Thermodynamics for Biological Systems:
Classical and Statistical Aspects

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Lecture – 43
Estimation of Fugacity Coefficient from P-V-T Data At Equilibrium

Welcome!

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. This is going to be another method from the P V T data at equilibrium.

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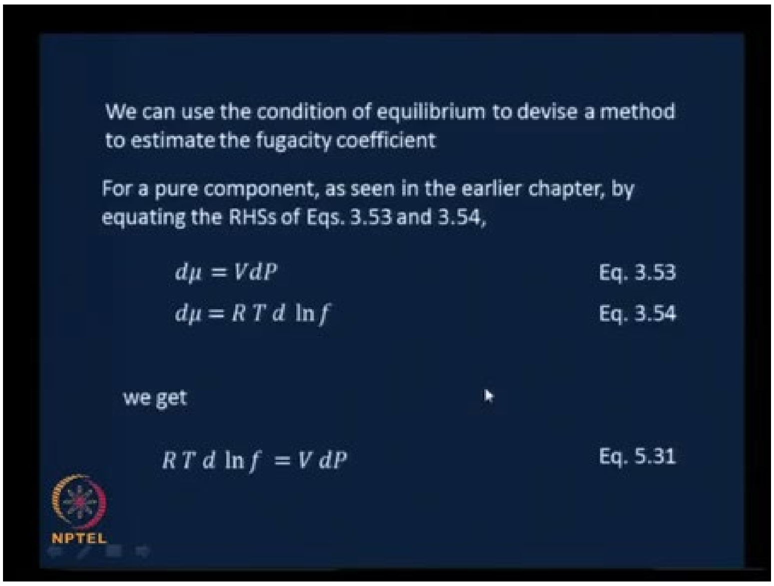

We can use the condition of equilibrium to devise a method to estimate the fugacity coefficient

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,

$$d\mu = VdP$$

This was 3 53. And,

$$d\mu = R\,T\,d\,\ln f$$

This was equation 3.54; f being fugacity. So since these are equal, if we equate these two, we would get

$$R\,T\,d\,\ln f = V\,dP$$

Let us call this equation 5.31.

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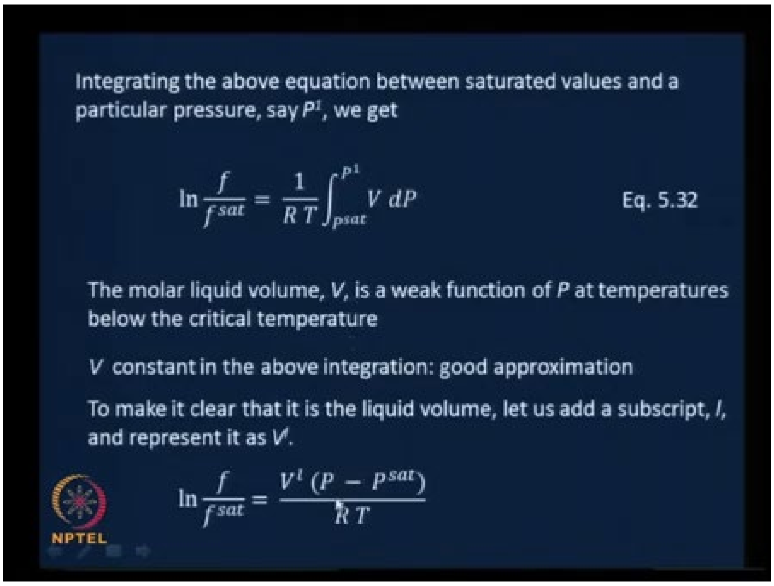

Integrating the above equation between saturated values and a particular pressure, say P^1, we get

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

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, we are going to integrate between a saturated pressure and a certain P1. Therefore, we will have to integrate the right hand side also.

$$\ln \frac{f}{f^{sat}} = \frac{1}{R\,T}\int_{Psat}^{P1} V\,dP$$

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

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

we just going to drop this `1' here.

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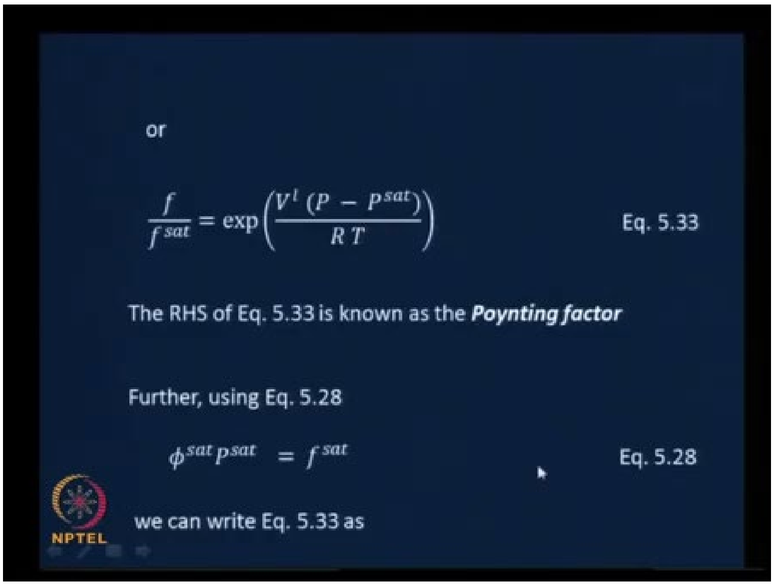

or

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

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,

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

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.

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. Further using equation 5.28 become clear right now. phi sat P sat was f sat? Now, this is again, a pure substance. So

$$\phi^{sat} P^{sat} = f^{sat}$$

This was 5.28.

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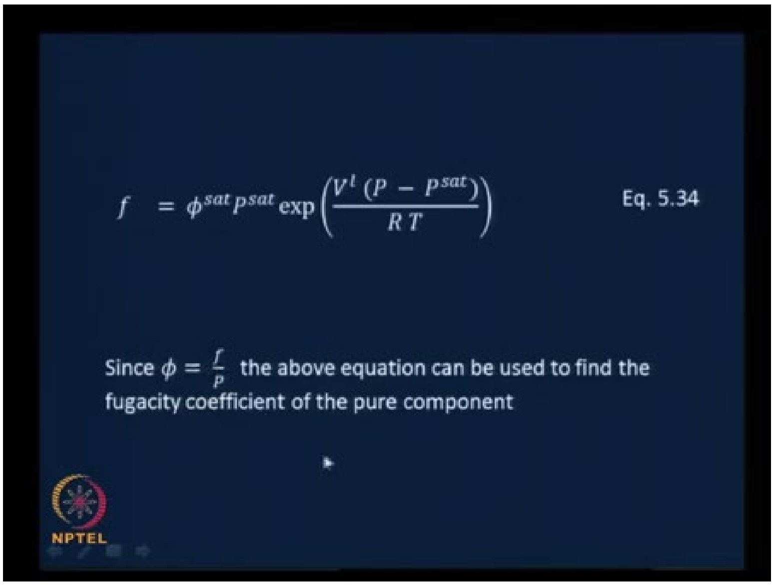

$$f = \phi^{sat} P^{sat} \exp\left(\frac{V^l (P - P^{sat})}{R\,T}\right)$$ Eq. 5.34

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

We can write 5.33 as

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

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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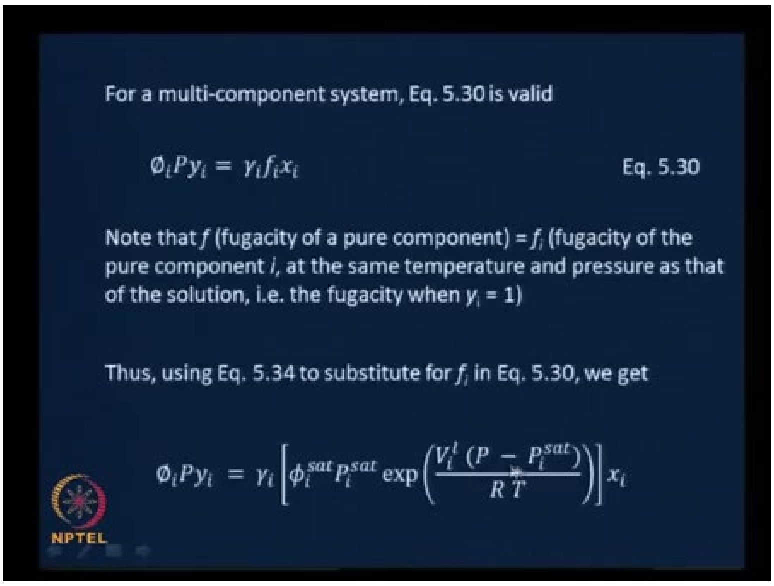

For a multi-component system, Eq. 5.30 is valid

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

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

$$\emptyset_i P y_i = \gamma_i f_i x_i$$

Note that the f which is fugacity of a pure component equals fi 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

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

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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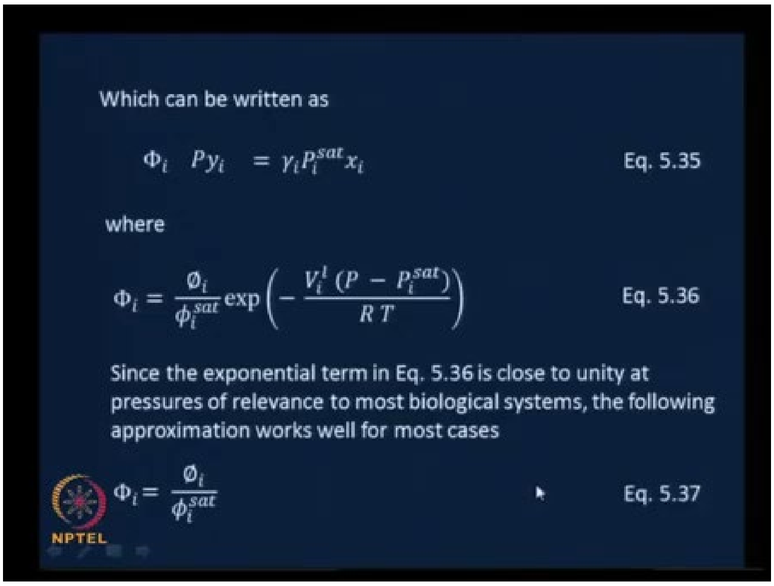

Which can be written as

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

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

$$\Phi_i \quad Py_i \; = \; \gamma_i P_i^{sat} x_i$$

This means the remaining terms have all been combined into fy i which is what will be shown here, where

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

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. Therefore, this term can just be replaced with a 1 for most biological systems. The following approximation works very well which is

$$\Phi_i \; = \; \frac{\emptyset_i}{\phi_i^{sat}}$$

equation 5.37.

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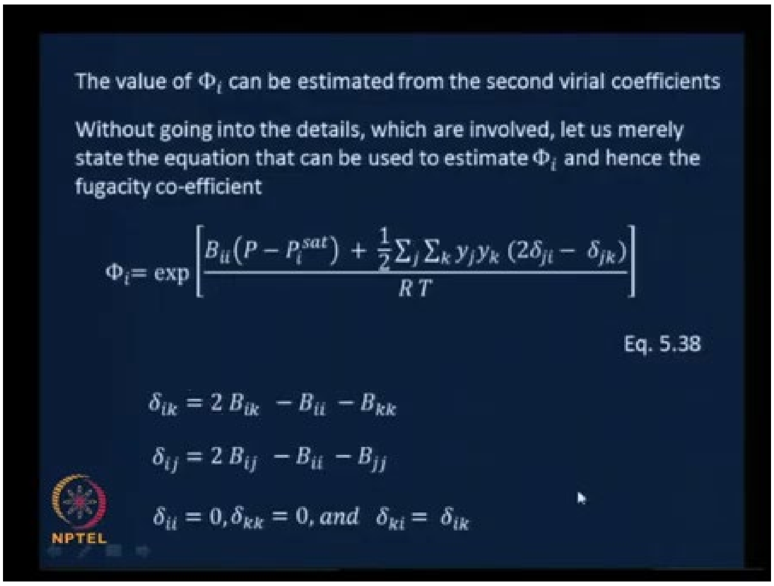

The value of Φ_i can be estimated from the second virial coefficients

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_{11}, B_{12} 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. I am just going to mention this here. fy i equals this complicated expression. Let me just read it out to you … equals

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

This is equation 5.38, where

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

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

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

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 in the next class.