# Chemical Engineering Thermodynamics
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## Lecture 59
## Solubility of gases in the liquid

Welcome back, last few lectures we have looked into vapor liquid equilibria, other concepts of fugacity and subsequently we have looked into the non-ideality in the liquid phase which is we represent in terms of activity. And used simple chemical potential equilibria represented that to fugacity and subsequently represented that to a fugacity coefficient for in the vapor phase and activity coefficient in the liquid phase.

For the liquid phase we consider two possible references one is Henry's law and the other is a Randall Lewis Randall reference which we often used as far as the examples are concerned. We also consider the case of eutectic mixtures. We looked into also the colligative properties however we did not look in to the gas solubility in the liquid phase which probably we should do that before we close this phase equilibria concepts in chemical engineering subject before we move into the reaction chemical reaction equilibria okay. So let me just focus on the solubility part and then we can close and then we can move on to the reaction part.

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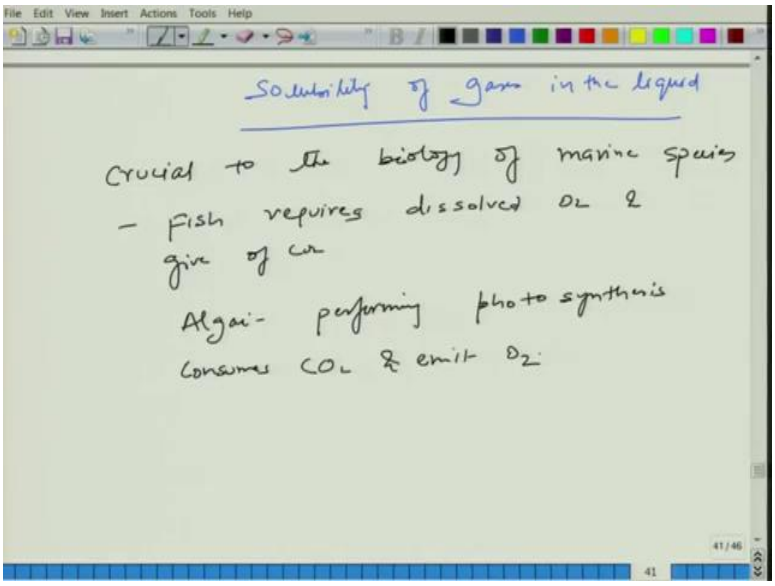
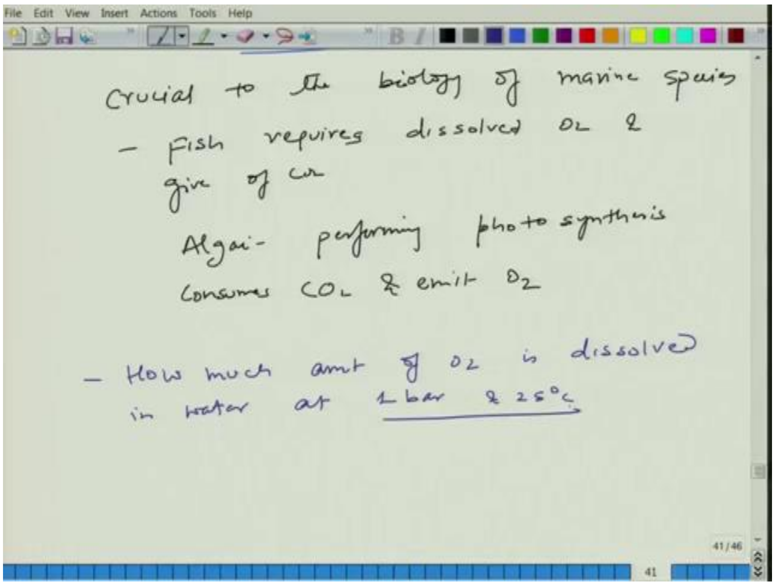


Solubility of gases in the liquid

Crucial to the biology of marine species

- Fish requires dissolved $O_2$ & give of $CO_2$

Algae - performing photosynthesis consumes $CO_2$ & emit $O_2$.

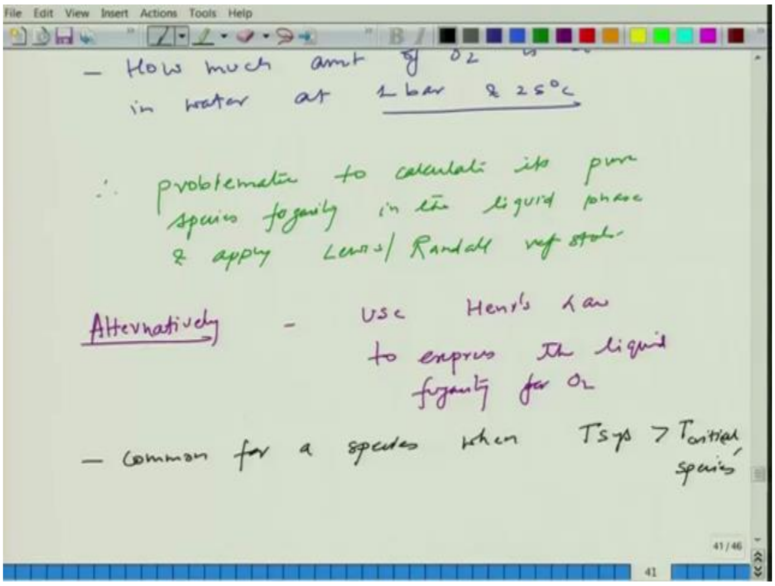


Crucial to the biology of marine species

- Fish requires dissolved $O_2$ & give of $CO_2$

  Algae- performing photosynthesis consumes $CO_2$ & emit $O_2$

- How much amt of $O_2$ is dissolved in water at 1 bar & 25°C



- How much amt of $O_2$ is dissolved in water at 1 bar & 25°C

∴ problematic to calculate its pure species fugacity in the liquid phase & apply Lewis/Randall ref state

Alternatively - use Henry's Law to express the liquid fugacity for $O_2$

- common for a species when $T_{sys} > T_{critical, species}$

Okay, so now this concept of solubility of gases in liquid plays an important role in many things. One of the primary importance are in the biological systems this is crucial okay to the biology of marine species right. So, this obviously you guess that for example, fish requires dissolved O2 okay. That is oxygen and releases and give off CO2 okay which is consumed by the algae. So, algae performing photosynthesis consumes CO2 and emit O2 okay.

So the question is if you would like to ask like what would be the appropriate or rather the amount of oxygen which can be dissolved in, let us say water. And then how do you find such a you know calculation? How do you calculate such a particular you know questions or rather solve such questions? So typical questions in the case of solubility would be let us say how much amount of O2 is dissolved or can be dissolved in water at a given temperature and pressure? Okay, now note that O2 oxygen at these conditions or is in supercritical states, okay.

So that is something which you should know which essentially means that even if you try to apply Randall and Louis it is basically it is not going to work out because this would be extremely small state in a liquid phase and that too it is a gaseous part. So this particular species will not exist in a liquid at that condition. So that is a way the problematic is that this is why it causes issue because oxygen will not be in a liquid state for this. Okay so this is a problematic to calculate its pure species fugacity in the liquid phase. And apply Louis-Randall reference state.

Okay, so at the end of the day if we are talking about the amount which is at equilibrium dissolved or amount of oxygen dissolved in the water at equilibrium which essentially means we can apply the concepts of equality of a chemical potential for sure. And then that can be converted into fugacity but the problem is that if you want to use the fugacity we cannot use Louise Randall reference straight because it is not in the liquid state you know for the particular gas this oxygen molecule.

So alternatively, what we can do is we can apply the Henrys' law okay, to express the liquid fugacity for O2 right. So, we can use this Henry's law and this is this particular approach is a common to the case where your t system that means your temperature of the system is greater than the critical temperature of the species of a species, okay.

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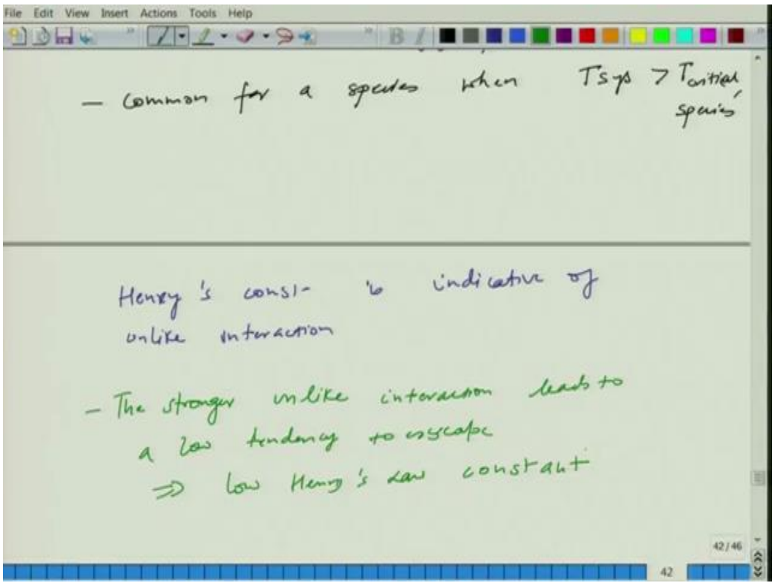

- common for a species when $T_{sys} > T_{critical, species}$

Henry's const. is indicative of unlike interaction

- The stronger unlike interaction leads to a low tendency to escape

$\Rightarrow$ low Henry's law constant

Now Henry's constant which we are going to use H here is indicative of the unlike interactions okay. So now what does it mean is that if the unlike interactions are strong which means the species has a lower tendency to escape and this would yield lower Henry's law constant. So the stronger unlike interaction leads to low tendency to escape. This would mean lower Henry's constant.

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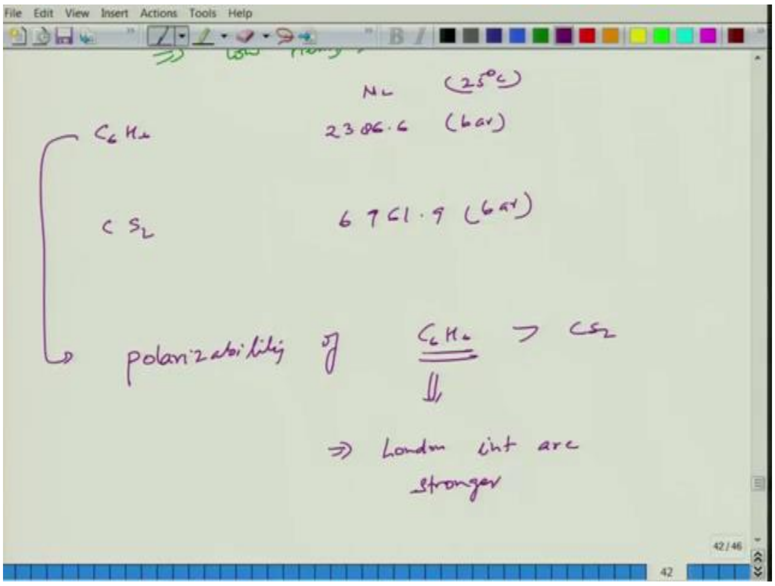

⇒ low

$N_2$ (25°C)

$C_6H_6$ 2386.6 (bar)

$CS_2$ 6961.9 (bar)

polarizability of $C_6H_6 > CS_2$

⇓

⇒ London int are stronger

So take an example this will give you a little bit of an idea. For example, you are talking about let us say and same C6 H6 and this is another solvent let us say CS 2 and we are talking about nitrogen solubility or in this solvent and then the corresponding Henry’s constant is 2386.6 in the units of bar okay at 25 degree Celsius.

And the corresponding Henry’s constant for N2 in CS 2 is 6961.9 bar, okay. Now this is so you can clearly see this has more Henrys constant here which means basically the tendency here the stronger as I said here the stronger unlike interaction is to lower a tendency to escape which indicates a lower Henry's law constant. So clearly this is a higher which essentially means this will be a weaker like interactions.

Now if you want to see this why this would be the case because the polarizablity, so apparently the polarizablity of C6 H6 is greater than CS 2 and essentially polarizablity will give you the indication that if it is a higher that means the disposition interaction or London interactions are going to be stronger which implies that London interaction for the like-like is going to be stronger. And I mean in general it is going to be stronger leading to lower Henrys constant here compared to CS 2.

So CS 2 being a weaker polarizablity will have a weaker unlike interaction and hence your Henrys law constant is more for the case of N2 in CS 2 compared to N2 in C6 H6 okay. So that was about simple understanding the Henrys law constant but this Henrys laws essentially their

H which we use often is related to the infinite dilute condition.

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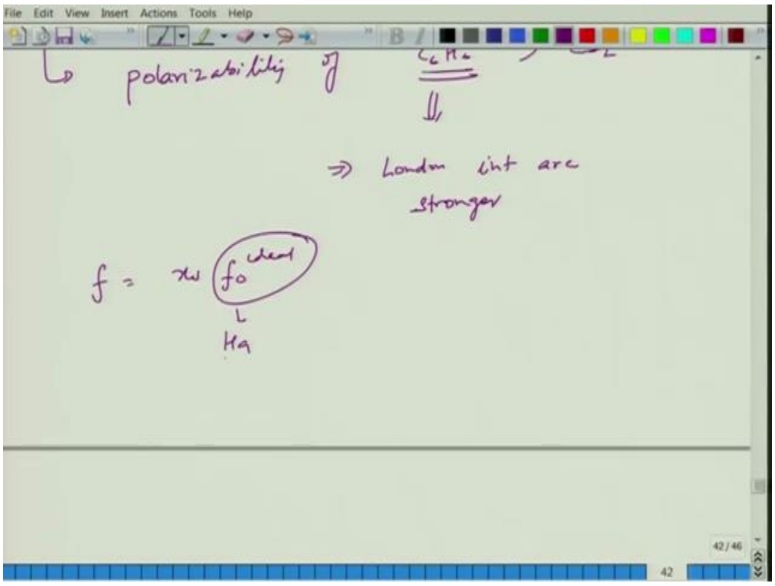

So let me again recall the fact that we have considered f fugacity is proportional to the composition for the case of ideal where we have considered f of 0 and ideal where this essentially could corresponds to Henrys law a or to correspond to the pure fugacity of the liquid phase so that will be your Randall. But in this case, when you have solubility of the gas and liquid as a problem, we use H here.

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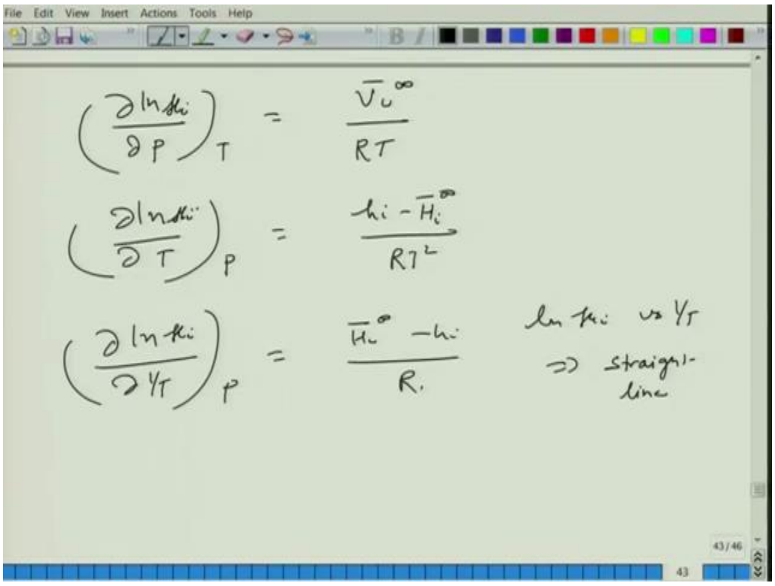

$$\left(\frac{\partial \ln H_i}{\partial P}\right)_T = \frac{\overline{V}_i^{\infty}}{RT}$$

$$\left(\frac{\partial \ln H_i}{\partial T}\right)_P = \frac{h_i - \overline{H}_i^{\infty}}{RT^2}$$

$$\left(\frac{\partial \ln H_i}{\partial 1/T}\right)_P = \frac{\overline{H}_i^{\infty} - h_i}{R.}$$

ln Hi vs 1/T

$\Rightarrow$ straight line

$$\left(\frac{\partial \ln H_i}{\partial P}\right)_T = \frac{\overline{V}_i^{\infty}}{RT}$$

$$\left(\frac{\partial \ln H_i}{\partial T}\right)_P = (h_i - \overline{H}_i^{\infty})/RT^2$$

$$\left(\frac{\partial \ln H_i}{\partial \left(\frac{1}{T}\right)}\right)_P = (\overline{H}_i^{\infty} - h_i)/R$$

$$f_i^v = f_i^l$$

$$y_i \phi_i P = x_i \gamma_i H_i$$

Now let shall again recall that this Henrys law or constant or the derivative of that in the log form with respect to p at a constant temperature is related to the partial molar volume at infinite dilution divided by RT and similarly you know dou ln Hi with respect to T at a constant p is equal to the Hi minus Hi infinity divided by RT square okay. Where let me just be very clear here that this is a Henrys constant but this is a enthalpy, so to avoid confusion let me try to use this as enthalpy and let me use a little bit differences symbol here Hi, okay.

So this I can rewrite here as dou of Ln Hi by dou 1 by T, P and this can be written as Hi infinity minus Hi by R okay. Which tells you that if you plot Henrys constant in the log form versus 1 by T is going to give you the straight line, okay right. So these are the something which we can expression which we can use in order to obtain the information of Henrys constants and something which would be useful.

So now one of the important parts is that given this expression the question is how do we now obtain the solubility amount of the gas? Okay now in this case, you can have many conditions where you can consider liquid phase to be ideal and vapor phase to be idle you can consider another case where can you have you can have a non-ideal liquid phase. But ideal vapor phase have you can have the case where we can have both the phases to be non-ideal.

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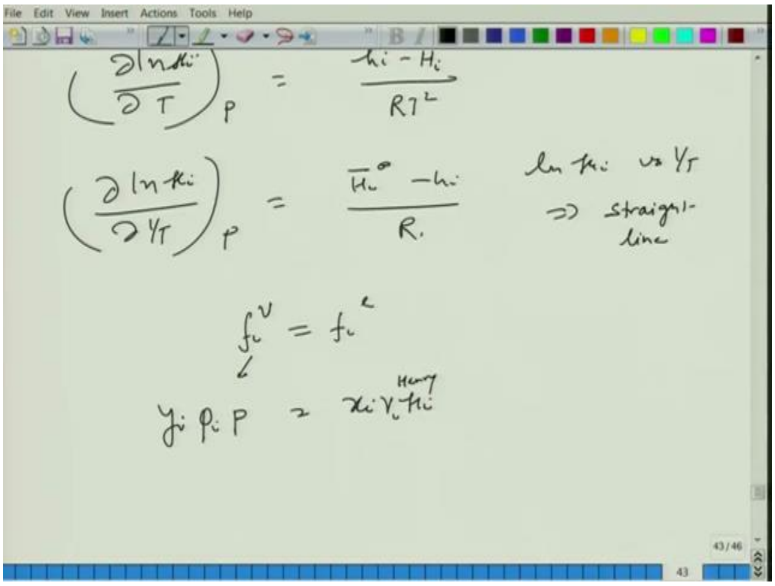

$$\left(\frac{\partial \ln \mathcal{H}_i}{\partial T}\right)_P = \frac{h_i - H_i}{RT^2}$$

$$\left(\frac{\partial \ln \mathcal{H}_i}{\partial 1/T}\right)_P = \frac{\bar{H}_i^{\infty} - h_i}{R.}$$

$\ln \mathcal{H}_i$ vs $1/T$

$\Rightarrow$ straight-line

$$f_i^V = f_i^L$$

$$y_i \phi_i P = x_i \gamma_i^{Henry} \mathcal{H}_i$$

So we will try to use this simple step by step cases here. So we will start with the basic equality of fugacity of this component here which basically would be the one which we are interested in obtaining the solubility. So but in general I can write fi is equal to fi vapor is equal to fi liquid and this can be written as y i Phi i p is equal to x i. Now here if it is an ideal part we are going to get right Hi. But then if it is non-ideal we are going to write gamma i but we will say that well this is a Henrys which essentially means that we are taking the reference of you know Henrys law, okay.

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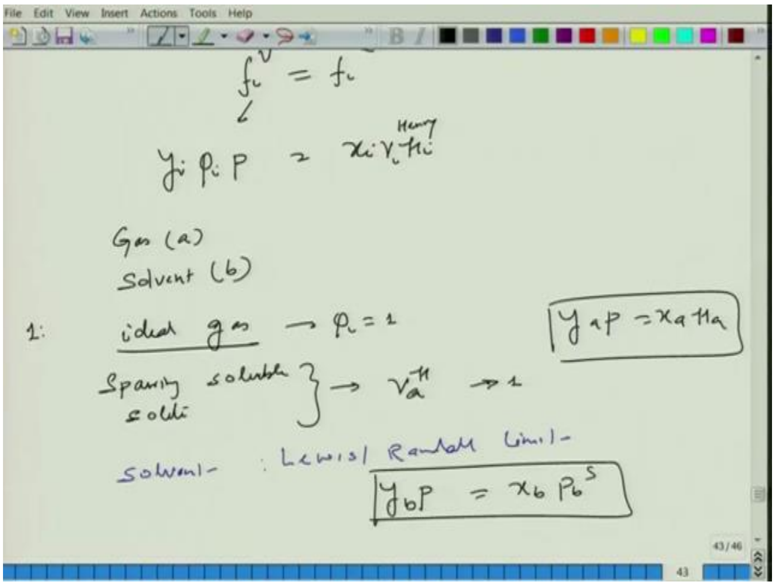


$f_i^V = f_i$

$y_i \phi_i P = x_i \gamma_i^{Henry} H_i$

Gas (a)

Solvent (b)

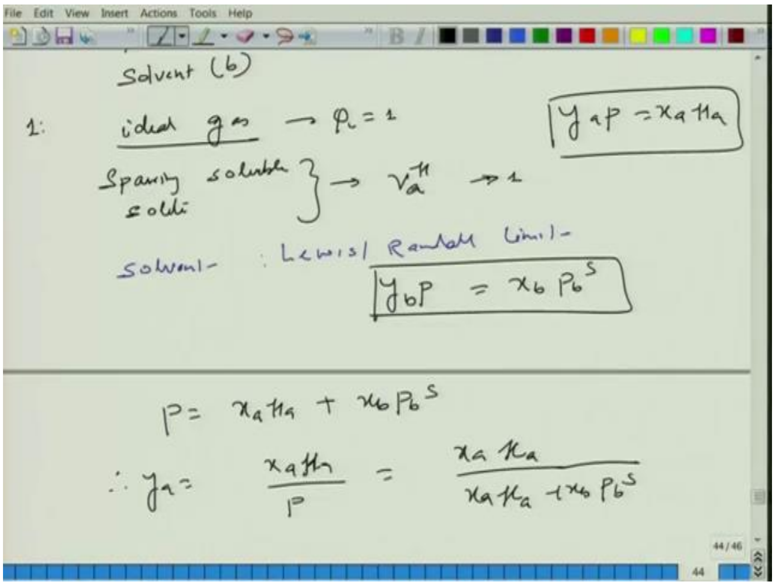
1: ideal gas → $\phi_i = 1$

$\boxed{y_a P = x_a H_a}$

Sparingly soluble solute } → $\gamma_a^H \to 1$

solvent : Lewis/Randall limit

$\boxed{y_b P = x_b P_b^S}$



Solvent (b)

1: ideal gas → $\phi_i = 1$

$\boxed{y_a P = x_a H_a}$

Sparingly soluble solute } → $\gamma_a^H \to 1$

solvent : Lewis/Randall limit

$\boxed{y_b P = x_b P_b^S}$

$P = x_a H_a + x_b P_b^S$

$\therefore y_a = \frac{x_a H_a}{P} = \frac{x_a H_a}{x_a H_a + x_b P_b^S}$

So consider a simple binary mixture here or where we are going to use the gas as component a and solvent as component b okay. So the first case which we are going to consider is ideal gas and sparingly soluble solute okay. Now if that is the case which essentially means that I am going to consider idle gas means I am going to consider Phi i is equal to 1 and I am going to consider gamma aH here which represent activity coefficient of gas and the Henrys limit that is going to be 1 also. Okay so which means I can write this as Yap is equal to Xa Ha so that is how equation 1.

What about for the solvent? Now for the case of the gas we have considered Henrys constant, for the case of solvent will be considering Louise Randall limit okay. So here considering this situation here or the assumptions which have considered here is that is going to be Yb p because ideal gas and then you have this Xb Pb s okay considering again that it is a low pressure and the solvent can be considered almost pure okay. So you have these 2 equations which you can solve and you can add this to equation.

If you add that you have the total pressure which is Ya p if you add this to the left hand side is total pressure and the right hand side is going to be Xa Ha plus Xp P b s okay. Therefore Ya is Xa Ha divided by p which is nothing but Xa Ha again I should be using not H here but something like this symbol okay and this is going to be Xa Ha plus Xb P b s okay. Similarly, I can do that for Ya also.

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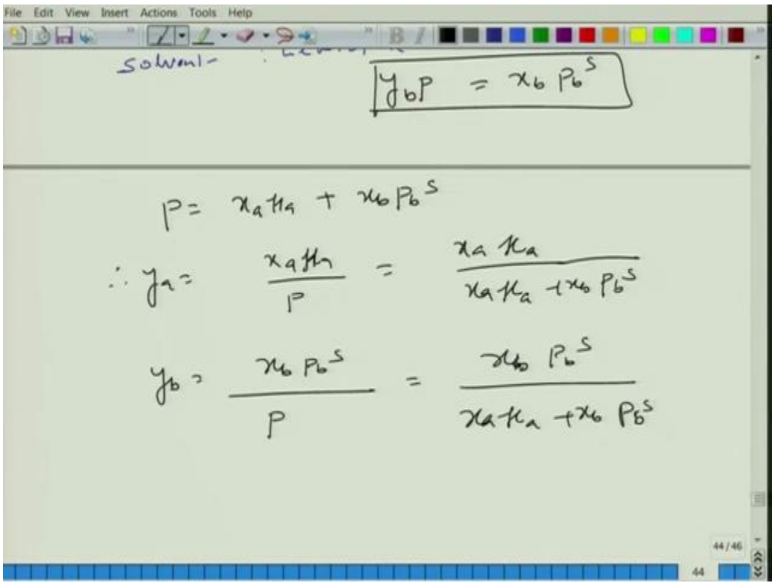

solvent

$$\boxed{y_b P = x_b P_b^S}$$

$$P = x_a H_a + x_b P_b^S$$

$$\therefore y_a = \frac{x_a H_a}{P} = \frac{x_a H_a}{x_a H_a + x_b P_b^S}$$

$$y_b = \frac{x_b P_b^S}{P} = \frac{x_b P_b^S}{x_a H_a + x_b P_b^S}$$

So Ya is going to be, sorry Yb is going to be Xb P b s divided by P which is going to be x b P b s, Xa Ha plus Xb P b s okay. So this is the case where we have considered ideal gas and sparingly soluble solute which essentially means that we can consider this assumption and we can go ahead with this to obtain the solubility information which is nothing here but Ya.

$$Gas\ (a); solvent\ (b)$$

1. $y_a P = x_a H_a; \quad y_b P = x_b P_b^s$

$$P = x_a H_a + x_b P_b^s$$

$$y_a = \frac{x_a H_a}{P} = \frac{x_a H_a}{x_a H_a + x_b P_b^s}$$

$$y_b = \frac{x_b H_b}{P} = \frac{x_b H_b}{x_a H_a + x_b P_b^s}$$

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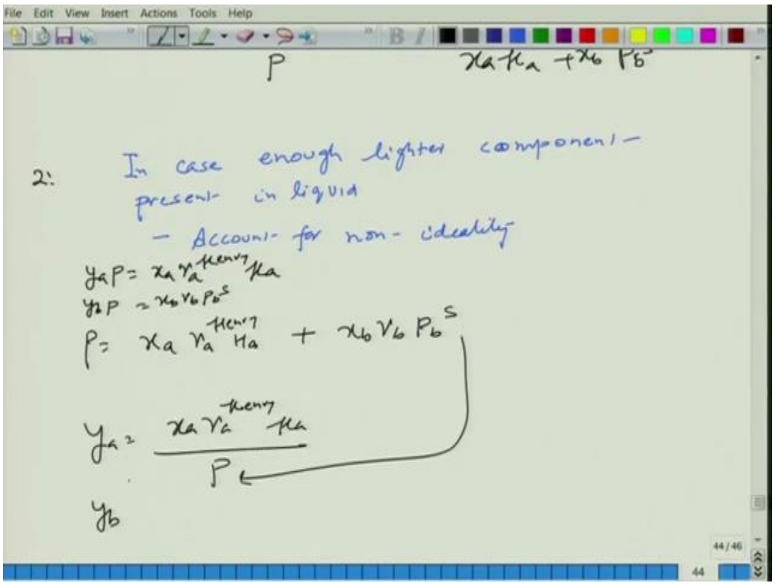


$P \quad x_a H_a + x_b P_b^s$

2: In case enough lighter component present in liquid

- Account for non-ideality

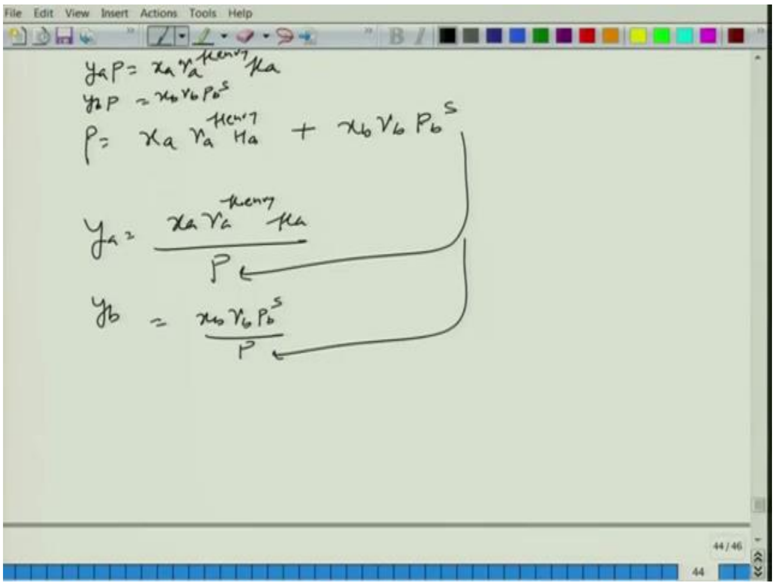
$y_a P = x_a \gamma_a^{Henry} H_a$

$y_b P = x_b \gamma_b P_b^s$

$P = x_a \gamma_a^{Henry} H_a + x_b \gamma_b P_b^s$

$y_a = \frac{x_a \gamma_a^{Henry} H_a}{P}$

$y_b$



$y_a P = x_a \gamma_a^{Henry} H_a$

$y_b P = x_b \gamma_b P_b^s$

$P = x_a \gamma_a^{Henry} H_a + x_b \gamma_b P_b^s$

$y_a = \frac{x_a \gamma_a^{Henry} H_a}{P}$

$y_b = \frac{x_b \gamma_b P_b^s}{P}$

Now let us consider the second case, so this would be the case where let us assume that if or in case enough lighter component that is your gas molecules. So in case, enough lighter component present in a liquid phase or solvent then consider or account for non-ideality okay. So which means I can now write pressure as Xa, okay and then since is a, so here in this case, you have to bring non-ideality and this case you will be having gamma a.

But since it is in the Henrys limit you say gamma a Henry to differentiate the gamma which comes here which is in the Louise Randall limit okay. So Xa, gamma a, H here, Ha here okay that comes out from the first component, component which is a lighter component plus Xb gamma b which is a liquid or solvent phase here P b s, so that is a pressure here.

Now using the same expression the rest of the things actually remains the same here, so because y a is going to be x a gamma H a divided b y P so let me also write down the equation for the sake of completion now you have y a P because the liquid phase still remains as idle gas okay. And we are still considering a low-pressure so that we can ignore the pointing correction. So with this you have Ya as Xa gamma a, Ha divided by pressure, now pressure you bring it here.

Similarly, you can do the same thing for Yb, so Yb is going to be Xb Pb Pb okay Xb gamma b P b s divided by P and now P of course is the same which you can use here. So with these 2 equations you can find out the compositions okay. Now I can consider another case, where we have now higher pressure which essentially means I have to bring the Pointing correction into account and ideal liquid.

$$2.\ y_aP = x_a\gamma_aH_a \quad y_bP = x_b\gamma_bP_b^S$$

$$P = x_a\gamma_aH_a + x_b\gamma_bP_b^S$$

$$y_a = \frac{x_a\gamma_aH_a}{P} \quad y_b = \frac{x_b\gamma_bP_b^S}{P}$$

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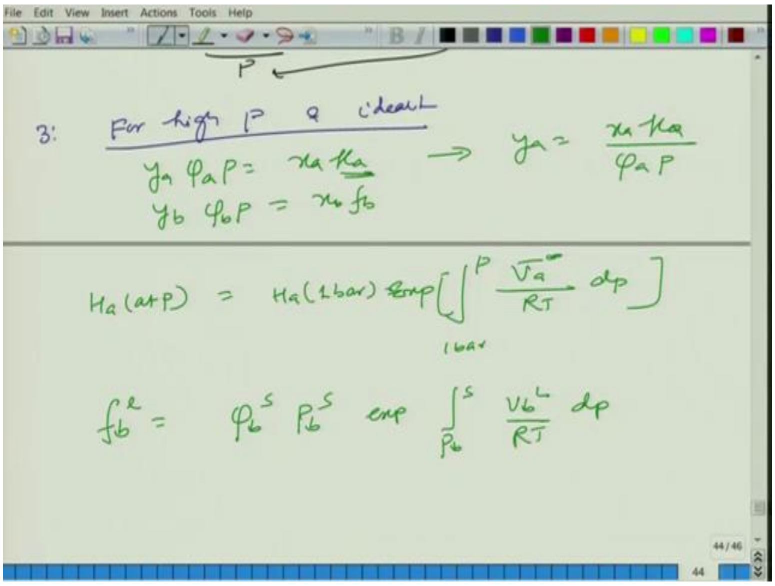

P

3: For high P & ideal

$$y_a \varphi_a P = x_a H_a \rightarrow y_a = \frac{x_a H_a}{\varphi_a P}$$

$$y_b \varphi_b P = x_b f_b$$

$$H_a (at\ P) = H_a (1\ bar)\ exp\left[\int_{1\ bar}^{P} \frac{\bar{V}_a^{\infty}}{RT}\, dp\right]$$

$$f_b^l = \varphi_b^s P_b^s\ exp \int_{P_b}^{s} \frac{V_b^L}{RT}\, dp$$

So let us consider another case, so this is a third case so for high pressure and ideal liquid okay. So if that is the case we have let us say we will write again for the component 1 or a here because ideal liquid then hence I can ignore the gammas here and this is your Yb phi b P because now I have to account for a high pressure and x b f p.

Now here Ha which is at high pressure I can calculate Ha at let us say P using one of these expressions which we have written earlier. We can keep the T fix here and integrate this part from 1 bar to the pressure which we are you want so this could be something like Ha at 1 bar is exponential integral of 1 bar to pressure and this Va infinity RT dp okay. So you can have H here. Similarly pointing correction can be consider for f b, f b l is Phi b s, P b s and then you have this exponential P b s V b l by RT dp.

So with these two consideration you have non-ideal liquid and as well as non-ideal gas and then your expressions would be more complete and then you can try to solve this, it will be more complicated but this is how it will go okay. So I am not doing any example to demonstrate this but you can if you have the information of course you can use excel sheets or you can write codes in order to solve this and obtain the Ya, Ya again will become like this we have to write Xa Ha divided by Phi a P and of course you have to use these two equation to get the pressure here okay.

$$3.\ For\ high\ pressure\ and\ ideal\ liquid$$

$$y_a \phi_a P = x_a H_a \quad y_b \phi_b P = x_b f_b$$

$$y_a = \frac{x_a H_a}{\phi_a P}$$

$$H_a(at\ P) = H_a(1\ bar)\exp\left[\int_{1\ bar}^{P} \frac{\overline{V_a}^{\infty}}{RT}\, dP\right]$$

$$f_b^l = \phi_b^s P_b^s \exp\int_{P_b}^{S} \frac{V_b^L}{RT}\, dP$$

Now given the information you have to rewrite or rearrange things in order to solve this equation okay. So I think I have covered all the aspects of as far as the vapor liquid, phase equilibria or in general phase equilibria which also include liquid-liquid and solid-liquid equilibria. So at this point I think we have covered as I said all aspect of it and some examples can be done which you can make use of the textbook which has plenty of examples and exercises. So let me stop here and then in the next lecture I will start a last topic of this particular course that will be your chemical reaction equilibrium. So I will see you in the next lecture.