Thermodynamics for Biological Systems:
Classical and Statistical Aspects

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Lecture – 42
Vapour Liquid Equilibrium (Contd.,)

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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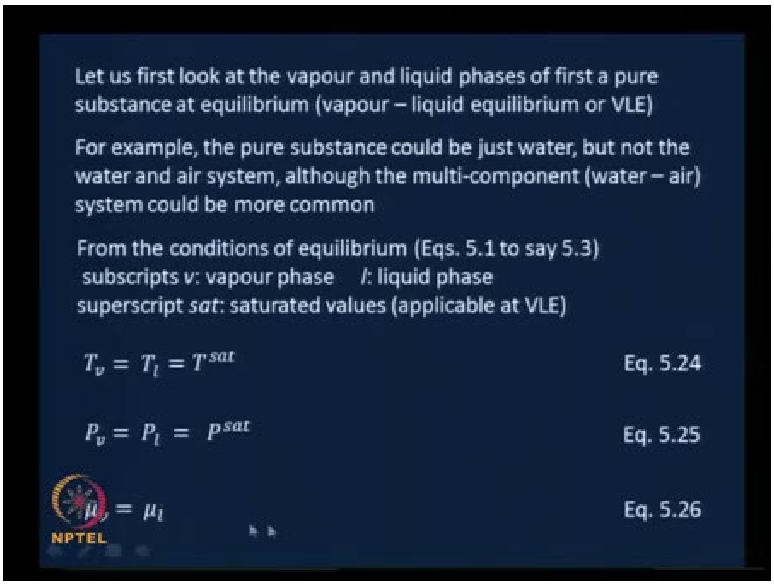

Let us first look at the vapour and liquid phases of first a pure substance at equilibrium (vapour – liquid equilibrium or VLE)

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)

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

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

$\mu_v = \mu_l$ Eq. 5.26

We said that the conditions of equilibrium need to be valid, therefore

$$T_v = T_l = T^{sat}$$
$$P_v = P_l = P^{sat}$$

This we … want to take as a given, and

$$\mu_v = \mu_l$$

that is what we said.

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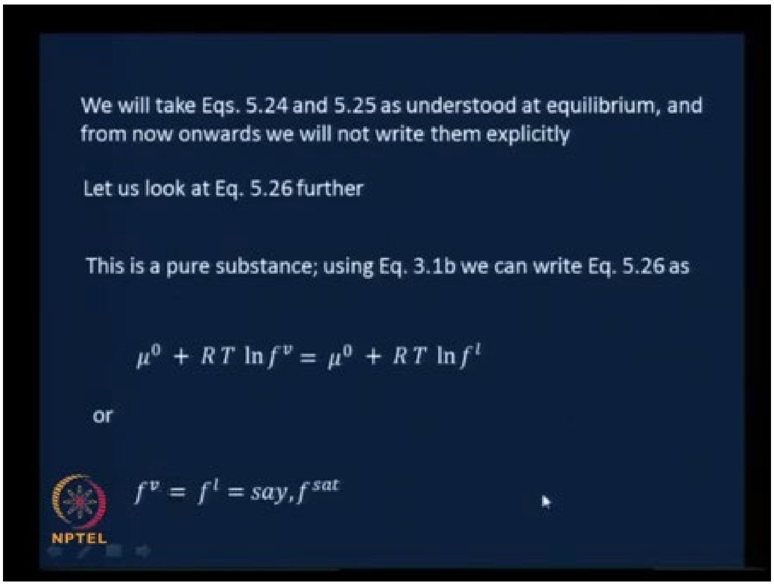

We will take Eqs. 5.24 and 5.25 as understood at equilibrium, and from now onwards we will not write them explicitly

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

$$f^v = f^l = say, f^{sat}$$

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

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

We could see that the fugacities are equal …. of the pure substance in the vapour phases and the liquid phases.

$$f^v = f^l = say,\ f^{sat}$$

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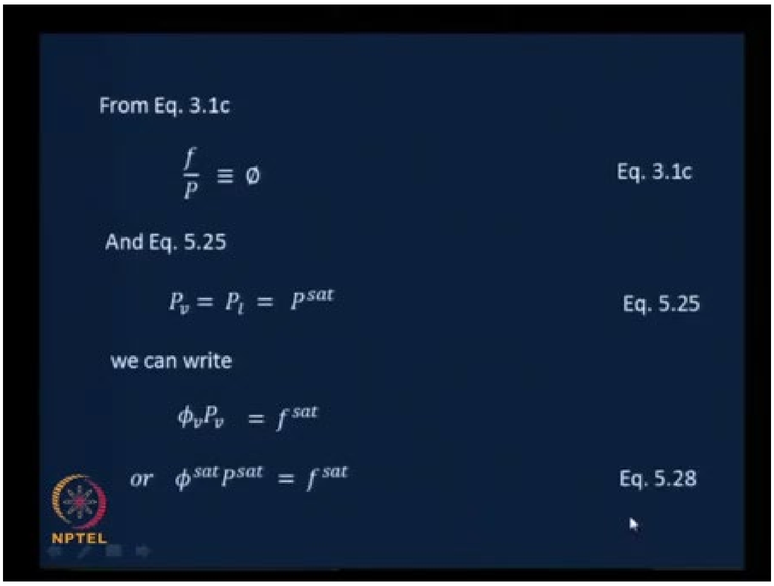

From Eq. 3.1c

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

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,

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

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,

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

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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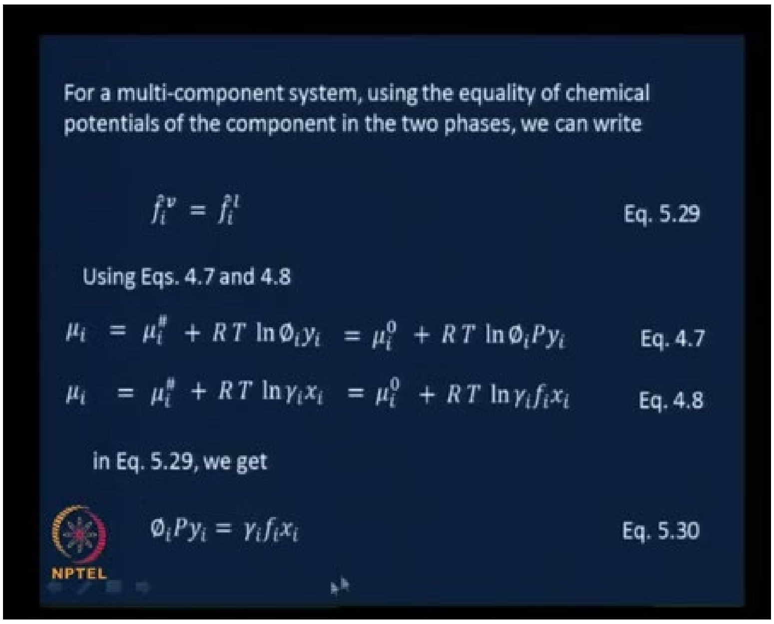

For a multi-component system, using the equality of chemical potentials of the component in the two phases, we can write

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

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. 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,

$$\hat{f}_i^v = \hat{f}_i^l$$

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 … this is what we got in 4 7 and 4 8.

That is

$$\mu_i = \mu_i^\# + RT\ ln\, \emptyset_i y_i = \mu_i^0 + RT\ ln\, \emptyset_i P y_i$$

This was equation 4.8 for the vapour phase. For the liquid phase:

$$\mu_i = \mu_i^\# + RT\ ln\, \gamma_i x_i = \mu_i^0 + RT\ ln\, \gamma_i f_i x_i$$

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,

$\phi_i P y_i = \gamma_i f_i x_i$

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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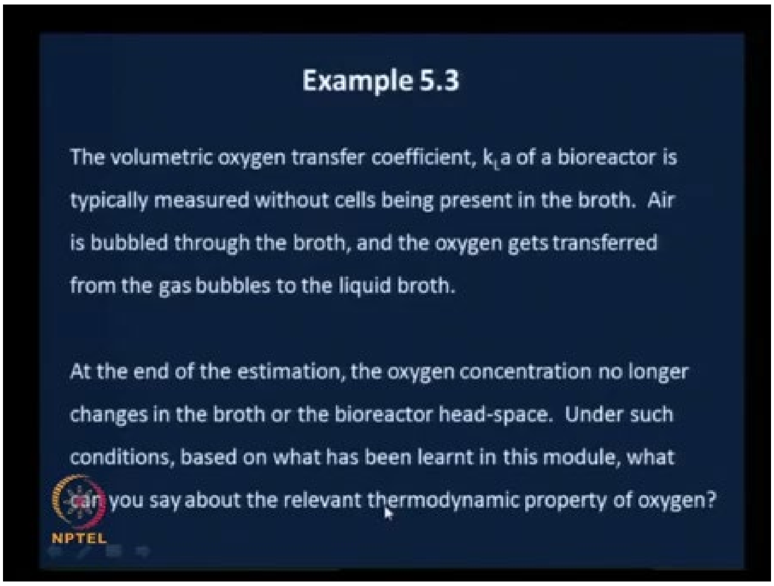

Example 5.3

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_La, of a bioreactor – volumetric oxygen transfer coefficient is denoted as k_La – 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 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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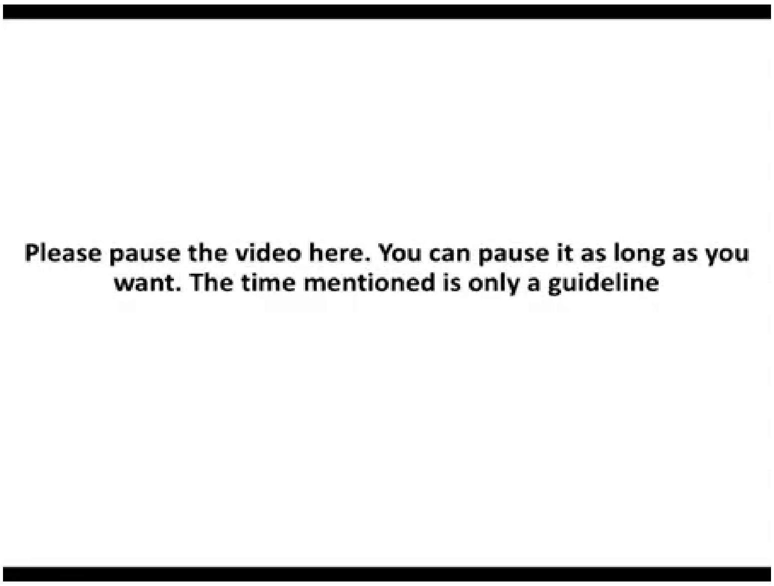

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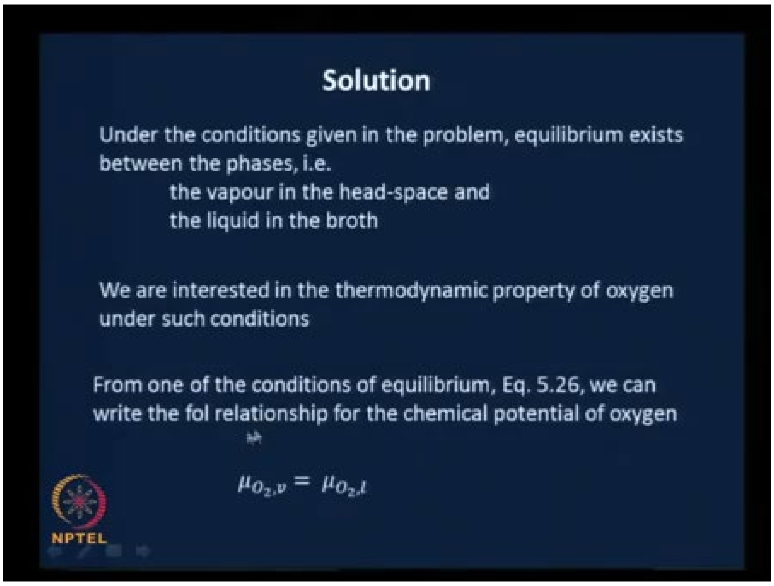

Solution

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

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.

See you in the next class.