Thermodynamics (Classical) for Biological Systems

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Module No. # 05

Phase Equilibria

Lecture No. # 31

Vapour-Liquid Equilibrium (continued) Estimation of Fugacity Coefficient from Equilibrium P-V-T Data

Welcome back!

In the last class, we had started looking at the specific equilibrium, which is the vapour-liquid equilibrium. We are going to derive useful relationships at vapour-liquid equilibrium conditions. We had already looked at a pure substance in vapour-liquid equilibrium.

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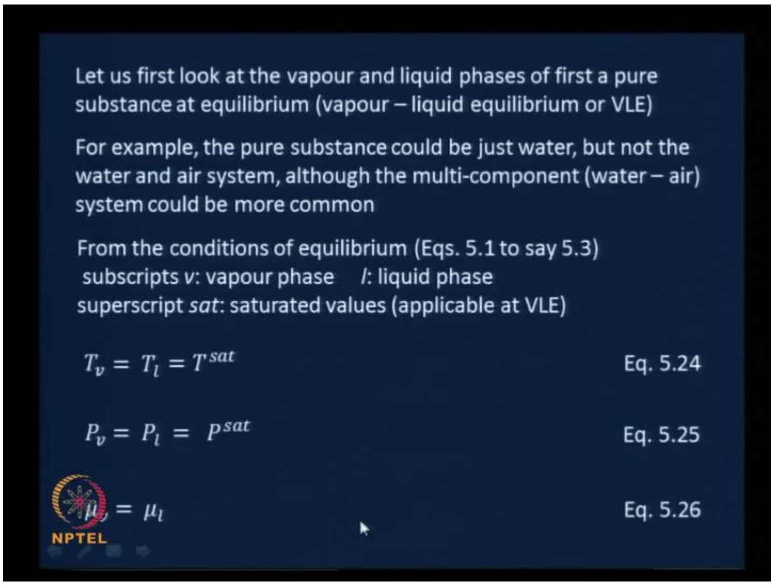

Let us first look at the vapour and liquid phases of first a pure substance at equilibrium (vapour – liquid equilibrium or VLE)

For example, the pure substance could be just water, but not the water and air system, although the multi-component (water – air) system could be more common

From the conditions of equilibrium (Eqs. 5.1 to say 5.3)
subscripts *v*: vapour phase *l*: liquid phase
superscript *sat*: saturated values (applicable at VLE)

$$T_v = T_l = T^{sat} \qquad \text{Eq. 5.24}$$

$$P_v = P_l = P^{sat} \qquad \text{Eq. 5.25}$$

$$\mu_v = \mu_l \qquad \text{Eq. 5.26}$$

We said that the conditions of equilibrium need to be valid, therefore T v equals T l equal say T sat, and P v equals P l equals say P sat. This we … want to take as a given, and mu v equals mu l – that is what we said.

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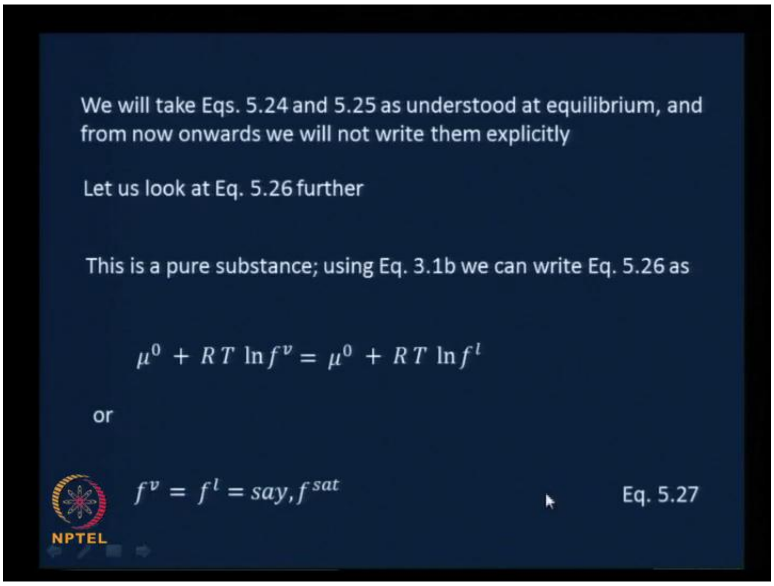

We will take Eqs. 5.24 and 5.25 as understood at equilibrium, and from now onwards we will not write them explicitly

Let us look at Eq. 5.26 further

This is a pure substance; using Eq. 3.1b we can write Eq. 5.26 as

$$\mu^0 + RT\ln f^v = \mu^0 + RT\ln f^l$$

or

$$f^v = f^l = say, f^{sat} \qquad \text{Eq. 5.27}$$

We looked at this particular equation further, and using the expansions or the definitions of the chemical potential in terms of fugacity that we had developed in, or that we had given in module 3, we wrote mu naught plus R T ln f v for mu v equals mu naught plus R T ln f l for mu l. … We could see that the fugacities are equal …. of the pure substance in the vapour phases and the liquid phases.

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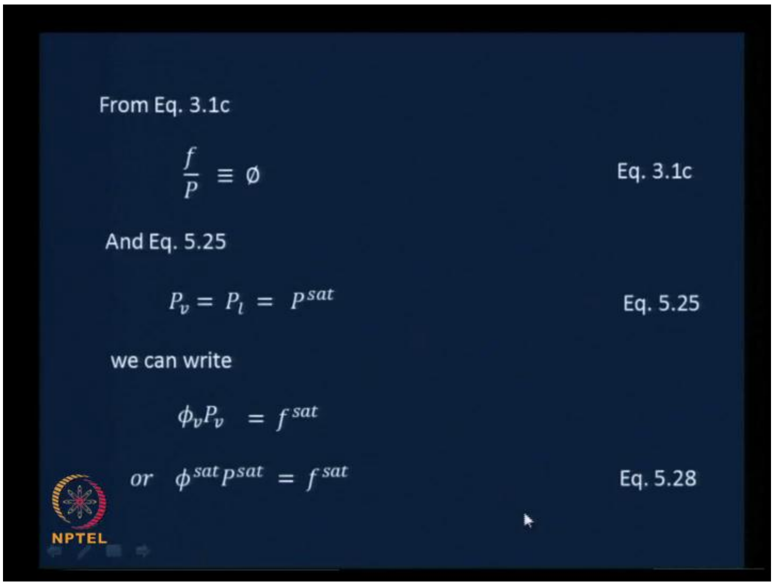

From Eq. 3.1c

$$\frac{f}{P} \equiv \emptyset \qquad \text{Eq. 3.1c}$$

And Eq. 5.25

$$P_v = P_l = P^{sat} \qquad \text{Eq. 5.25}$$

we can write

$$\phi_v P_v = f^{sat}$$

$$or \quad \phi^{sat} P^{sat} = f^{sat} \qquad \text{Eq. 5.28}$$

From this and just the definition of the fugacity coefficient we could write a relationship between the fugacity coefficient and pressure, phi v P v equals f sat. Or, in other words, phi sat you know phi v is nothing but, the value at the saturated value under the conditions of vapour-liquid equilibrium, phi sat P sat equals f sat. This was equation 5.28, and what was the left as an assignment for you was to develop similar expressions for a multi-component system. This is … for a pure component system, and you are asked to develop equations for a multi-component systems. Hopefully, you could do that.

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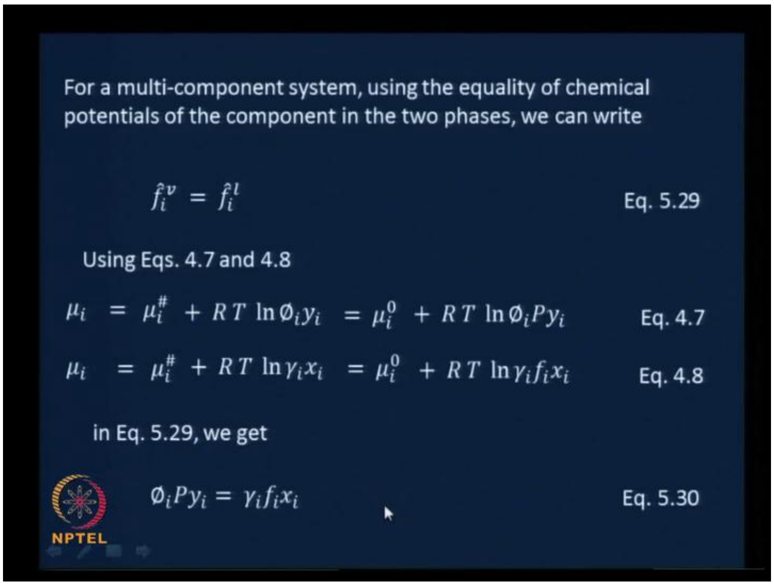

For a multi-component system, using the equality of chemical potentials of the component in the two phases, we can write

$$\hat{f}_i^v = \hat{f}_i^l \qquad \text{Eq. 5.29}$$

Using Eqs. 4.7 and 4.8

$$\mu_i = \mu_i^\# + RT\ln \emptyset_i y_i = \mu_i^0 + RT\ln \emptyset_i P y_i \qquad \text{Eq. 4.7}$$

$$\mu_i = \mu_i^\# + RT\ln \gamma_i x_i = \mu_i^0 + RT\ln \gamma_i f_i x_i \qquad \text{Eq. 4.8}$$

in Eq. 5.29, we get

$$\emptyset_i P y_i = \gamma_i f_i x_i \qquad \text{Eq. 5.30}$$

And, let us see how they look at, now. From … mu i v equals mu i l, for a multi-component system, that is a chemical potential of the species i in the vapour phase must equal the chemical potential of the species i in the liquid phase. And if you expand it as mu naught plus R T ln f i v hat, you know that is how we write … the chemical potential is related to fugacity in the case of a multi-component system. Therefore, f i v hat equals f i l hat is what follows from mu i v equals mu i l we will call this equation 5.29. Using equations 4 7 and 4 8 from module 4 … you will realize what those expressions are; mu i equals mu i hash plus R T ln phi i y I … you know this is what we got in 4 7 and 4 8.

That is mu i naught plus R T ln phi i P y I – 4.7, and mu i equals mu i hash plus R T ln gamma i x i. This is for the liquid phase and this is for the vapour phase. … For the liquid phase, this further equals mu i naught plus R T ln gamma i f i x i. This is equation 4.8, or this was equation 4.8. We said that this is the condition, and if we even if we do not look at it … if we just go ahead and equate these two, … mu i naught, mu i naught will cancel out; R T, R T will cancel out.

Therefore, phi i P y i equals gamma i f i x i. This equation 5.30 is the condition for equilibrium … for a species i. You can write this for a species i at vapour-liquid equilibrium conditions. So, hopefully you would have gotten at this. If not, this is the kind of expression that we were looking for.

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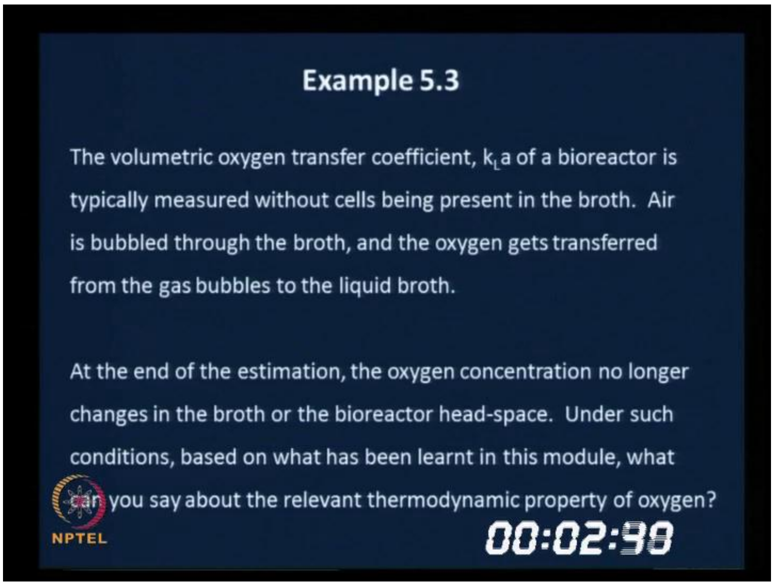

Example 5.3

The volumetric oxygen transfer coefficient, k_La of a bioreactor is typically measured without cells being present in the broth. Air is bubbled through the broth, and the oxygen gets transferred from the gas bubbles to the liquid broth.

At the end of the estimation, the oxygen concentration no longer changes in the broth or the bioreactor head-space. Under such conditions, based on what has been learnt in this module, what can you say about the relevant thermodynamic property of oxygen?

Now let me give you some sort of a real world example, and give you some time to work it out. The answer is very simple, but it requires some bit of thinking. So, I am going to give you enough time for that. The example 5.3 reads as the volumetric oxygen transfer coefficient, k L a, of a bioreactor – volumetric oxygen transfer coefficient is denoted as k L a – k L a of a bioreactor is typically measured without cells being present in the broth. Air is bubbled through the broth, and the oxygen gets transferred from the gas bubbles to the liquid broth.

At the end of the estimation, the oxygen concentration no longer changes in the broth or the bioreactor head-space. Under such conditions, based on what has been learnt in the module, what can you say about the relevant thermodynamic property of oxygen? I have worded it this way for a specific reason, I would like you to go through what we have covered in this module and come up with the solution. The solution is a very, very simple. It is a straightforward thing. It is a very simple thing, but it will require some bit of thought especially, when you are doing it for the first time. And I will just show you the solution when we come back.

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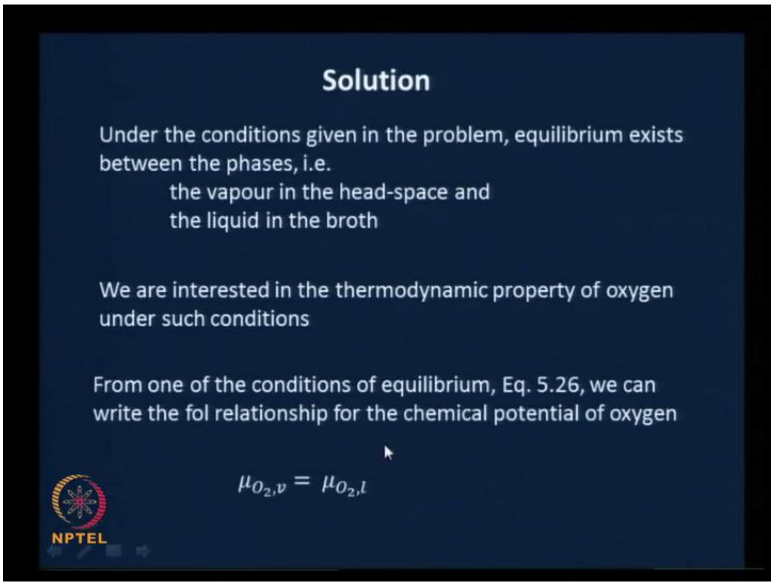

Solution

Under the conditions given in the problem, equilibrium exists between the phases, i.e.

the vapour in the head-space and
the liquid in the broth

We are interested in the thermodynamic property of oxygen under such conditions

From one of the conditions of equilibrium, Eq. 5.26, we can write the fol relationship for the chemical potential of oxygen

$$\mu_{O_2,v} = \mu_{O_2,l}$$

Hopefully you got that simple solution. If not, the thinking is something like this: under the conditions given in the problem equilibrium exists between the phases. Note that there was oxygen that was transferring from the gas bubbles to the liquid phase. And then, after a while, there was no consumption of oxygen anyway, and therefore, the concentration of oxygen in the broth is not going to change.

Therefore, consequently, the head-space oxygen concentration is also going to remain the same. Therefore there has been a condition of equilibrium reached between the liquid and the vapour phases. Or oxygen in the broth and oxygen in the vapour phase reaches a … certain state of equilibrium. These are the phases that are of interest here, the vapour in the head-space and the liquid in the broth. We are interested in the thermodynamic property under such conditions. Of course, the temperature and pressure you need to appropriately look at. But, we are not really going to focus on that.

From one of the conditions of equilibrium, equation 5 26, we can write the relationship for the chemical potential of oxygen. This is what we are looking for, and this is what we are going to write. The relationship for the chemical potential of oxygen is going to be that, the chemical potential of oxygen in the vapour phase must equal the chemical potential of oxygen in the liquid phase. This is the condition that will be valid, under the situation given in the problem. And, from this you can come up with something useful, but that is not in the scope of this particular problem.

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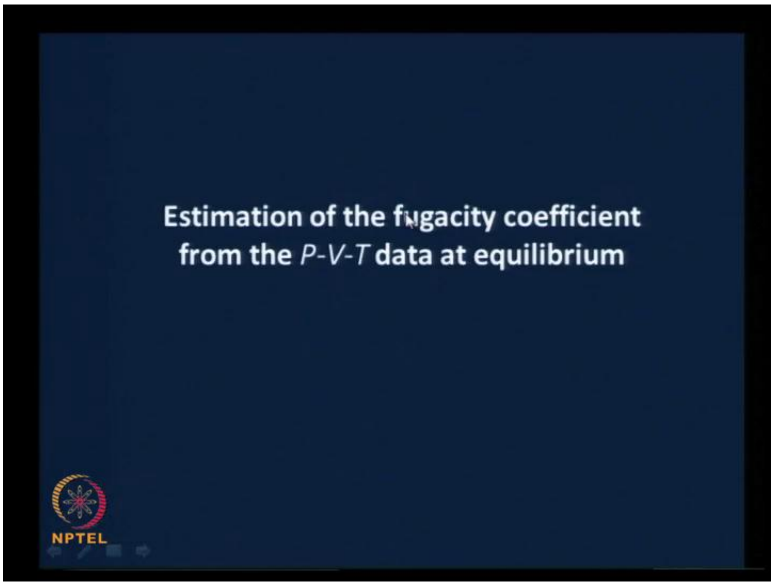

Estimation of the fugacity coefficient from the *P*-*V*-*T* data at equilibrium

So, you would have had a chance to look at whatever we have developed in the context of a real situation. Let us move forward.

What we are going to see next is the estimation of the fugacity coefficient from the pressure, specific volume and temperature data at equilibrium. Note that we have already seen a method of estimating the fugacity coefficient at the end of a previous module. And this is going to be another method from the P V T data at equilibrium.

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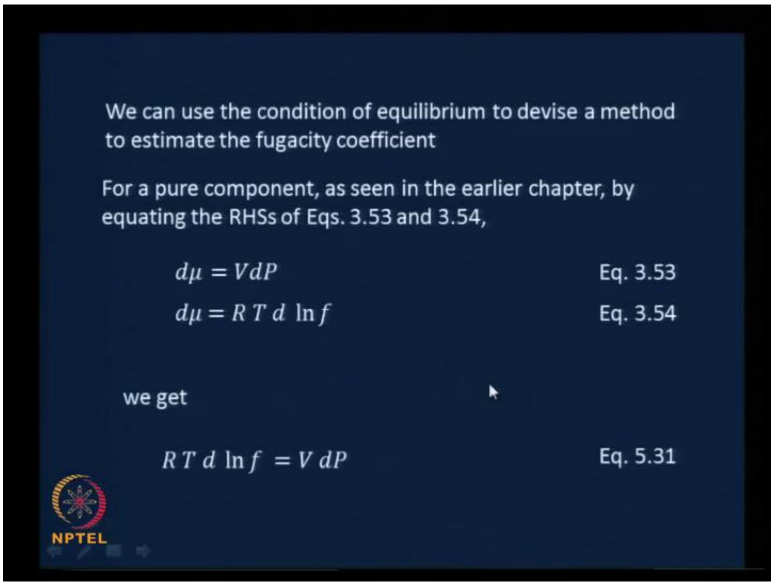

We can use the condition of equilibrium to devise a method to estimate the fugacity coefficient

For a pure component, as seen in the earlier chapter, by equating the RHSs of Eqs. 3.53 and 3.54,

$$d\mu = VdP \qquad \text{Eq. 3.53}$$

$$d\mu = R\,T\,d\,\ln f \qquad \text{Eq. 3.54}$$

we get

$$R\,T\,d\,\ln f = V\,dP \qquad \text{Eq. 5.31}$$

So, we are going to use the condition of equilibrium to devise a method to estimate the fugacity coefficient. For a pure component, we have already seen this equation in module three, d mu equals V d P under certain conditions, this was 3 53. And, d mu equals RT d ln f. This was equation 3.54; f being fugacity. So since these are equal, if we equate these two, we would get R T d ln f equals V dP. Let us call this equation 5.31.

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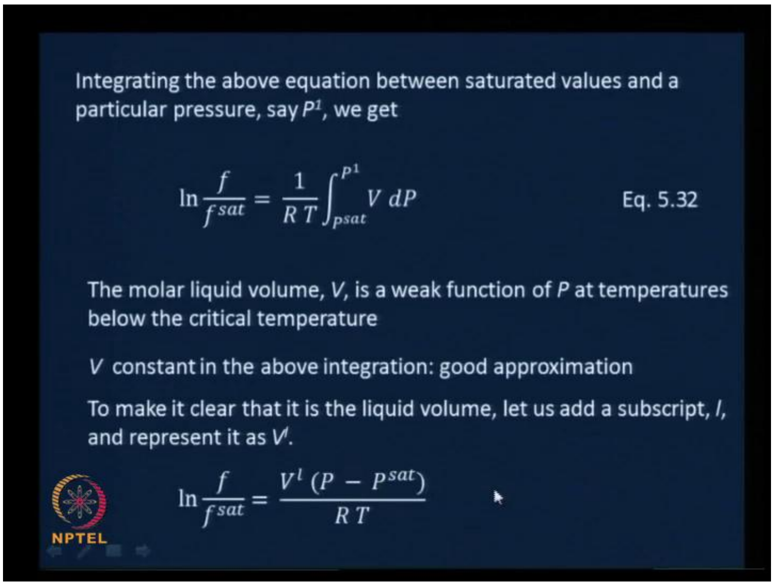

Integrating the above equation between saturated values and a particular pressure, say P^1, we get

$$\ln\frac{f}{f^{sat}} = \frac{1}{R\,T}\int_{P^{sat}}^{P^1} V\,dP \qquad \text{Eq. 5.32}$$

The molar liquid volume, V, is a weak function of P at temperatures below the critical temperature

V constant in the above integration: good approximation

To make it clear that it is the liquid volume, let us add a subscript, l, and represent it as V^l.

$$\ln\frac{f}{f^{sat}} = \frac{V^l\,(P - P^{sat})}{R\,T}$$

If we integrate this expression between saturated value and a particular pressure, let us say, P 1, we would get … this is R T d ln f; we are going to integrate between a saturated pressure and a certain P 1. Therefore, we will have to integrate the right hand side also. First, let us see the left hand side. d ln f – therefore, ln of f by f sat, ln f minus ln f sat, which is going to be ln of f by f sat. That equals 1 by R T integral from P sat to P 1 V dP. Let us call this equation 5.32. If you recall, this is the molar liquid volume. The molar liquid volume is typically a weak function of pressure. At the temperatures well below the critical point, we really do not have to worry about its variation with pressure. Therefore, for all practical purposes of interest, this V can be taken to be a constant in this particular integral – is a very good approximation. What we are going to do now is to avoid the … confusion between the vapour and the liquid phase volumes. We are going to use another subscript l to represent or to make it clear that it is the molar liquid volume. Therefore, we are going to call it as V l – this is actually a superscript; superscript l, and we are going to call it as V l. Therefore, we will get ln of f by f sat equals … this is 1 by R T, … V l is a constant that has come out. Therefore, V l by R T and integral of P sat to P 1 dP is nothing but, … P 1 minus P sat – we just going to drop this `1’ here.

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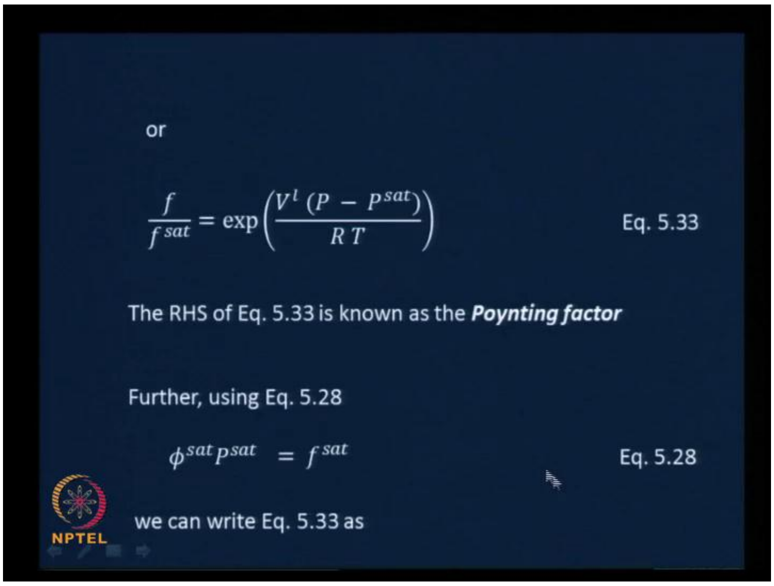

or

$$\frac{f}{f^{sat}} = \exp\left(\frac{V^{l}\,(P - P^{sat})}{R\,T}\right) \qquad \text{Eq. 5.33}$$

The RHS of Eq. 5.33 is known as the ***Poynting factor***

Further, using Eq. 5.28

$$\phi^{sat} P^{sat} = f^{sat} \qquad \text{Eq. 5.28}$$

we can write Eq. 5.33 as

Therefore, P minus P sat. Or f by f sat equals exponential of V l into P minus P sat by RT. Earlier, there was a log here. Therefore, f by f sat becomes exponential of the right hand side. Let us call this equation 5.33. And while we are doing all this, our main aim is to get at an estimate of the fugacity coefficient. Let see, how to go about doing that. This right hand side of this expression is actually called as the Poynting factor. f by f sat equals this exponential of V l P minus P sat by R T – this is the Poynting factor. Further using equation 5.28 become clear right now. phi sat P sat was f sat? Now, this is again, a pure substance.

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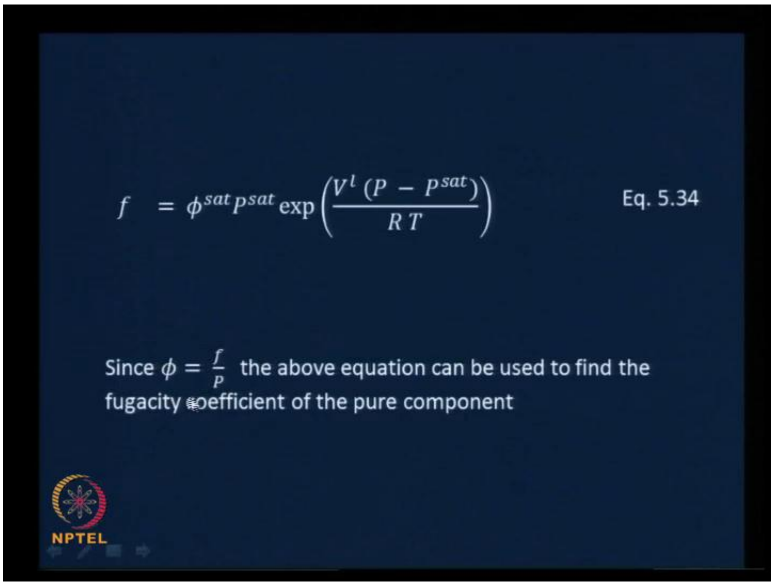

$$f = \phi^{sat} P^{sat} \exp\left(\frac{V^l\,(P - P^{sat})}{R\,T}\right)$$ Eq. 5.34

Since $\phi = \frac{f}{P}$ the above equation can be used to find the fugacity coefficient of the pure component

So phi sat P sat equals f sat is valid here, this was 5.28. We can write 5.33 as f equals phi sat P sat exponential V l, P minus P sat by R T .Now f sat f by f sat was exponential V l P minus P sat by R T. Therefore, f equals f sat exponential V l P minus P sat by R T. We have just replaced f sat by phi sat P sat. Let us call this equation 5.34. Now, phi is nothing but the fugacity coefficient, which is nothing but f by P. Therefore, the above equation can be used to find the fugacity coefficient of a pure component. And that we have somehow arrived at. But, let us clarify that a little further.

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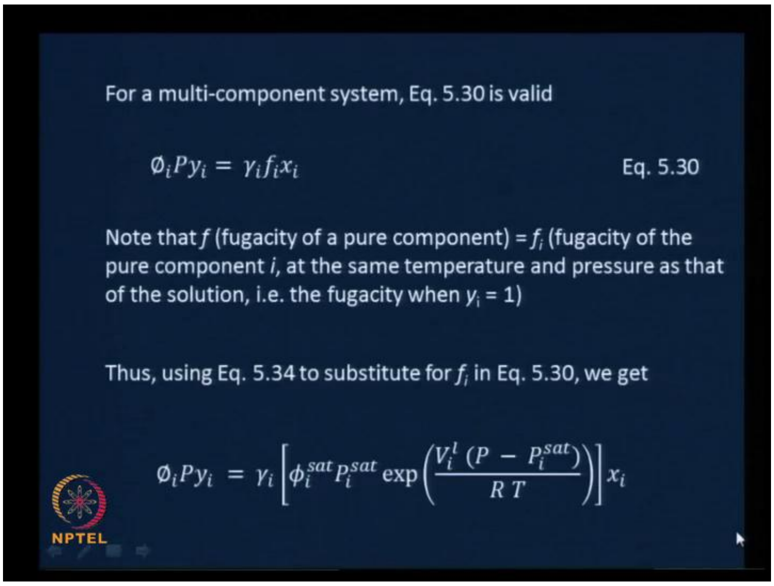

For a multi-component system, Eq. 5.30 is valid

$$\emptyset_i P y_i = \gamma_i f_i x_i \qquad \text{Eq. 5.30}$$

Note that *f* (fugacity of a pure component) = f_i (fugacity of the pure component *i*, at the same temperature and pressure as that of the solution, i.e. the fugacity when $y_i = 1$)

Thus, using Eq. 5.34 to substitute for f_i in Eq. 5.30, we get

$$\emptyset_i P y_i = \gamma_i \left[\phi_i^{sat} P_i^{sat} \exp\left(\frac{V_i^l \, (P - P_i^{sat})}{R\,T} \right) \right] x_i$$

That was for a pure system. We need … to look at a multi-component system – that is what I meant by clarifying further – we need to do it for a multi-component system. For a multi-component system, this equation 5.30 is valid, which is phi i P y i equals gamma i f i x i. This is what we derived … in fact, you had derived, for a multi-component system the condition for equilibrium being this phi i P by i equals gamma i f i x i; equation 5.30.

Note that the f which is fugacity of a pure component equals f i which is the fugacity of the pure component i at the same temperature and pressure as that of the solution; that is the fugacity when y i equals 1, when the mole fraction equals 1.

Therefore, using equation 5 34 to substitute for f i in 5 30, we get phi i P y i that is a left hand side, equals gamma i – same as gamma i here, x i – same as x i here, instead of f i, we are going to write phi i sat P i sat exponential of V i l into P minus P i sat divided by R T. We just substituted f i with the one that includes the Poynting factor here, which can further be written as phi i into P y i which is the left hand side equals gamma i P i sat x i.

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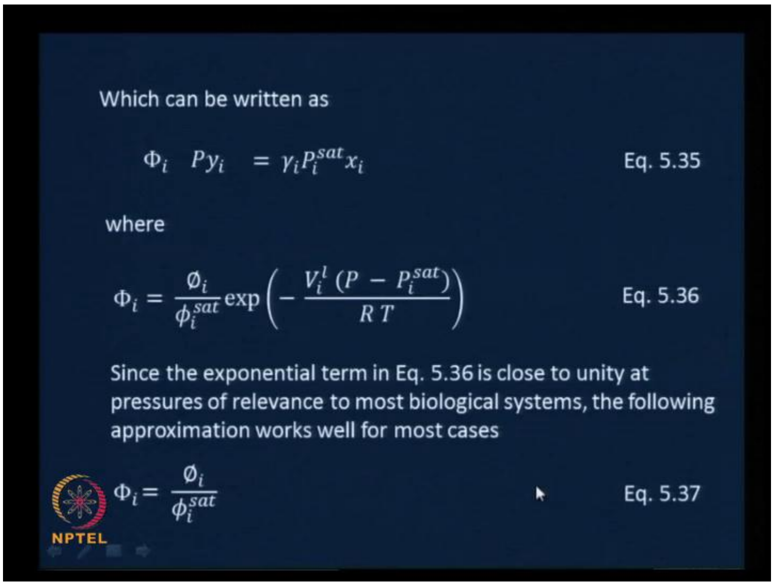

Which can be written as

$$\Phi_i \quad P y_i \; = \gamma_i P_i^{sat} x_i \qquad \text{Eq. 5.35}$$

where

$$\Phi_i = \frac{\emptyset_i}{\phi_i^{sat}} \exp\left(-\frac{V_i^l \,(P - P_i^{sat})}{R\,T}\right) \qquad \text{Eq. 5.36}$$

Since the exponential term in Eq. 5.36 is close to unity at pressures of relevance to most biological systems, the following approximation works well for most cases

$$\Phi_i = \frac{\emptyset_i}{\phi_i^{sat}} \qquad \text{Eq. 5.37}$$

Now, … if you are able to see this … let me show you what phi i is. Then it will become easier. This is what we have here. We have written this expression as … let us call this phi. This is not phi … let us call this fy… fy i into P y i equals gamma i P i sat x i. This means the remaining terms have all been combined into fy i which is what will be shown here, where fy i equals phi i divided by phi i sat exponential of minus V i l P minus P i sat by R T. Let us call this equation 5.36.

What usually happens is that the exponential term is close to unity at pressures of relevance to most biological systems, which is typically atmospheric pressures and so on and so forth. Therefore, this term can just be replaced with a 1 for most biological systems. The following approximation works very well which is fy i equals phi i by phi i sat – equation 5.37.

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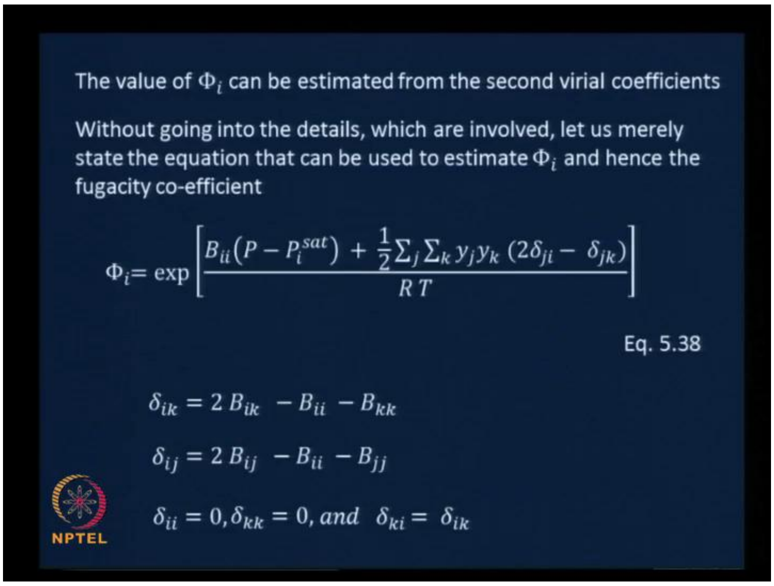

The value of Φ_i can be estimated from the second virial coefficients

Without going into the details, which are involved, let us merely state the equation that can be used to estimate Φ_i and hence the fugacity co-efficient

$$\Phi_i = \exp\left[\frac{B_{ii}(P - P_i^{sat}) + \frac{1}{2}\Sigma_j \Sigma_k y_j y_k\,(2\delta_{ji} - \delta_{jk})}{R\,T}\right]$$

Eq. 5.38

$$\delta_{ik} = 2\,B_{ik} - B_{ii} - B_{kk}$$

$$\delta_{ij} = 2\,B_{ij} - B_{ii} - B_{jj}$$

$$\delta_{ii} = 0, \delta_{kk} = 0, \text{ and } \delta_{ki} = \delta_{ik}$$

The value of fy i can be estimated from the second virial coefficients. Remember that B 1 1, B 1 2 and so on so forth; we can use that to estimate fi i, I am just going to state it here. I am not going to derive it here. Derivation requires probably some understanding of statistical mechanics. So, since that is outside the scope of this course, I am just going to mention this here. fy i equals this complicated expression. Let me just read it out to you … equals exponential of B i i P minus P i sat plus half and twice sum over j and k y j y k 2 delta j i minus delta j k. I will tell you what deltas are delta 2 delta j i minus delta j k divided by R T. This is equation 5.38, where delta i k equals 2 B i k minus B i i minus B k k and delta i j equals 2 B i j minus B i i minus B j j, and delta i i equals 0, delta k k equals 0, and delta k i equals delta i k. Therefore, there is a way of estimating this fy i from the second virial coefficients. And going back, you can get the other quantity that we are looking for.

What we did in this particular section is to look at a way or a method of estimating the fugacity coefficient from the conditions of vapour-liquid equilibrium. Since the other things are slightly different, let us start them in the next class. We will stop here for this class. See you then.