Thermodynamics for Biological Systems:
Classical and Statistical Aspects
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Lecture – 17
Volume Estimation

Welcome!

In the last class, we looked at two cubic equations of state. We said the advantages in using cubic equations are that it can handle both gases and liquid behaviour or predictions. The two equations that we saw among the many there are available, were the Vander Waals equation of state, which you may have some familiarity with from the some earlier classes, and also the Redlich-Kwong equation of state. And we also saw a means by which we can calculate the constants a, and b in those two equations. And the rationale for that calculation was left as an exercise towards the end of the class, last class.

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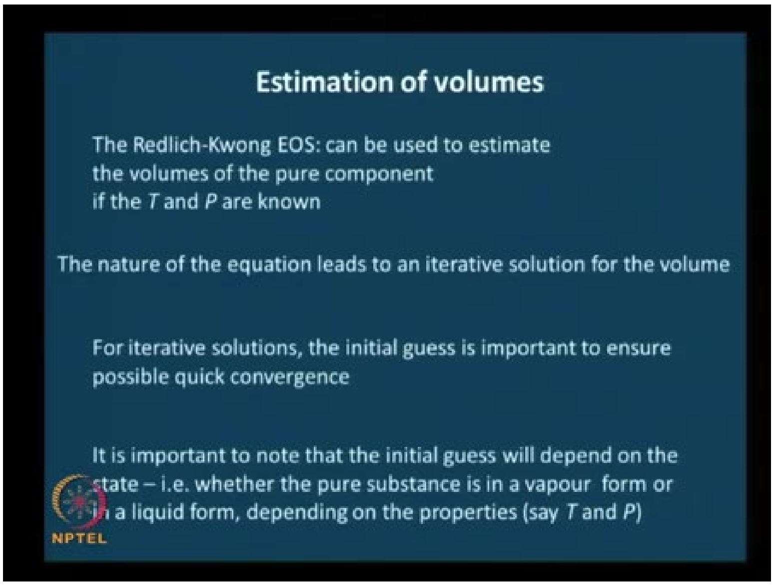

Now, we will start looking at estimation of volumes using the cubic equations of state. Let me use the Redlich-Kwong equation of state to estimate the volumes; it is a little new. You can use a similar thing for Vander Waals also. So, the Redlich-Kwong educational state can be used to estimate the volumes of pure substances. … Recall that the module deals only with pure substances – this module, if the temperature and pressure are known. We know that … from the very name that these are cubic equations; and therefore, we need to necessarily solve them iteratively for volume. So, we will write equations appropriately, and then solve it. And, we also saw from the previous exercise that for iterative solutions, the initial guess is very important to ensure quick convergence, as well as correctness of the values.

Suppose, the function is like this and you start with a different initial value, you might end up with a solution that may not be even relevant for the case in question. Therefore, some more insights are required apart from a regular mathematical treatment to know where you are operating. More importantly, we said that the cubic equations can handle both, the vapour behaviour or the gas behaviour as well as the liquid behaviour.

The vapour volumes are going to be very different from the liquid volumes. May be hundreds of times more one volume of liquid approximately 500 to 800 volumes of the gas. Therefore, they could be two or three orders of magnitude different. And therefore, the initial guess depends on the state that we are dealing with. In other words whether the pure substance is in a vapour form or in a liquid form will determine the initial guess that we are going to make. And this of course, will depend on the properties, temperature and pressure. Later in the course, we will see how to actually fix the number of variables that are required to know this state of a system.

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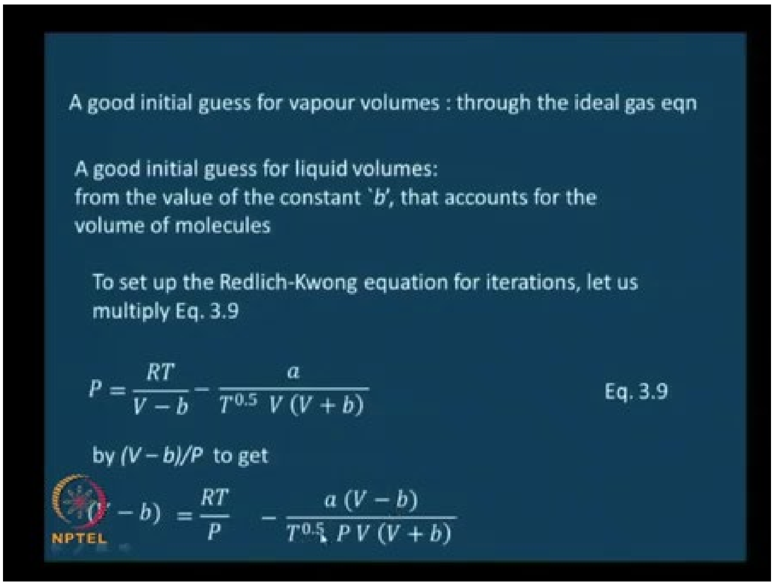

Let us first consider vapour volumes. A good initial guess for vapour volumes is very easy; this is what we chose in the last exercise also. That is the volume that comes from the application of the ideal gas equation. And a good initial guess for liquid volumes may not be that obvious right now. But consider the constant b that appears in the Vander Waals equation for example, Vander Waals, we are familiar with. You know there is a V minus b that comes in there. That b essentially accounts for the volume of molecules in the gas and we are subtracting that to get if of the form that was suitable for that equation of state. Therefore, the value of b that accounts for the volume of molecules could be a very good initial value or an initial guess to start with, if one is interested in finding out liquid volumes. Therefore, for a gas volume or a vapour volume it is an ideal gas equation, the volume come that comes out of that, and for the liquid volumes the constant b is a good initial gas.

Now, let us set up the Redlich-Kwong equation for iterations. In the last exercise, we set up something else for iterations. Here we will set up the Redlich-Kwong equation for iterations. To do that this is the Redlich Kwong equation

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}\ V\,(V+b)}$$

this is nothing but equation 3.9, the Redlich-Kwong equation. We will multiply both sides by V minus b by P. Note, we need to have V on this side as well as V on this side for an iterative solution. The iterative solution becomes necessary, because the cubic nature of the equation.

So, if we focus on V on this side and V on this side to get rid of P, let us multiply V minus b by P. If we do that here, we need to do that on the right hand side also. And if we do that, P and P will get cancelled, V minus b would remain, here V minus b V minus b would get cancelled and the first term would be R T by P. And, here again, we need to multiply by V minus b by P which would result in

$$(V - b) = \frac{RT}{P} - \frac{a\,(V-b)}{T^{0.5}\ P\,V\,(V+b)}$$

Therefore, we can transpose this equation, and also write it in terms of n plus 1, and n, which will be suitable for iterations. We always said that we have a guessed value, then we calculate the value, then we compare … a calculated value to guessed value till a certain level of convergence.

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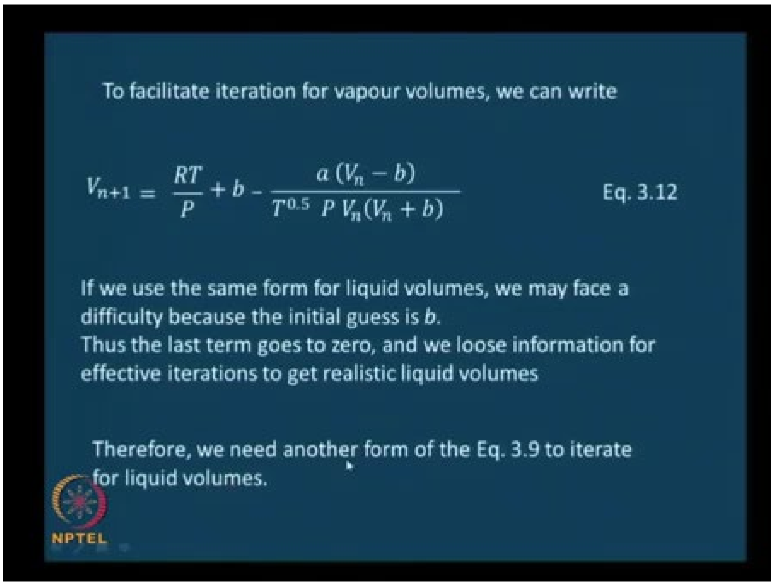

And therefore, the guessed value could be n and calculated value could be n plus one. If we do that, this equation becomes

$$V_{n+1} = \frac{RT}{P} + b - \frac{a\,(V_n - b)}{T^{0.5}\ P\, V_n (V_n + b)}$$

Let us call this equation 3.12. Now, this is fine for vapour volumes; and with an initial guess that comes out of the ideal gas equation of state, we had been able to ultimately get to the actual molar volume.

Whereas, note the form of the equation here, we have a V n minus b. Therefore, if our initial guess is going to be b, this term is going to get out completely. And therefore, this is a big loss of information here, to get … to be able to do effective iterations to get realistic liquid volumes. Therefore, this is not the form that we would like to employ for doing iterations to get to liquid volumes.

Therefore, we need another form of this equation, either equation 3.9, which is the Redlich-Kwong equation. I think that is the better place to start. Here, we cannot really do much. Therefore, let us start with the Redlich-Kwong equation itself, which is 3.9 and write in a form that will allows us to overcome this difficulty and iterate to get the liquid volumes.

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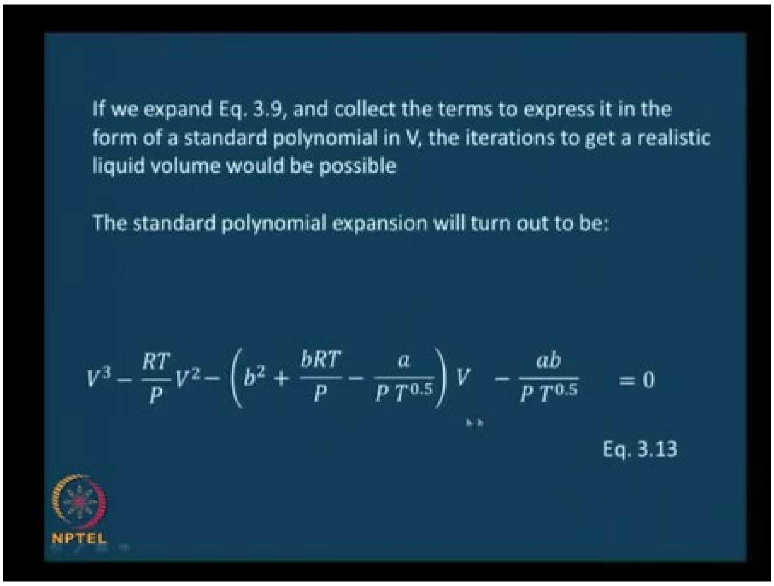

If we expand 3.9, you know we had 3.9 was this … P equals R T into V minus b minus a by T power 0.5 V into V plus b. Now, multiply … reduce this side to a common denominator, then cross multiply here, and so on and so forth. If we do all that we will get a polynomial expression in terms of V and that polynomial expression would turn out to be … please do this exercise and convince yourself that this is indeed what you are getting, and also check whether there are any errors in this … we will get

$$V^3 - \frac{RT}{P}V^2 - \left(b^2 + \frac{bRT}{P} - \frac{a}{P\,T^{0.5}}\right)V - \frac{ab}{P\,T^{0.5}} = 0$$

It comes from nothing but a regular production … or simplification initially and then, an expansion of the Redlich-Kwong equation, algebraically speaking. Let us call this equation 3.13.

For the iteration itself, we said we could have it of the form of V n plus 1 and V n. Let us write it as V n plus 1, you know … this was where does the V occur here – it occurs here. And therefore, we could write this as V n here. And, by a suitable transposition all these terms could go to the other side – these two terms and this term, and therefore, this becomes the denominator on the other side.

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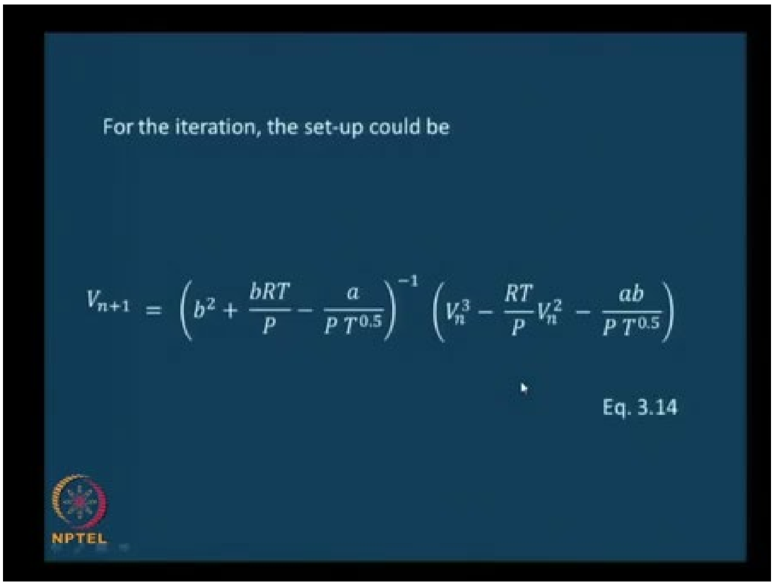

$$V_{n+1} = \left(b^2 + \frac{bRT}{P} - \frac{a}{P\,T^{0.5}}\right)^{-1}\left(V_n^3 - \frac{RT}{P}V_n^2 - \frac{ab}{P\,T^{0.5}}\right)$$

This is a nice way to set up the equation, you could write a program to do this, so that you do not have to go and the calculations, for finding out liquid volumes. Let us call this equation 3.14.

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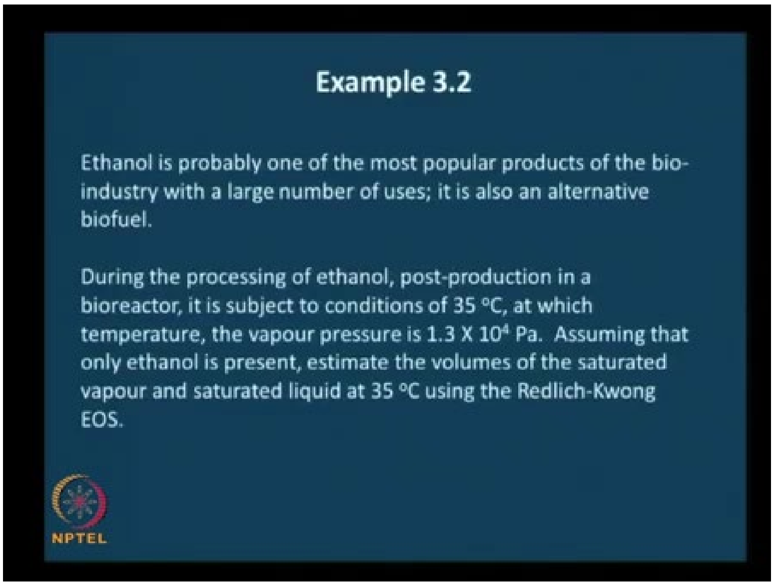

To see how to apply this … to get more comfortable with the process itself, iterative process, and to recognize that gases volumes and liquid volumes are two distinct entities that could be obtained from the same equation, let us do this example 3.2. Ethanol is probably one of the most popular products of the bioindustry with a large number of uses. This I do not have to tell you already know that ethanol is a very popular product. It is also an alternative biofuel. You know the blending of ethanol with gasoline is done very routinely nowadays in some countries to the extent of about 15 to 20 percent and some other countries, 5 to 10 percent. They have different targets to meet by which … to the extent to which they can blend ethanol, so that they could reduce the cause of the fossil fuel … the amount of fossil fuel that is being used.

As you all know ethanol comes predominantly from a biological route; *Saccharomyces cerevisiae* produces ethanol, and that produces your alcoholic beverages also. During the processing of ethanol, post production in a bioreactor, after being produced in a bioreactor, it is subject to conditions of 35 degree C, at which temperature, the vapour pressure is 1.3 into 10 power 4 Pascals. Assuming that only ethanol is present, you know we are dealing with pure substances in this module. So, let us make an assumption here that only ethanol is present in this particular process, in this particular situation.

Assuming that only ethanol is present, estimate the volumes of the saturated vapour and the saturated liquid at 35 degrees C using the Redlich-Kwong equation of state. Go ahead think about this for 5 minutes and then I will give you a couple of hints. 5 minutes please.

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Now, that you have thought through it, if you have an idea to work it out, go ahead and work it out. Stop the lecture and here and work it out. If not, you can make use of this hint, I am going to give you one hint at a time. First I will you about 5 minutes to process it and then ultimately much longer time before I present the complete solution to you.

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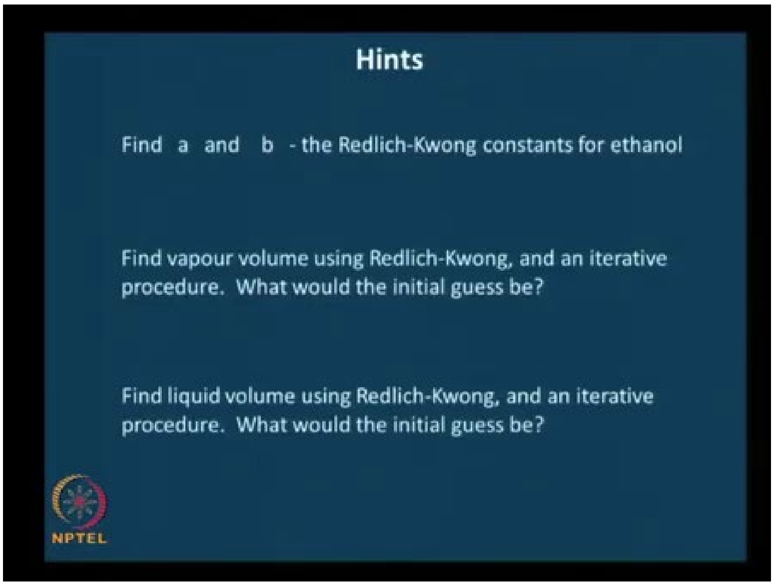

The next hint, find vapour volume using Redlich-Kwong equation of state, and an iterative procedure; and I would like you to think about what would the initial guess be? Think about this and solve this. It so, happens that this particular iteration, if we choose appropriate initial guess, converges within two steps. And, therefore, take about 5 minutes to do this. Then I will give you the next hint.

Now, go ahead and solve or complete the process for these two steps, if you have not already done so. And since this involves some calculations, I think you should take about 10 minutes to do it. Go ahead please.

Now, let me give you the next hint, and also give you the remainder of the class, which has another 5 minutes left. And whatever time it needs to completely solve the problem. Why I need to give you that much time? I will tell you in a minute, I will tell you very shortly. The next hint is to find the liquid volume using the Redlich-Kwong equation of state and an iterative procedure. And what would the initial guess be in this case is something that you would want to consider.

This iteration takes about five or six steps for convergence. And therefore, take the remainder of this class, and whatever time it takes as home work, to complete the solution. In the next class, I will start by presenting the solution.

See you in the next class.