correction but that we found very small, so that is also taken off that is also not considered here. Why we are doing such simplification here itself before going into the details of solution because we understand this problem is a kind of trial and error problem, right? y_2 you need to find out, but without ϕ_2 you cannot find out y_2 because ϕ_2 is function of y_2, same is that x_2 also, x_2 is now function of y_2 and all those things all there.

So, because of such relations you know x_2 but that means $1 - x_1$ and then x_1 is related to the y_1 and then y_1 is nothing but $1 - y_2$ these are interrelated as we have seen. So, that is the reason we are going to do a kind of trial and error solution as we have discussed in a few slides before, okay? So, that is the reason in order to reduce the calculation load by taking so many terms, wherever possible we are neglecting those terms that is the only reason and then we are not blindly neglecting those items.

Here, we can see that here this $\bar{v}_1$ infinity is not given, right? And then H_{12} also, pressure corrector is needed only, is up to 20 bars, so that is not far away from 1 bar basic value. So that way also it is not required. So, that is the reason that we have taken and then here in this case anyway exponential this Poynting correction 1.035 is coming, so that also not taken. So, blindly we are not striking off, we are striking off these 2 term logically, just simplifying.

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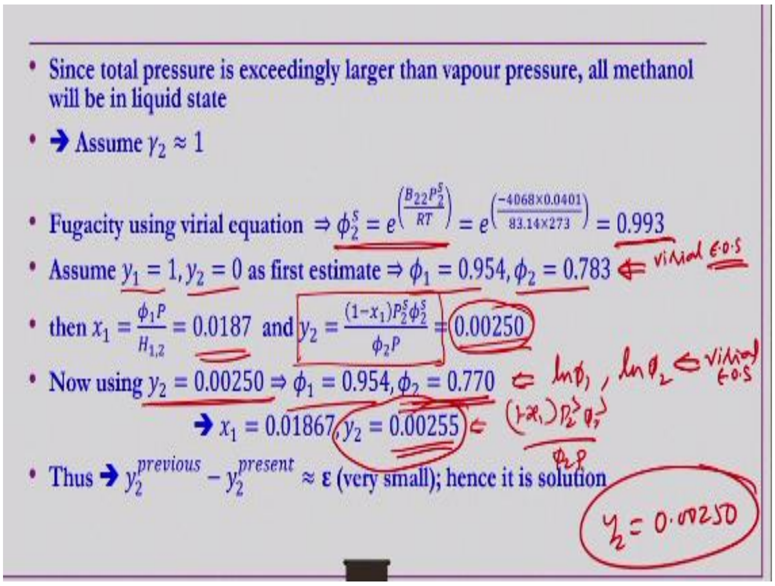

- Since total pressure is exceedingly larger than vapour pressure, all methanol will be in liquid state
- ➔ Assume $\gamma_2 \approx 1$
- Fugacity using virial equation $\Rightarrow \phi_2^S = e^{\left(\frac{B_{22}P_2^S}{RT}\right)} = e^{\left(\frac{-4068\times0.0401}{83.14\times273}\right)} = 0.993$
- Assume $y_1 = 1, y_2 = 0$ as first estimate $\Rightarrow \phi_1 = 0.954, \phi_2 = 0.783 \Leftarrow$ virial E.O.S
- then $x_1 = \frac{\phi_1 P}{H_{1,2}} = 0.0187$ and $\boxed{y_2 = \frac{(1-x_1)P_2^S\phi_2^S}{\phi_2 P}} = 0.00250$
- Now using $y_2 = 0.00250 \Rightarrow \phi_1 = 0.954, \phi_2 = 0.770 \Leftarrow \ln\phi_1, \ln\phi_2 \Leftarrow$ virial E.O.S

  ➔ $x_1 = 0.01867, y_2 = 0.00255 \Leftarrow \frac{(1-x_1)P_2^S\phi_2^S}{\phi_2 P}$
- Thus ➔ $y_2^{previous} - y_2^{present} \approx \varepsilon$ (very small); hence it is solution

$y_2 = 0.00250$

So, total pressure is exceedingly larger than the vapor pressure, all methanol will be in liquid state then you can take $\Gamma_2 = 1$, right? Then ϕ_2^S we have to find out from the virial equation that is nothing but $e^{\left(\frac{B_{22}P_2^S}{RT}\right)}$ that you get 0.993 and then assume $y_1 = 1$, $y_2 = 0$ as the first case. Then find out ϕ_1, ϕ_2 this expression for the virial equation of state whatever ln ϕ_1, ln ϕ_2 expressions are there. Those things you solve by taking $y_1 = 1$ and then $y_2 = 0$ because we do not know.

So, we are starting with this trail, right? So, once we have these things, ϕ_1 is known, so the next one you can find it out by $x_1 = \frac{\phi_1 P}{H_{1,2}}$ by the previous relation, previous slide we have seen that comes out to be 0.0187. Once x_1 is there, so you can correct y_2 from the modified Raoult's law that we have written in the previous slide that is $y_2 = \frac{(1-x_1)P_2^S\phi_2^S}{\phi_2 P}$. So, ϕ_2^S also we calculated. So y_2 it is coming out 0.0025, 0.0025 and then 0.0 is not very far, we cannot say it is a conversed to kind of solution.

It has to be further trialed, one more trial we have to do it. So next trial what we do? We take y_2 as a kind of 0.00250 as a second trial, this is for the second trial. Then again virial equation of state whatever the ln ϕ_1, ln ϕ_2 expressions are there for virial equations of state. So those you solve by using $y_2 = 0.00250$ and then y_1 is nothing but $1 - y_2$. Then you get ϕ_1, ϕ_2 like this. So, once you have this ϕ_1, ϕ_2, then x_1 is nothing but again $\frac{\phi_1 P}{H_{1,2}}$ if you do, ϕ_1 P in the second case is 0.954.

After second iteration, it has not changed much. So you are getting x_1 same value, but in the second trial, ϕ_2 has changed significantly. First trial ϕ_2 is 0.783. Now, second trial ϕ_2 by the second assumptions y_2 is 0.0025 it has come as a 0.770. So, this one if you again you make use here $y_2 = \frac{(1-x_1)P_2^S\phi_2^S}{\phi_2 P}$ you do, then you get 0.00255. So, this value is not far away from the second trial value of 0.0025. So, that means error is very small, so the solution has conversed. So, the solution is nothing but whatever this 0.00250 is the solution. This is how we can solve the problems, right?

Now, we have almost solved everything related to the fugacity, the non-ideality in the vapor phase. Now, next lecture onwards, we will be discussing about the non-ideality in the liquid phase, okay? After that, we go to the phase equilibrium problem solutions.

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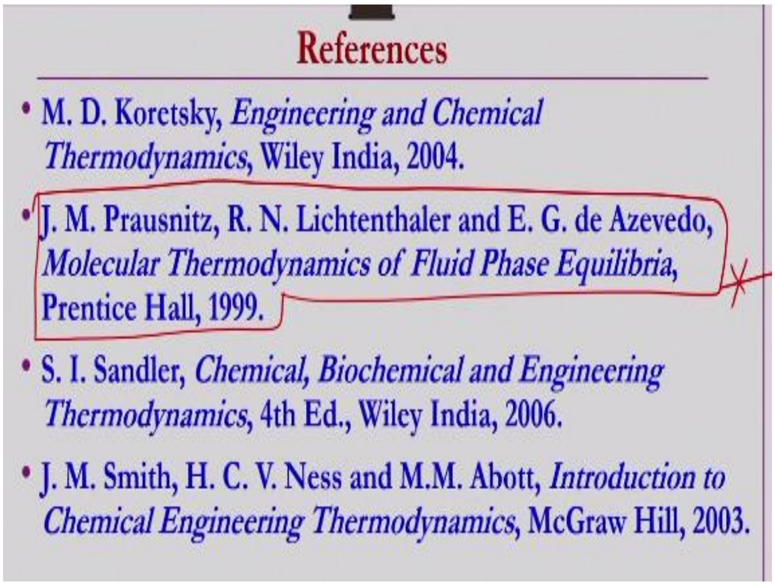

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References are given here, but most of the lecture is prepared from this reference book and then problems discussed in this lecture are kind of exercise problems given in this particular book.

Thank you.