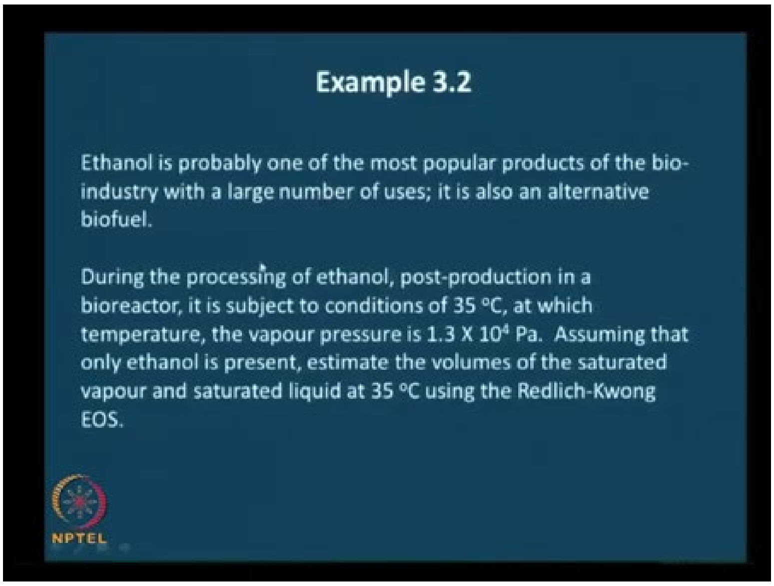
Thermodynamics for Biological Systems:
Classical and Statistical Aspects
Prof. G.K. Suraishkumar
Department of Biotechnology
Indian Institute of Technology - Madras

Lecture – 18
Volume Estimation Contd.,

Welcome back!

We had started to look at this problem yesterday, example 3.2. Let me read it out again for completeness, today.

(Refer Slide Time: 00:27)

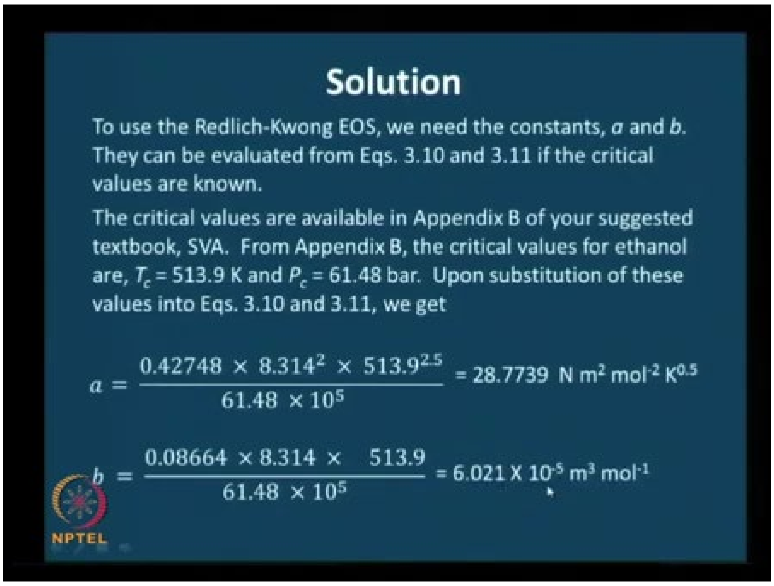


Ethanol is probably one of the most popular products in the bio industry with the large number of uses. It is also an alternative bio fuel. During the processing of ethanol post production in the bioreactor, it is subject to conditions of 35 ^{o}C, at which temperature, the vapour pressure is 1.3 X 10^4 pascals. Assuming that only ethanol is present, estimate the volumes of the saturated vapour and the saturated liquid at 35 degree C using the Redlich-Kwong equation of state. This was the problem or the example that was presented. And then, I had also given you some hints and time to work it out. Hopefully you had worked out the solution in full. We will any way present the solution now, after these hints.

(Refer Slide Time: 01:04)

The hints were to use the Redlich-Kwong equation, we need to find the Redlich-Kwong constants, constants a, and b for ethanol, and I had asked you to find that out first. You had to look at the appropriate appendix. And then find the vapour volume using the Redlich-Kwong equation, and an iterative procedure. The question was what would the initial guess be? The initial guess is the ideal … the volume that one obtains from the ideal gas equation. And then the other hint was to find out the liquid volume, which is the next part of the solution using the Redlich-Kwong equation of state and an iterative procedure. In this case, the initial guess was going to be the volume of the molecules as given by the constant b.

(Refer Slide Time: 02:11)



So, the solution itself in terms of numbers to for you, to verify yours. The constants a, and b can be obtained from the equations that give the constants in terms of the critical values. The critical values are available in the appendix B, this is the actual appendix … of Smith, VanNess, and Abbott, which gives you the values of the critical parameters, critical temperature, critical pressure. And from appendix B, the critical values of ethanol are critical temperature T_c is 513.9 Kelvin and the critical pressure is 61.48 bar. It will be good to visualize, what exactly these mean in terms of your P V diagram, P versus v diagram. The top point of the dome with under which you have the saturated region. Or in the P T diagram it is essentially the point at the end point of the line, the vaporisation line there.

Upon substitution of these values into equation 3.10 and 3.11, which give you the expressions for a, and b.

$$a = \frac{0.42748 \times 8.314^2 \times 513.9^{2.5}}{61.48 \times 10^5} = 28.7739 \text{ N m}^2 \text{ mol}^{-2} \text{ K}^{0.5}$$

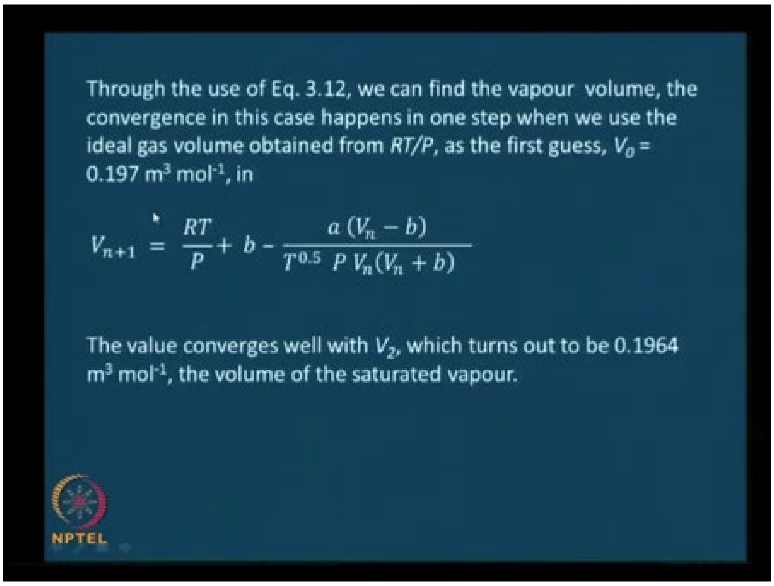
I am giving you 4 digits here, because this is the calculation, 4 is reasonably fine. When you are working with experimental values you need to be a little careful with the number of digits that you get here. Although your calculations would give you a large number of digits, your calculator would give you a large number of digits, they usually do not make much sense given the accuracy with which the measurements can themselves be made.

The confidence with which measurements can be made is probably limited to 1 or 2 decimal places after this and therefore, it may not make sense to give experimental values in terms of a large number of decimal places. Whenever, it becomes relevant I will mention it again. But, in this case it is OK. `a' turns out to be 28.7739 … Newton meter squared per mole squared Kelvin to the power of 0.5. Similarly,

$$b = \frac{0.08664 \times 8.314 \times 513.9}{61.48 \times 10^5} = 6.021 \text{ X } 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

This is the volume of the molecules.

(Refer Slide Time: 05:28)



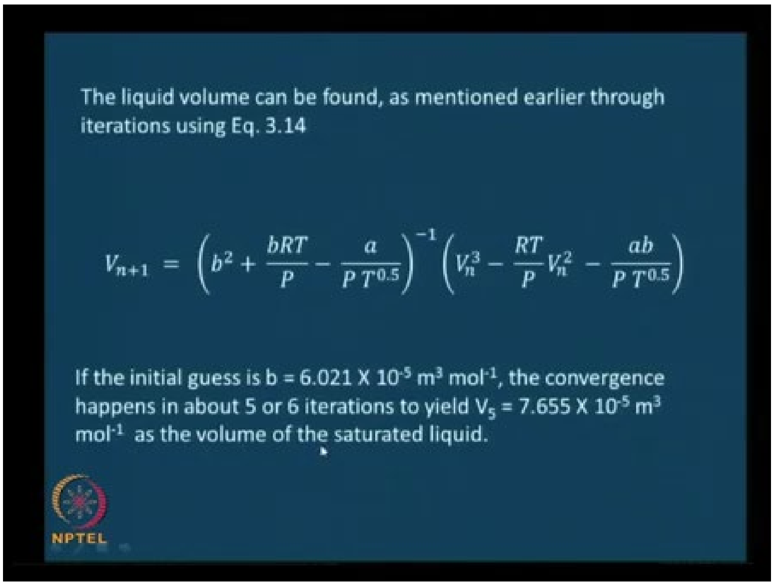
Now, that we have this, the second part is to find out the gas volumes and that can be … or the vapour volume, and that can be done through the equation of 3.12. You can go back and check it is essentially an equation that is set up to find out volumes for a gas. The convergence in this case for this iterative solution happens in one step or in two steps.

When we use the ideal gas volume, … if we look at RT by P as the initial guess V_0, which is the initial guess turns out to be 0.197 meter cubed per mole. And this is the equation that we considered for the iteration.

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

V 2, which is after two iterations turns out to be 0.1964 meter cubed per mole; and since the difference between this and the V 1 value is less than certain acceptable percent in this case very less, this can be taken as the volume of the saturated vapour. This is nice – it just turned out that the solution was close to the initial guess. So, we did not have to do too many iterations. Sometimes we may have to do a large number of iterations, in which case it is best to feed this into a computer that does it or write a program, computer program, that does it in terms of excel and so on so forth … MS excel. Or, write a program to do it in terms of any of these standard programming languages.

(Refer Slide Time: 07:14)



So, this is the second part. The third part was to find out the liquid volume. This … again … the liquid volume, we needed to use another formulation to avoid the dropping of the second term, because you had a V minus V term earlier, if you recall that. You can go back and check why we had used a different polynomial formulation for this iterations … this set of iterations.

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

If we do the iterations here with an initial guess, as b t,he volume of the molecules 6.021 X 10^{-5} m^3 mol^{-1}, the convergence happens in about 6 iterations to give you a value of 7.655 X 10^{-5} m^3 mol^{-1} as the volume of the saturated liquid.

So, that is the numerical solution. Please check it. If you have any doubts, any clarifications that are needed you can always get back.

See you in the next class.