Chemical Engineering Thermodynamics
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Lecture – 29
Fugacity

Right now let us get an example.

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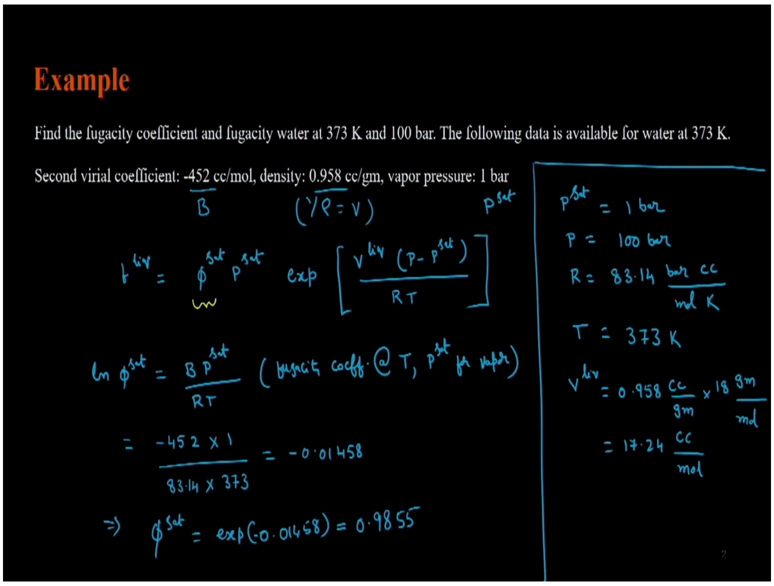

Example

Find the fugacity coefficient and fugacity water at 373 K and 100 bar. The following data is available for water at 373 K.

Second virial coefficient: -452 cc/mol, density: 0.958 cc/gm, vapor pressure: 1 bar

B $\quad (1/\rho = V) \quad P^{sat}$

$$f^{liq} = \phi^{sat} P^{sat} \exp\left[\frac{V^{liq}(P - P^{sat})}{RT}\right]$$

$$\ln \phi^{sat} = \frac{B P^{sat}}{RT} \quad (\text{fugacity coeff. @ } T, P^{sat} \text{ for vapor})$$

$$= \frac{-452 \times 1}{83.14 \times 373} = -0.01458$$

$$\Rightarrow \phi^{sat} = \exp(-0.01458) = 0.9855$$

$P^{sat} = 1 \text{ bar}$

$P = 100 \text{ bar}$

$R = 83.14 \frac{\text{bar cc}}{\text{mol K}}$

$T = 373 \text{ K}$

$V^{liq} = 0.958 \frac{\text{cc}}{\text{gm}} \times 18 \frac{\text{gm}}{\text{mol}}$

$= 17.24 \frac{\text{cc}}{\text{mol}}$

We have water at 373 Kelvin and a 100 bar and we want to estimate the fugacity coefficient and fugacity for this water. The following data is given the second virial coefficient is given, this is B this is the density for water or rather inverse of density I should say this is in cc program. So, this is actually the molar volume. So, this is inverse of density and then this is the vapor pressure. So, essentially the saturation pressure this is the information given to us we can also call this as V the specific volume, and based on this information we are to calculate the fugacity and fugacity coefficient for water this is liquid water 373 Kelvin alright.

So, the first thing we do is we will write the equation we just derived which reads the fugacity of liquid, I will omit the subscript I we just have one species anyway is the fugacity at the saturation conditions. So, it is the fugacity coefficient times the saturation pressure, times the pointing correction factor which reads exponential of the volume of the liquid P minus P sat over RT this is the expression we have just derived.

So, we have to use this expression and calculate the fugacity of the liquid phase. We will take each term at a time P sat is given to us all that is right what is known P sat is given to us it is 1 bar, P also is given to us it as a 100 bar R is 83.14 bar cc per mol per Kelvin and the temperature is 373 Kelvin. The volume of the liquid is 0.958 cc per gram, but remember we work with molar quantities in all these equations. So, this is a specific volume what we will do is we will multiply with the molecular weight for water which is 18 grams per mole.

So, that will be equal to 17.24 cc per mole this is a molar volume at the given condition we have converted it from the specific volume two molar volume. So, I have V liquid. So, I have everything that I need to calculate the pointing correction factor. The only thing that is missing in this on the right hand side of this equation is the saturation vapor pressure, how do we get the saturation vapor pressure? If you recall we said at the saturation condition because we are at equilibrium between the vapor and liquid phases, the fugacity of the liquid will be equal to the fugacity of the vapors which we are calling it as the saturation fugacity or fugacity coefficient.

So, what we will do is we will use the vapor phase and the second virial coefficient to estimate the fugacity coefficient in the vapor phase, and we will use that value for the saturation condition. So, l n phi for pure species if you recall is BP and because we are at the saturation condition I will use P sat R T. This will be fugacity coefficient at T and P sat for vapor. And once we calculate it for vapor it is of course, going to be same for the liquid as well, but this is our going to a calculate the fugacity coefficient at the saturation condition.

So, B is given to us negative 452 cc per mole multiplied with 1 bar over 83.14 bar cc per mole per Kelvin multiplied with 373 and if I simplify this numerical value, what I will get is negative 0.01458 what; that means, is the fugacity coefficient will be exponential of this value, negative 0.01458 which will be 0.9855 this will be the fugacity coefficient.

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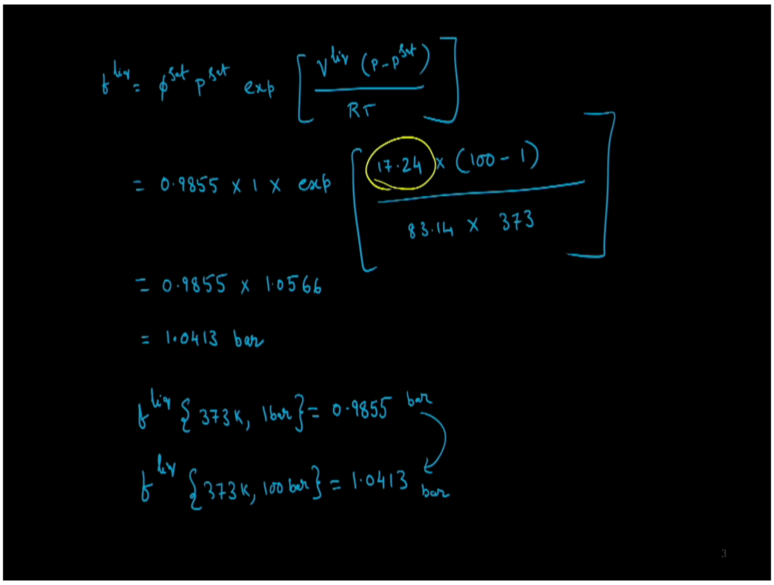

$$f^{liq} = \phi^{sat} P^{sat} \exp\left[\frac{V^{liq}(P - P^{sat})}{RT}\right]$$

$$= 0.9855 \times 1 \times \exp\left[\frac{\boxed{17.24} \times (100 - 1)}{83.14 \times 373}\right]$$

$$= 0.9855 \times 1.0566$$

$$= 1.0413 \text{ bar}$$

$$f^{liq}\{373\text{K}, 1\text{bar}\} = 0.9855 \text{ bar}$$

$$f^{liq}\{373\text{K}, 100\text{ bar}\} = 1.0413 \text{ bar}$$

Now, I have everything I need to calculate f liquid f liquid we said is phi sat P sat exponential V for the liquid P minus P sat over RT this value the first value was 0.9855 times P sat is 1 times exponential of V liquid is 17.24 cc per mole times 100 is the value for pressure 1 bar is the value for P sat 83.14 is the value for R in bar cc per mole per Kelvin, and the temperature is 373 Kelvin. With these numbers the first two numbers the product of those is 0.9855 of course, multiplied with the exponential value, I have is 1.0566. So, this pointing correction factor as you can see even when the pressure changes by about a 100 bar, the pointing correction factor is only 1.05 for this liquid volume and this is typically the case for 100 bar we have bar 5 percent change in the molar volume for typical liquids, we encounter in the industry.

So, this is a number we are looking at in terms of pointing condition factor and if you guessed yet saturation conditions and once we multiply these two, we will get the fugacity of the liquid 1.0413 bar. So, as you can see the fugacity of the liquid at 373 Kelvin and 1 bar which is the saturation condition is about 0.9855 and the fugacity of the liquid when we change the pressure from 1 bar to about a 100 bar, right a 100 bar is 1.0413 and like I said it is about a 5 percent change in that is the only change we get for a change in pressure of 100 about 99 bar right.

So, of course, both these units are in bars right. So, those are the type of numbers we are looking at when we talk about fugacities of the liquid phase. This of course, comes with the assumption that liquid is fairly incompressible. So, going from 1 bar to 100 bar the average molar volume will be more or less constant at that number of 17.24 if that is not the case of course, we see a slight change in these numbers,, but they are fairly incompressible the molar volume does not change much at these conditions. So, that is how we use the concept of vapor liquid equilibrium and use it in calculation of fugacity of the liquid phase we are the pointing correction factor.

Now, once we look at this, this expression is going to be useful for the discussion we are going to do in our next section right. The next section will be talking about the vapor liquid equilibrium in general, how we go about modeling vapor liquid equilibrium for non ideal solutions and how we collect experimental data to obtain the excess Gibbs free energy values. Remember when we talked about the excess properties, we said the excess Gibbs free energy comes from vapor liquid equilibrium data typically and the excess enthalpy comes from the mixing experiments.

So, we will start our discussion on vapor liquid equilibrium modeling for non ideal solutions and then look at how experimental data is collected to obtain the excess R Gibbs free energy.

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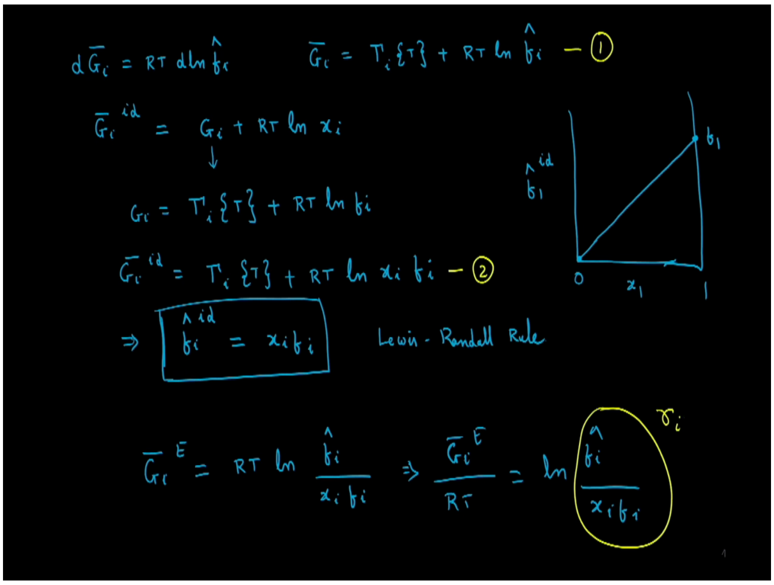

$$d\bar{G}_i = RT\, d\ln \hat{f}_i \qquad \bar{G}_i = \Gamma_i\{T\} + RT\ln \hat{f}_i \quad - ①$$

$$\bar{G}_i^{id} = G_i + RT\ln x_i$$

$$\downarrow$$

$$G_i = \Gamma_i\{T\} + RT\ln f_i$$

$$\bar{G}_i^{id} = \Gamma_i\{T\} + RT\ln x_i f_i \quad - ②$$

$$\Rightarrow \boxed{\hat{f}_i^{id} = x_i f_i}$$

Lewis - Randall Rule

$$\bar{G}_i^{E} = RT\ln \frac{\hat{f}_i}{x_i f_i} \Rightarrow \frac{\bar{G}_i^{E}}{RT} = \ln \overset{\gamma_i}{\left(\frac{\hat{f}_i}{x_i f_i}\right)}$$

Recall that the Gibbs free energy d G i bar the partial molar Gibbs free energy is related to fugacity of species i in a mixture we are this relation right. I can integrate this is at constant temperature I can integrate this and what we get is G i bar is some function for that species i some constant which is a function of temperature for that species i plus R T l n f i hat also recall that for an ideal solution G i bar ideal we have written it as G i plus RT l n x i.

Now, this is how we have defined an ideal solution. Now if I can expand G i right it will be for a pure species, it will be the constant gamma i it is same it is only dependent on the temperature T and the species i as long as it is the same species i and we are at the same temperature, then it will be same value of gamma i plus because it is for a pure species all I will have is simply RT l n f i right. So, this will be G i. So, then G i bar for ideal solution will be gamma i T plus RT l n x i f i right and if you compare these two equations what we get is f i hat in an ideal solution should be equal to x i times f i right both these equations are identical, one is for written for ideal solution one is a general equation. So, what this essentially implies is that for an ideal solution f i hat ideal should be equal to x i f i and we call this as Lewis Randall rule.

So, an ideal solution the fugacity of species in the mixture is going to be proportional to the pure component fugacity or its going to sorry it is going to be proportional to the mole fraction and the constant of proportionality is of course, the pure component fugacity because at one end, it has to be the pure component fugacity right and we call this as the Lewis Randall rule. So, if I were to if I were to draw a picture of f i hat ideal in a binary mixture let us say this is x 1 going from 0 to 1, and this is f 1 hat right. If I were to draw how f 1 hat changes with the composition x 1 it will look something like that. At one end when x 1 is 0 f 1 hat is going to be 0 because of Lewis Randall rule at the other end it will be same as f 1 that is for pure species 1.

So, this is of course, only true if Lewis Rendell rule is valid or if it is an ideal solution f i f 1 hat ideal will look something like that. That is how it changes with mole fraction of that particular species in the mixture. In general though if we take these two equations here right for a non-ideal solution, if I take this equation 1 and this equation 2 right and I subtract one from the other, what I get on the left hand side is G i bar E that is the excess Gibbs free energy G i minus G i ideal is the excess Gibbs free energy is going to be equal to RT l n f i hat over x i f i. Or, if I were to write it in a better way, G i bar E over RT is going to be l n f i hat over x i f i right. We call this quantity on the right hand side as gamma i or the activity coefficient.

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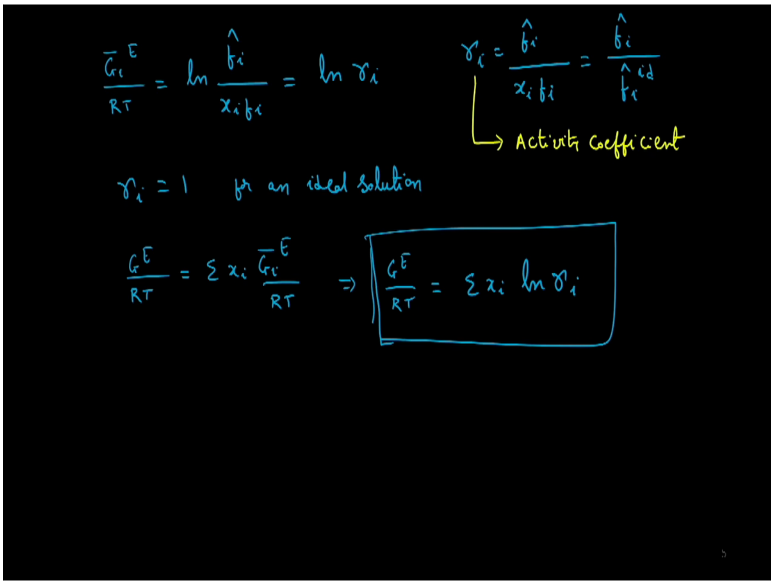

$$\frac{\bar{G}_i^E}{RT} = \ln \frac{\hat{f}_i}{x_i f_i} = \ln \gamma_i$$

$$\gamma_i = \frac{\hat{f}_i}{x_i f_i} = \frac{\hat{f}_i}{\hat{f}_i^{id}}$$

Activity coefficient

$\gamma_i = 1$ for an ideal solution

$$\frac{G^E}{RT} = \sum x_i \frac{\bar{G}_i^E}{RT} \Rightarrow \boxed{\frac{G^E}{RT} = \sum x_i \ln \gamma_i}$$

So, let us rewrite that equation one more time. G i bar e over RT is equal to l n of f i hat by x i f i and we will call that as activity coefficient gamma i, it is the ratio of the fugacity of species in the mixture over what is given by the ideal solution. So, it is f i hat over f i hat ideal right and we call this as the activity coefficient; obviously, gamma i equals 1 for an ideal solution because f i hat will be equal to f i hat ideal otherwise, it will not be unity will have value that is not equal to unity and the and that number will denote how non-ideal the solution s right. If it is 1 we have an ideal solution if it is not 1 we have a non ideal solution right.

And also note that G i bar E over RT is a partial molar property. So, G E by RT will be equal to sigma x i G i bar E over RT this is using the summability relation right. If we add the partial molar properties multiplied with the mole fraction we get the total property, what this means is G E over RT is going to be sigma x i l n gamma i. So, if I know the activity coefficient of the species in the solution, I can calculate the excess Gibbs free energy for that particular solution. We will come back and see how we can obtain this value of gamma i from experiments.

But that is the essential idea of introducing activity coefficients just like a compressibility factor for ideal gases it is 1, for non ideal gases we deviate from one similarly for ideal solutions the activity coefficient is 1, for non-ideal solutions we are going to deviate from 1. And, like we said the excess Gibbs free energy itself can have positive or negative deviations from ideality similarly gamma i can be greater than 1 or less than 1 depending on whether we have positive or negative deviations from ideality for that particular solution.

Now, since we talked about the excess Gibbs free energy and fugacity of and how the fugacity of species in a solution is related to the excess Gibbs free energy. Now, let us go back to our original problem of how to obtain G E by RT from vapor liquid equilibrium data. To do that what we need to do is formulate the vapor liquid equilibrium problem.

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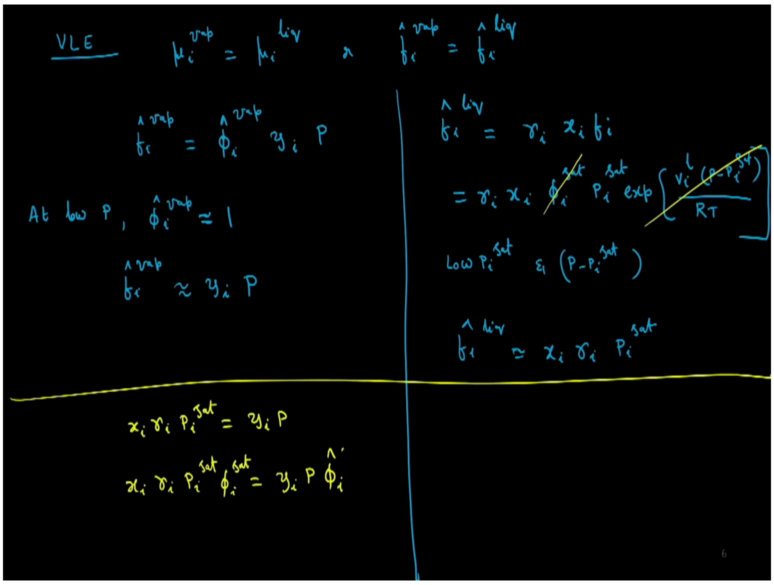

VLE $\quad \mu_i^{vap} = \mu_i^{liq} \quad \text{or} \quad \hat{f}_i^{vap} = \hat{f}_i^{liq}$

$$\hat{f}_i^{vap} = \hat{\phi}_i^{vap} y_i P$$

At low P, $\hat{\phi}_i^{vap} \simeq 1$

$$\hat{f}_i^{vap} \approx y_i P$$

$$\hat{f}_i^{liq} = \gamma_i x_i f_i$$

$$= \gamma_i x_i \cancel{\phi_i^{sat}} P_i^{sat} \cancel{\exp\left[\frac{V_i^l (P - P_i^{sat})}{RT}\right]}$$

Low P_i^{sat} & $(P - P_i^{sat})$

$$\hat{f}_i^{liq} \simeq x_i \gamma_i P_i^{sat}$$

$$x_i \gamma_i P_i^{sat} = y_i P$$

$$x_i \gamma_i P_i^{sat} \phi_i^{sat} = y_i P \hat{\phi}_i'$$

If you recall we said for vapor liquid equilibrium mu i in the vapor phase should be equal to mu i in the liquid phase or f i hat in the vapor phase should be equal to f i hat in the liquid phase. We have derived this equation we said the chemical potential should be equal or in other words the fugacities of each of the species in both the phases need to be equal.

Now, let us take each one of these fugacities and see how we can obtain them. The vapor phase fugacity is fairly straightforward to obtain what we will do is we will write it as the fugacity coefficient of that species in the vapor mixture multiplied with the partial pressure of that species y i times P. At low pressures for some most of our industrial applications, we might be able to use. Now, this is fugacity of species in the vapor at low pressures most gases behave as ideal gases. So, the fugacity coefficient for the species can be approximated to 1 and if we do that, the fugacity in the vapor phase will simply be equal to y i times P.

Now, when we look at the fugacity of the liquid, we said this will be by definition of the activity coefficient. So, let us write gamma i first multiplied with the fugacity of the ideal solution which is x i times f i. f i is the fugacity of the pure species i and for the pure species i, we can write that fugacity as the fugacity at the saturation conditions phi i sat P i sat multiplied with the pointing correction factor P minus P i sat over RT.

And as we have seen in the example we worked using the pointing correction factor even for a change of 100 bar, the pointing correction factor is less than 5 percent for smaller changes the pointing correction factor can be safely ignored for smaller changes from P to P i sat that is. And if the saturation pressure also is low P i sat and P minus P i sat also being or the difference between P and P i sat also being low, what we can do is we can safely ignore the pointing correction factor and we can also assume that the gas phase itself is going to be ideal.

So, we can ignore the fugacity coefficient at the saturation condition for the vapor phase because P i sat itself is and if that happens we can approximate f i had liquid to be x i gamma i P i sat. Now, remember for this to happen the vapor phase at the saturation condition needs to behave as an ideal gas and the pointing correction factor should be small enough, that we can ignore it and when that happens f i hat liquid will be this.

So, once we have this, we can equate the vapor and liquid phase fugacities with the approximations we have made that equation becomes x i gamma i P i sat will be equal to y i times P if we only ignore the pointing correction factor and do not ignore the non-idealities in the vapor phases. Then this equation will become x i gamma i P i sat times phi sat for non-ideality at the saturation conditions will be equal to y i P times phi i hat for the vapor phase.

So, depending on the pressures and the saturation conditions we will choose one of these equations and try to work with them accordingly. So, what we have done via this exercise is we have related the vapor and liquid phase fugacities in terms of quantities we can easily work with. The only thing we still did not talk about is gamma i the activity coefficient which we related it to the excess Gibbs free energy.

Now, remember when we said one of the ways to obtain the excess Gibbs free energy is using the vapor liquid equilibrium data.

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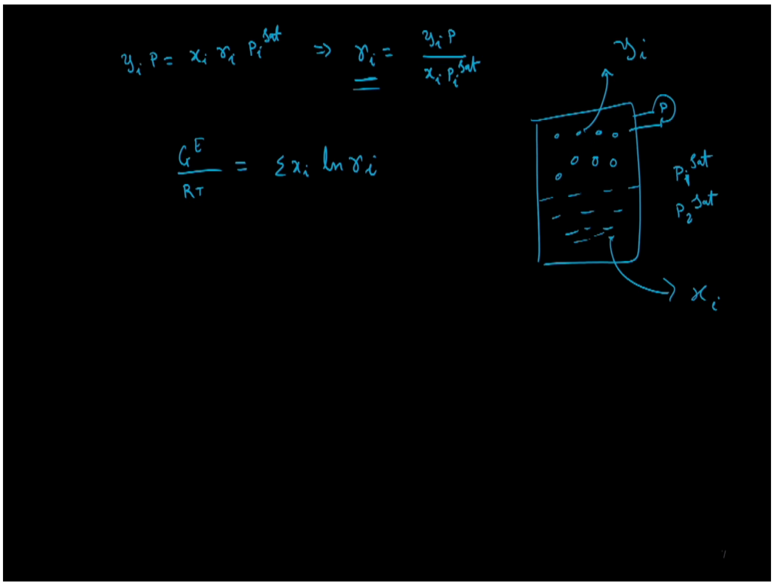

$$y_i P = x_i \gamma_i P_i^{sat} \Rightarrow \underline{\underline{\gamma_i}} = \frac{y_i P}{x_i P_i^{sat}}$$

$$\frac{G^E}{RT} = \sum x_i \ln \gamma_i$$

So, if you look at the previous equation or the simplified version of the previous equation, it reads y i P is x i gamma i P i sat when we ignore the non idealities in the vapor phases. When that happens this means gamma i is going to be y i P by x i P i sat, I can perform a vapor liquid equilibrium experiment obtain the composition of the liquid phase which x I, the composition of the vapor phase which is y i the total pressure P and I know the pure component vapor pressures P i sat, and if I have this information I can calculate the activity coefficient gamma i. And, once I calculate gamma i remember we said G E over RT is sigma x i l n gamma i.

So, I can do an experiment I can take a closed vessel fill it with pure species and note the put it in an isothermal bath nor the pressure, that will give me P i sat at that temperature change the liquid, but it will give me P 2 sat the first one was P P 1 sat. And, then I can put a mixture of both the liquids and allow it to attain equilibrium and at equilibrium I will have both the liquid and the vapor phases each with different compositions the vapor phase composition is y i the liquid phase composition is x i I can sample them obtain the composition or mole fraction in the vapor and the liquid phases. And, once I have all this information, I can go back and calculate the activity coefficient and once I have the activity coefficient I can calculate the excess Gibbs free energy. So, this is one of the ways to obtained excess Gibbs free energy, using the vapor liquid equilibrium data in this case.

Once we have that information we can build models for excess Gibbs free energies just like we have equation of state for PVT relationship we can build a model that relates a excess Gibbs free energy to the compositions. And once we have that model, we can use that to obtain the fugacity coefficients and obtain vapor liquid equilibrium behavior for that particular mixture. Let us talk about one final thing before we stop the lecture today.

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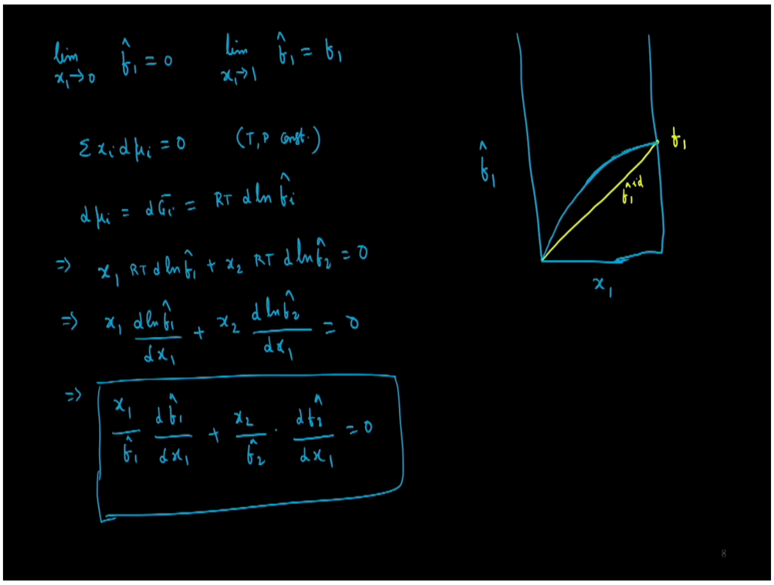

$$\lim_{x_1 \to 0} \hat{f}_1 = 0 \qquad \lim_{x_1 \to 1} \hat{f}_1 = f_1$$

$$\sum x_i \, d\mu_i = 0 \qquad (T, P \text{ const.})$$

$$d\mu_i = d\bar{G}_i = RT \, d\ln \hat{f}_i$$

$$\Rightarrow \quad x_1 RT \, d\ln \hat{f}_1 + x_2 RT \, d\ln \hat{f}_2 = 0$$

$$\Rightarrow \quad x_1 \frac{d\ln \hat{f}_1}{dx_1} + x_2 \frac{d\ln \hat{f}_2}{dx_1} = 0$$

$$\Rightarrow \quad \boxed{\frac{x_1}{\hat{f}_1} \frac{d\hat{f}_1}{dx_1} + \frac{x_2}{\hat{f}_2} \cdot \frac{d\hat{f}_2}{dx_1} = 0}$$

This relates to the behavior of the systems at the ends of the composition diagram. We said that the fugacity varies with composition f 1 hat varies with composition linearly if it is an ideal solution, this is f 1 hat ideal and this value then needs to be f for pure one at the temperature and pressure of interest. But in real life the solutions are not ideal. If they are not ideal f 1 hat ideal will not fall along this line it might look something like that right.

So, let us join them. So, there is a deviation from ideality for f 1 hat. Nevertheless at d ends of the composition limit x 1 going to 0 f 1 hat should go to 0 and limit x 1 going to 1 f 1 hat should approach f 1 right. The other thing we can note from this particular diagram is sigma x i d mu i is 0 because mu i is a partial molar property and Gibbs Duhem equation as to hold at constant temperature and pressure.

Since, d mu I is d G i bar mu i and G i bar are same is RT d l n f i hat what this means in a binary system is x 1 RT d l n f 1 hat plus x 2 RT d l n f 2 hat should be equal to 0 we can get rid of R T. So, what it means is x 1 d l n f 1 hat over d x 1 f 1 hat varies with composition it either d x 1 or d x 2 in a binary does not matter plus x 2 d l n f 2 hat with respect to the same x, x 1 in this case equals 0 this means x 1 over f 1 hat d f 1 hat over d x 1 plus x 2 over f 2 hat times d f 2 hat over d x 1 should be equal to 0. So, this is a requirement because Gibbs Duhem equation always needs to be satisfied. So, f 1 hat and f 2 hat in that sense are not completely independent they are somehow related to one another.

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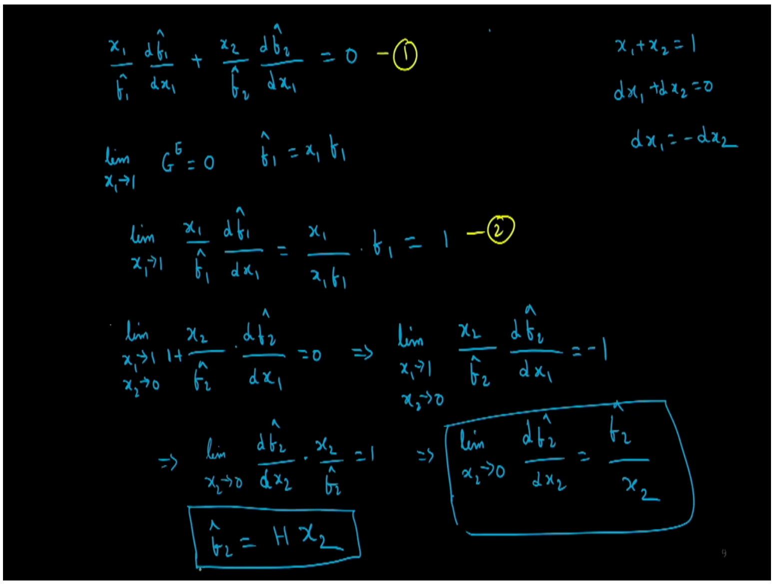

$$\frac{x_1}{\hat{f}_1}\frac{d\hat{f}_1}{dx_1} + \frac{x_2}{\hat{f}_2}\frac{d\hat{f}_2}{dx_1} = 0 \quad -①$$

$$x_1 + x_2 = 1$$

$$dx_1 + dx_2 = 0$$

$$dx_1 = -dx_2$$

$$\lim_{x_1 \to 1} G^E = 0 \qquad \hat{f}_1 = x_1 f_1$$

$$\lim_{x_1 \to 1} \frac{x_1}{\hat{f}_1}\frac{d\hat{f}_1}{dx_1} = \frac{x_1}{x_1 f_1} \cdot f_1 = 1 \quad -②$$

$$\lim_{\substack{x_1 \to 1 \\ x_2 \to 0}} 1 + \frac{x_2}{\hat{f}_2} \cdot \frac{d\hat{f}_2}{dx_1} = 0 \Rightarrow \lim_{\substack{x_1 \to 1 \\ x_2 \to 0}} \frac{x_2}{\hat{f}_2}\frac{d\hat{f}_2}{dx_1} = -1$$

$$\Rightarrow \lim_{x_2 \to 0} \frac{d\hat{f}_2}{dx_2} \cdot \frac{x_2}{\hat{f}_2} = 1 \Rightarrow \boxed{\lim_{x_2 \to 0} \frac{d\hat{f}_2}{dx_2} = \frac{\hat{f}_2}{x_2}}$$

$$\boxed{\hat{f}_2 = H x_2}$$

So, let us rewrite that reemphasize that again. So, this equation one is the Gibbs Duhem equation. Now, at the limit of x 1 going to 1 the solution becomes ideal we have mostly pure one and the excess Gibbs free energy will be equal to 0 and because the solution becomes ideal f 1 hat will be equal to x 1 times f 1 because that is the property of an ideal solution as we have seen a minute ago. When that happens the limit at x 1 going to 1 x 1 over f 1 hat d f 1 hat over d x 1 will be x 1 by x 1 f 1 and the derivative of f 1 hat with respect to x 1 will be f 1. So, this value turns out to be 1.

Now, from 1 and 2; 1 is applicable everywhere 2 is applicable at a particular limit. So, limit as x 1 going to 1 x 2 will go to 0 at this limit x 2 over f 2 hat, d f 2 hat over d x 2 and the first term at this limit is 1. So, 1 plus this should equal 0 or what this means is limit x 1 going to 1 x 2 going to 0, x 2 by f 2 hat d f 2 hat over d x 1 should be equal to negative 1.

Now, recall that x 1 plus x 2 in a binary system is 1. So, d x 1 plus d x 2 is 0 or d x 1 is negative of d x 2. So, I can easily replace this d x 1 here with d x 2 and what; that means, is limit as x 2 goes to 0 d f 2 hat over d x 2 times x 2 over f 2 hat will be equal to 1 or limit as x 2 goes to 0, d f 2 hat over d x 2 will be equal to f 2 hat over x 2. What this means is that the slope will be same as the ratio of f 2 hat to x 2 or f 2 hat will be the slope whatever that value is multiplied with x 2 we call that slope as h or the Henrys constant. Let us see what it means.

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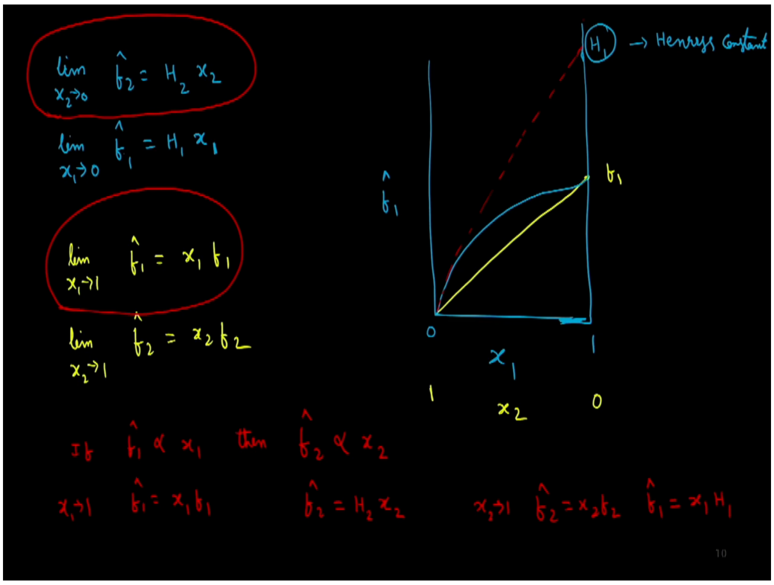

$$\boxed{\lim_{x_2 \to 0} \hat{f}_2 = H_2 x_2}$$

$$\lim_{x_1 \to 0} \hat{f}_1 = H_1 x_1$$

$$\boxed{\lim_{x_1 \to 1} \hat{f}_1 = x_1 f_1}$$

$$\lim_{x_2 \to 1} \hat{f}_2 = x_2 f_2$$

If $\hat{f}_1 \propto x_1$ then $\hat{f}_2 \propto x_2$

$x_1 \to 1$ $\hat{f}_1 = x_1 f_1$ $\hat{f}_2 = H_2 x_2$ $x_2 \to 1$ $\hat{f}_2 = x_2 f_2$ $\hat{f}_1 = x_1 H_1$

Let us draw a diagram of how things change with composition x 1 0 and one and what I will do is are also indicate x 2 on this particular diagram x 2 is 1 here and 0 here and let me write f 1 hat here; f 1 hat when this is 0 we will start here. And, as we have seen the ideal solution line or the Lewis Rendell line will go like this until this point which is f for pure one if the solution is non ideal it will go like this and then go like that.

Now, as you have seen here limit as x 2 goes to 0 f 2 hat is H times x 2 similarly at the limit as x 2 goes to 0, f 2 hat is some constant H for 2 times x 2 similarly limit we can also show that limit as x 1 goes to 0, f 1 hat will be H for 1 times x 1. So, that is the slope of this line for f 1 hat at the 0 composition. So, if I draw the slope here right that is the slope that slope will meet the line x equal to 1 at H 1. H 1 is called as the Henrys constant. These are the two limits at the compositions going to 0; the other two limits we have seen are at the compositions going to one limit as x 1 goes to 1, f 1 hat will be an ideal solution. So, it will be x 1 times f 1 similarly limit as x 2 goes to 1 f 2 hat will be equal to x 2 times f 2.

So, these are the two ends of the composition diagram what I have shown here is for f 1 hat we can draw a similar diagram for f 2 hat, in that case we will have the slope to be the Henrys constant for species 2 or H 2 right. We have obtained this using the Gibbs Duhem equation what it means is that, in the region where f 1 hat is proportional to the composition x 1 which is in this region. At the same region f 2 hat because x 1 is going to one in the same region x 2 is going to 0 in the same region f 2 hat also needs to be proportional to x 2 this is stipulated by the Gibbs Duhem equation.

So, let us write that done if f 1 hat is proportional to x 1 then f 2 hat will be proportional to x 2. This is a stipulation we can obtain from Gibbs Duhem equation. The constant of proportionality here will be the pure component fugacity at one limit as x 1 goes to 1 and at the same limit the constant of proportionality as x 1 goes to 1, it is almost pure 1 we have infinite dilution of 2 and the constant of proportionality at infinite dilution we are going to call it as the Henrys constant for 2 H 2. Similarly at the other limit at x 2 going to 1 we have almost pure 2. So, f 2 hat will be x 2 times f 2 the constant of proportionality is f 2 and as x 2 goes to 1 x 1 goes to 0 we have infinitely dilute 1 and f 1 hat will be x 1 times h one or the Henry constant for 1.

So, this is the overall summary of how the fugacities are going to behave at the two ends of the composition diagrams. And as you see the fugacity of both the species are related they cannot independently behave. So, with that we stop the lecture today when we come back, we will try to look at the application of what we have derived today in terms of activity coefficients and how we go about using this data or using this model for obtaining the vapor liquid equilibrium behavior.

Thank you.