Thermodynamics for Biological Systems:
Classical and Statistical Aspects
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Lecture – 41
Vapour Liquid Equilibrium

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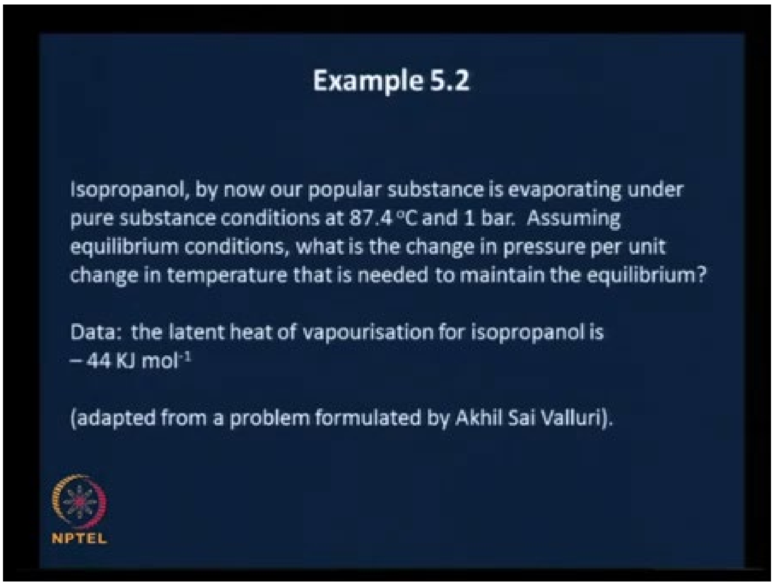

Example 5.2

Isopropanol, by now our popular substance is evaporating under pure substance conditions at 87.4 °C and 1 bar. Assuming equilibrium conditions, what is the change in pressure per unit change in temperature that is needed to maintain the equilibrium?

Data: the latent heat of vapourisation for isopropanol is – 44 KJ mol^{-1}

(adapted from a problem formulated by Akhil Sai Valluri).

Welcome!

We were looking at the solution to this example problem, which involved the use of the Clausius-Clapeyron equation. The problem itself was isopropanol is evaporating under pure substance conditions at 87.4 degree C and 1 bar. Assuming equilibrium conditions, what is the change in pressure per unit change in temperature that is needed to maintain equilibrium, and the latent heat of vaporization of isopropanol is given.

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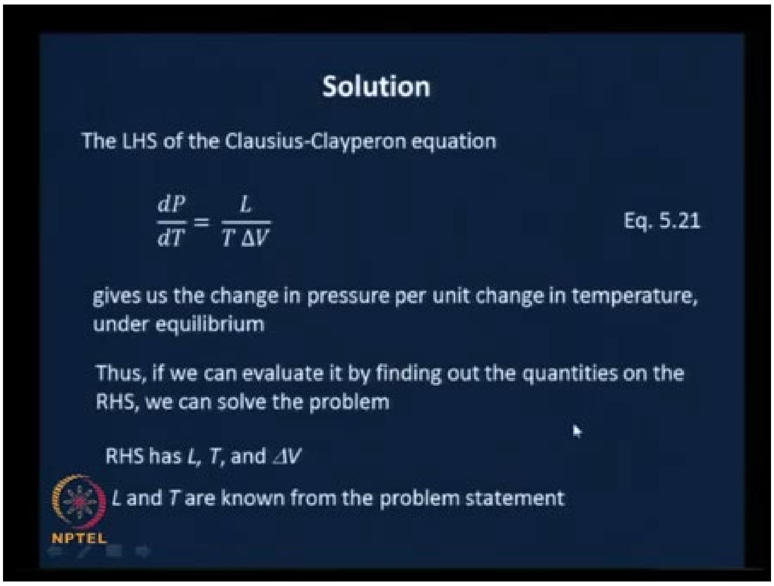

Solution

The LHS of the Clausius-Clayperon equation

$$\frac{dP}{dT} = \frac{L}{T\,\Delta V} \qquad \text{Eq. 5.21}$$

gives us the change in pressure per unit change in temperature, under equilibrium

Thus, if we can evaluate it by finding out the quantities on the RHS, we can solve the problem

RHS has L, T, and ΔV

L and T are known from the problem statement

We saw that we needed to use the Clausius-Clapeyron equation, to get $\frac{dP}{dT}$, which is the quantity that we need. … We also … realized that the values of L and T are given; and therefore, if we know delta V, which is V of the gas or V of the vapour minus V of the liquid, the molar volume differences, then, we can find $\frac{dP}{dT}$, and get the quantity of interest. … We also noted or recognized that the way to go about finding out the volumes of the gas, and the liquid was through the use of an equation of state, a suitable equation of state.

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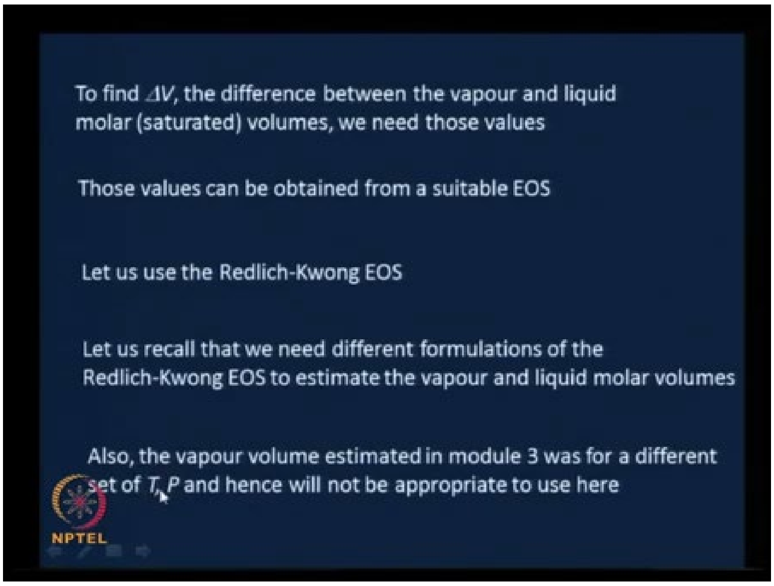

To find ΔV, the difference between the vapour and liquid molar (saturated) volumes, we need those values

Those values can be obtained from a suitable EOS

Let us use the Redlich-Kwong EOS

Let us recall that we need different formulations of the Redlich-Kwong EOS to estimate the vapour and liquid molar volumes

Also, the vapour volume estimated in module 3 was for a different set of T, P and hence will not be appropriate to use here

Now, let me give you some more details, and then let you work out the actual numbers. For this particular problem, since we have seen the Redlich-Kwong equation of state earlier, as some sort of an improvement over the initial equations of state, we will use the Redlich-Kwong equation of state here. If you recall what we did in module 3, we actually needed different formulations of the Redlich-Kwong equation of state to estimate the vapour and liquid molar volumes, because the formulation for the vapour volume had a V minus b term. If we had used that with an initial guess of V equals b, then that term would have completely gone to 0. … We would have completely eliminated that term and not had the benefit of the contribution of that term into our estimations.

Also, the vapour volume estimated was for a different set of temperature and pressure. If you recall we had estimated the vapour volume in module 3. We cannot use it here, because that was for a different temperature and pressure; if we recall correctly, it was around 200 degrees C and a pressure of 10 bar. At that pressure it is going to be a complete vapour. It is not going to be in a state of equilibrium between the liquid and vapour phases.

… Here, in this problem, it is vaporizing, which means it is in a state of equilibrium between the liquid and vapour phases. This point is somewhere, along the vaporization line in the P T diagram. Therefore, we cannot use the value that we calculated earlier. We will have to do the estimations all over again.

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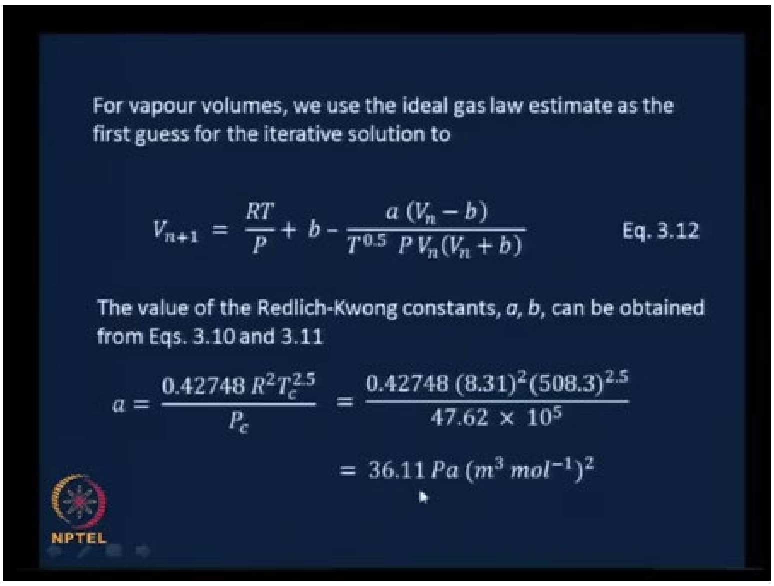

For vapour volumes, we use the ideal gas law estimate as the first guess for the iterative solution to

$$V_{n+1} = \frac{RT}{P} + b - \frac{a\,(V_n - b)}{T^{0.5}\;P\,V_n(V_n + b)} \qquad \text{Eq. 3.12}$$

The value of the Redlich-Kwong constants, *a*, *b*, can be obtained from Eqs. 3.10 and 3.11

$$a = \frac{0.42748\,R^2 T_c^{2.5}}{P_c} = \frac{0.42748\,(8.31)^2(508.3)^{2.5}}{47.62 \times 10^5}$$

$$= 36.11\,Pa\,(m^3\,mol^{-1})^2$$

Therefore, let us start with the iterations… This is the iterative form that we found to be most useful for finding out the vapour volumes

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

So, we saw that if we put in a guessed value of V n, we get a calculated value of V n plus 1.

By calculating the right hand side, and if we find out the difference between the calculated value and the guessed value to be close enough or the difference to be negligible enough, then we can stop the iterations. `Negligible enough' – we said it should be, let us say, within 1 or 2 percent of the guessed value. The value of the Redlich-Kwong constants, a and b, can be obtained from equations 3 10 and 3 11 in module 3. We have already done this as a part of an earlier solution in module 3. I would like you to go back and revisit that if you have forgotten, and to get back into the frame of mind for solving this particular problem.

$$a = \frac{0.42748\,R^2 T_c^{2.5}}{P_c} = \frac{0.42748\,(8.31)^2 (508.3)^{2.5}}{47.62 \times 10^5} = 36.11\ Pa\,(m^3\,mol^{-1})^2$$

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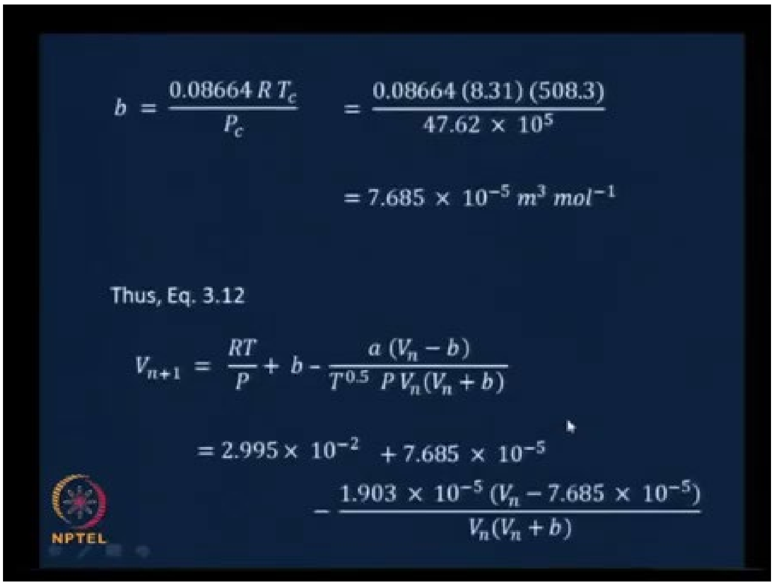

$$b = \frac{0.08664\,R\,T_c}{P_c} = \frac{0.08664\,(8.31)\,(508.3)}{47.62 \times 10^5}$$

$$= 7.685 \times 10^{-5}\ m^3\,mol^{-1}$$

Thus, Eq. 3.12

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

$$= 2.995 \times 10^{-2} + 7.685 \times 10^{-5} - \frac{1.903 \times 10^{-5}\,(V_n - 7.685 \times 10^{-5})}{V_n(V_n + b)}$$

And

$$b = \frac{0.08664\,R\,T_c}{P_c} = \frac{0.08664\,(8.31)\,(508.3)}{47.62 \times 10^5} = 7.685 \times 10^{-5}\ m^3\,mol^{-1}$$

Now we have a and b values; we can iterate the Redlich-Kwong equation, written appropriately for iterations, to get the vapour volume which is this. This is the equation that we are going to use.

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

$$2.995 \times 10^{-2} + 7.685 \times 10^{-5} - \frac{1.903 \times 10^{-5}\,(V_n - 7.685 \times 10^{-5})}{V_n(V_n + b)}$$

This V n is our first guessed value, and we said we could use the ideal gas equation value for the first guess, because this is the vapour phase.

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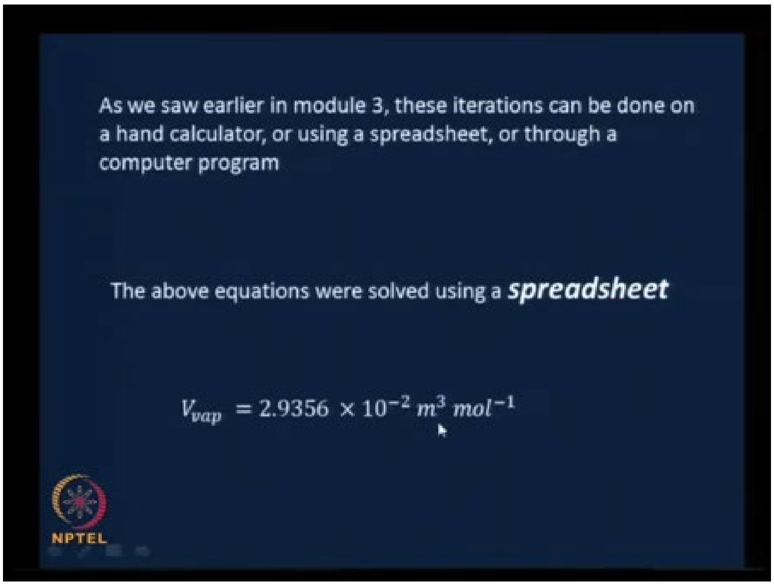

As we saw earlier in module 3, these iterations can be done on a hand calculator, or using a spreadsheet, or through a computer program

The above equations were solved using a ***spreadsheet***

$$V_{vap} = 2.9356 \times 10^{-2}\ m^3\ mol^{-1}$$

So, if we do that … first estimate using the ideal gas equation. Then, use that as the first guess and then, calculate the value. Find out the difference between the values. See whether it is acceptable. If it is not acceptable, use the calculated value as the next guessed value, and so on and so forth … then we can get the solution. … We also saw that these iterations can be done on either a hand calculator or a spreadsheet or a computer program … you can do it whichever way you want it. But what I am going to show you here is the use of a standard spreadsheet for doing these calculations. … I will show you one, and probably let you do the other.

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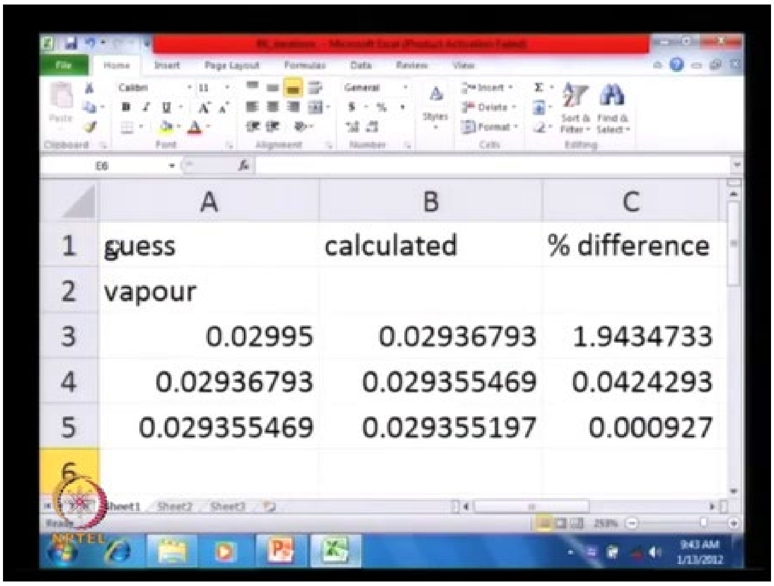

	A	B	C
1	guess	calculated	% difference
2	vapour		
3	0.02995	0.02936793	1.9434733
4	0.02936793	0.029355469	0.0424293
5	0.029355469	0.029355197	0.000927
6			

To look at this spreadsheet … you know, this is the first column is the guess value, the second column is going to be the calculated value. Guess value, you know, our initial guessed value is going to be 0.02995, which comes from the ideal gas equation P V equals R T. Therefore, V equals R T by P, and that is going to be 0.02995.

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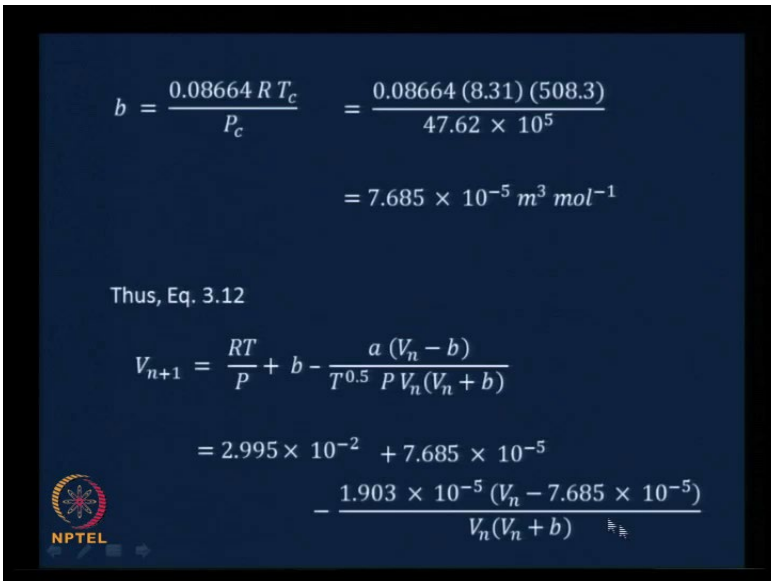

$$b = \frac{0.08664\, R\, T_c}{P_c} = \frac{0.08664\,(8.31)\,(508.3)}{47.62 \times 10^5}$$

$$= 7.685 \times 10^{-5}\ m^3\ mol^{-1}$$

Thus, Eq. 3.12

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

$$= 2.995 \times 10^{-2} + 7.685 \times 10^{-5} - \frac{1.903 \times 10^{-5}\,(V_n - 7.685 \times 10^{-5})}{V_n (V_n + b)}$$

You can recall this … this R T by P is 2.995×10^{-2} and this is our nothing but our ideal gas volume.

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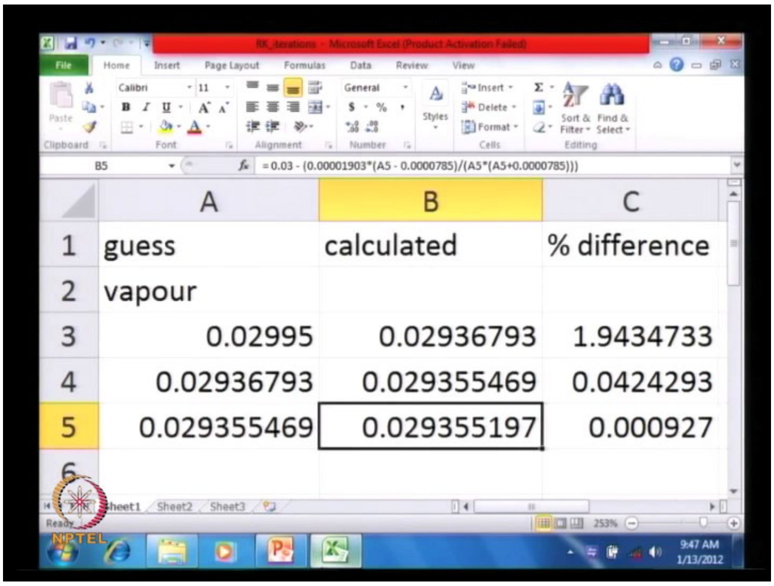

B5 =0.03 - (0.00001903*(A5 - 0.0000785)/(A5*(A5+0.0000785)))

	A	B	C
1	guess	calculated	% difference
2	vapour		
3	0.02995	0.02936793	1.9434733
4	0.02936793	0.029355469	0.0424293
5	0.029355469	0.029355197	0.000927
6			

Therefore, this is what we are going to use as the first guess, 0.02995, this value. Then, if we calculate all those R T by P plus b and so on, and so forth, whatever was in the right hand side, we would get 0.0293673. … The way we calculated is given here. You know … these are the terms on the right hand side. I just substituted these terms; 0.02995 I have approximated as 0.03 minus the a into A 3. This happens to be the volume that is guessed minus b divided by V n into V n plus b. So, this turns out to be 0.0293 and so on.

So, now the main thing is, "what is your percentage difference? It turns out to be 1.94 percent which is reasonably fine". In fact, we can stop our iterations here, if about 2 percent is allowed. But, let us go little further since we seem to have hit upon the value within 1iteration. Let us go about further and improve the accuracy of our value. And also this helps to demonstrate how to do the iterations. Now let us assume that this is not an acceptable percentage. Let us say that we are looking for a percentage which is less than 10 power minus 3 or 10 power minus 4; 10 power minus 3 is a good value.

So, we take the calculated value, put it into the guessed value, calculate the value again. This is the same equation that was used to calculate the value. Now you find that the guessed value was 0.02936 so on. And the calculated value turns out to be 0.029355 so on. And the percentage difference is… a percentage difference was calculated as A4, which is this minus B4, which is this difference divided by a 4 into hundred; that turns out to be 0.042, which is a very small percentage – acceptable here. But we said 10 power minus 3 in this case. Well … it is still not

10 power minus 3 here.

So, we go through the next iteration 0.029355. So, on we put in here we calculate the value again. Here, you … can simply calculate the value by control-d – copies the formula, from here to here, and calculates this value. Here it turns out to be 0.029355197 … very close to this. And actually, the percentage difference turns out to be 9.27 X 10^{-4}. This is definitely less than 10^{-3}. Therefore, this becomes acceptable, and we can choose this as our gas volume.

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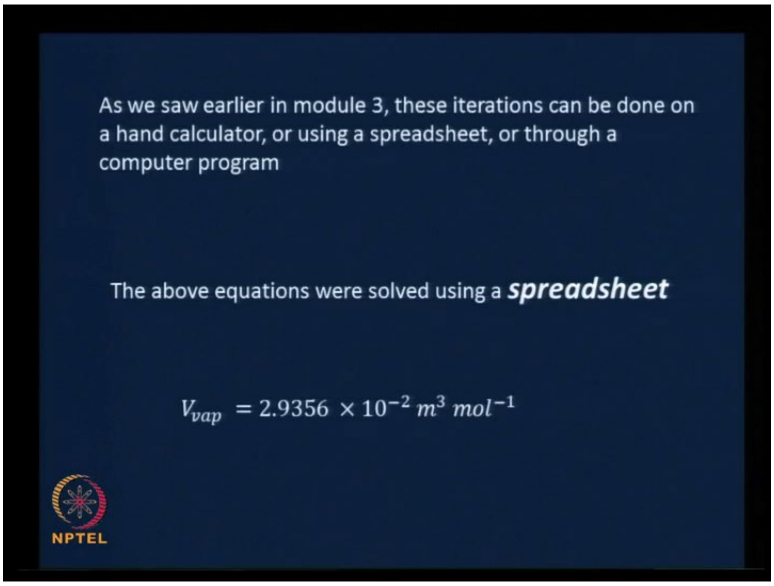

As we saw earlier in module 3, these iterations can be done on a hand calculator, or using a spreadsheet, or through a computer program

The above equations were solved using a ***spreadsheet***

$$V_{vap} = 2.9356 \times 10^{-2}\, m^3\, mol^{-1}$$

So, that is what have done. We have chosen V vapour as $V_{vap} = 2.9356 \times 10^{-2}\, m^3\, mol^{-1}$. Now, this is only the vapour volume, we still need the liquid volume. the liquid volume, we said, requires a different frame work; we have already seen this. So, I am just going to state it here.

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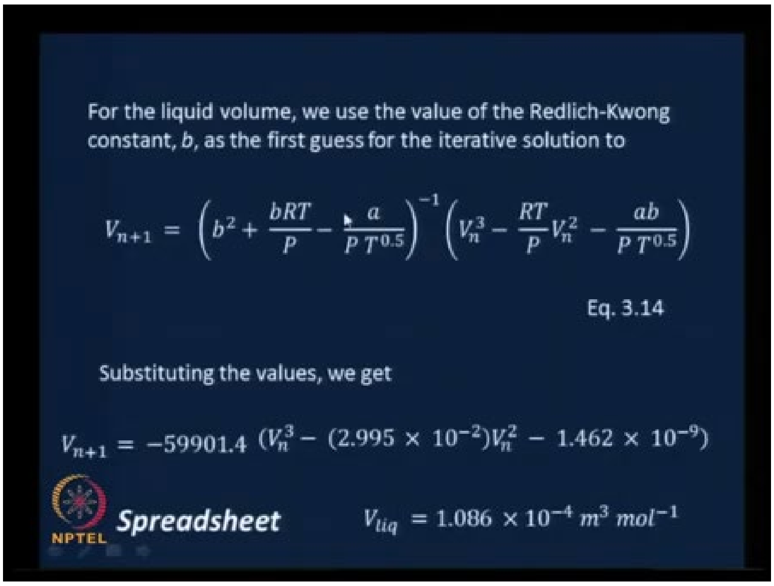

For the liquid volume, we use the value of the Redlich-Kwong constant, *b*, as the first guess for the iterative solution to

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

Eq. 3.14

Substituting the values, we get

$$V_{n+1} = -59901.4\,(V_n^3 - (2.995 \times 10^{-2})V_n^2 - 1.462 \times 10^{-9})$$

Spreadsheet $V_{liq} = 1.086 \times 10^{-4}\ m^3\ mol^{-1}$

This was the way in which, we have cast the Redlich-Kwong equation by an appropriate manipulation, to overcome the difficulty that was posed by the previous … iterative formulation. And we have seen this earlier – equation 3 14; you can go back and check how we got this. … To be able to do this, I think, we have all the values. We have b, we have R T …yes, a. As long as we keep substituting the appropriate guessed values, we will get the calculated value. And we said that the first guessed value, a first good guess would be the value of b, which represents the volume of molecules that are present in the liquid – present in the pure substance. In a liquid form,these would be close together and therefore, the volume of molecules can be approximated to the volume of the liquid, and that is how we take b as the first guess here.

… What I would like you to do now … I am going to give you another 20 minutes this time, because these are calculations and you are going through this. Please set up iteration scheme on this spreadsheet that I have shown earlier and do the calculations. Use b as the first guessed value and see how you get. I will show you the calculations when we come back. Please go ahead and do this. This will help you get used to the iterations, and spreadsheet is a nice way of doing the iterations. Go ahead please, 20 minutes.

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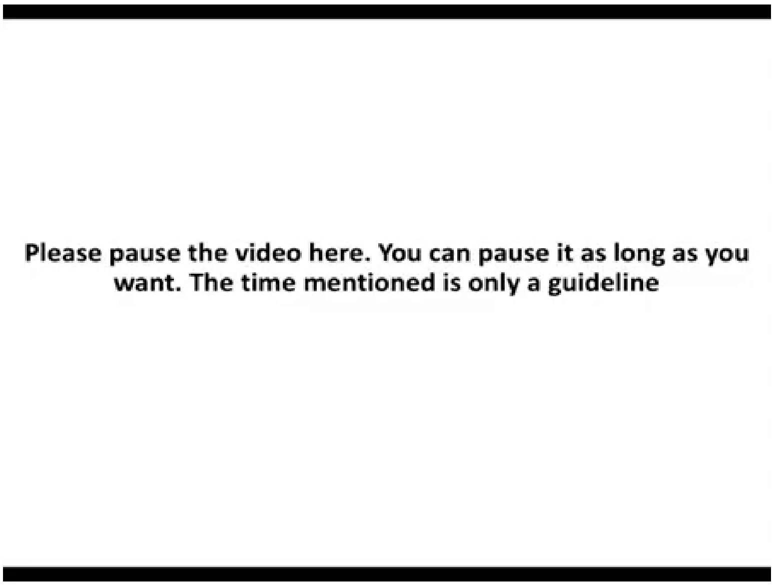

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You would have had a chance to first calculate the right hand side, substitute the b value. And also set up spreadsheet iterations … set up iterations. And, you would have hopefully gotten the final value. In this case, it takes about 5 or 6 iterations to get to the … acceptable final value. The details are as follows V n plus 1, if you substitute b and so on

$$V_{n+1} = -59901.4\left(V_n^3 - \left(2.995 \times 10^{-2}\right)V_n^2 - 1.462 \times 10^{-9}\right)$$

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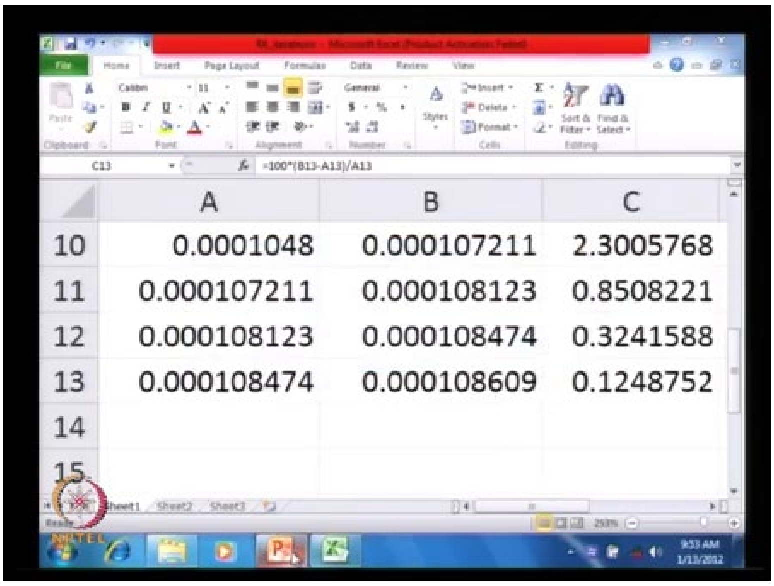
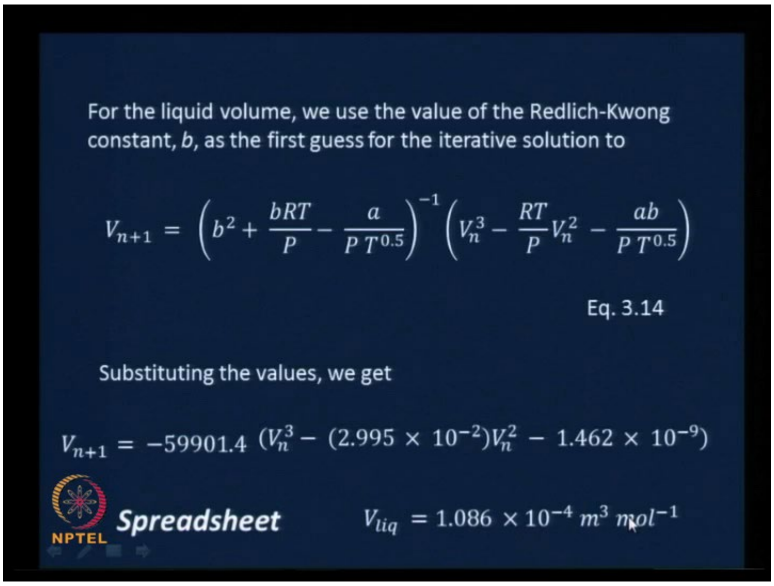


C13 =100*(B13-A13)/A13

	A	B	C
10	0.0001048	0.000107211	2.3005768
11	0.000107211	0.000108123	0.8508221
12	0.000108123	0.000108474	0.3241588
13	0.000108474	0.000108609	0.1248752
14			
15			

Now, let us look at this spreadsheet that I have. You can compare it with this spreadsheet that you have. You know this is the first column, it is the guessed value; the second column is the calculated value, third column is the percentage difference. These are the vapour values. Now let us look at the liquid values.



For the liquid volume, we use the value of the Redlich-Kwong constant, *b*, as the first guess for the iterative solution to

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

Eq. 3.14

Substituting the values, we get

$$V_{n+1} = -59901.4\,(V_n^3 - (2.995 \times 10^{-2})V_n^2 - 1.462 \times 10^{-9})$$

Spreadsheet $V_{liq} = 1.086 \times 10^{-4}\ m^3\ mol^{-1}$

First, b 0.00007685, and then the calculated value is 9.81 to 10 power minus 5; the percentage difference is 27.7. This is clearly unacceptable. Therefore, we put the calculated value – the calculations are given here – … that was the previous one. … This was the equation that we saw for the liquid volume iterations: minus 59901.4 into the one inside the brackets.

Now, we substitute the calculated value … or, take the calculated value as the second guessed value. Calculated value happens to 0.0001 and so on. The percentage error is 6.78; still clearly unacceptable. Therefore, we do another iteration. Take … the calculated value, put it into the next guessed value, and here the percentage difference comes down to 2.3. The next time you do it, the percentage is somewhat acceptable 0.85. And then if we want to continue and improve our accuracy, one more iteration … it comes down to 0.324. And, we will stop here. You could have even stopped here; let us do couple more and we will stop at … $V_{liq} = 1.086 \times 10^{-4}\ m^3\ mol^{-1}$. So, this is how … a slightly lengthy procedure too. But it is an iterative procedure. Explanation takes time, but if you do it yourself it is much faster. So, we have the vapour volume and the liquid volume the molar … vapour and the molar liquid volumes. Substitute this back, take the difference between the two.

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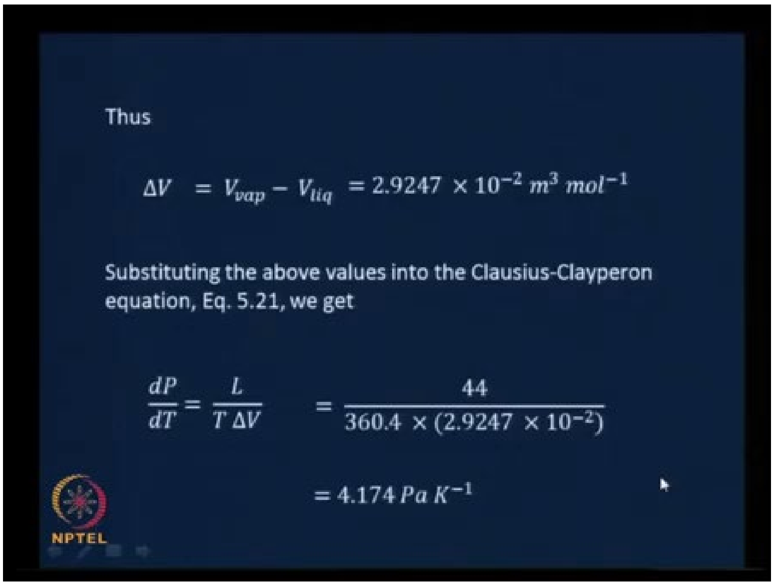

Thus

$$\Delta V = V_{vap} - V_{liq} = 2.9247 \times 10^{-2}\ m^3\ mol^{-1}$$

Substituting the above values into the Clausius-Clayperon equation, Eq. 5.21, we get

$$\frac{dP}{dT} = \frac{L}{T\,\Delta V} = \frac{44}{360.4 \times (2.9247 \times 10^{-2})}$$

$$= 4.174\ Pa\ K^{-1}$$

It turns out to be

$$\Delta V = V_{vap} - V_{liq} = 2.9247 \times 10^{-2}\ m^3\ mol^{-1}$$

This was the only thing that was needed

$$\frac{dP}{dT} = \frac{L}{T\,\Delta V} = \frac{44}{360.4 \times (2.9247 \times 10^{-2})} = 4.174\ Pa\ K^{-1}$$

This is the amount of pressure for a unit change in temperature that is required to maintain equilibrium, when this process is taking place. That is one of the interpretations of the left hand side of the Clausius-Clapeyron equation.

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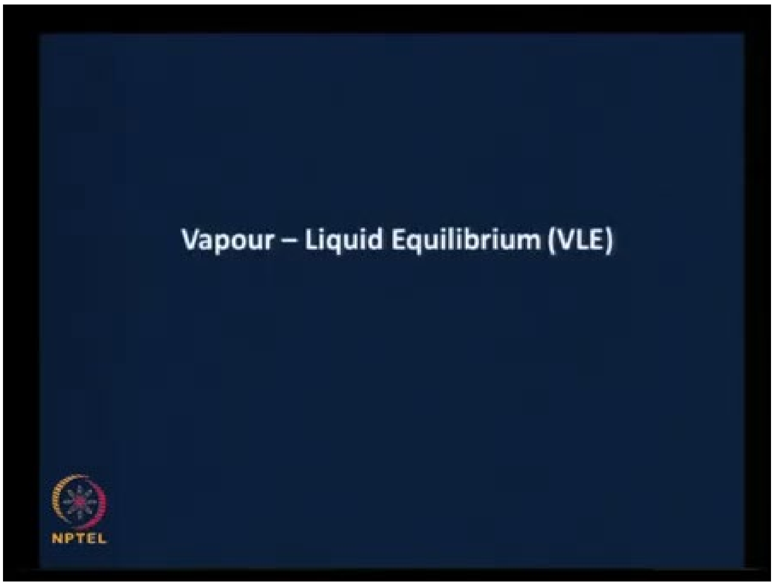

Vapour – Liquid Equilibrium (VLE)

Let us go on to the next thing which is vapour liquid equilibrium; the last example was also an example of vapour liquid equilibrium. But that we saw as a specific case of phase equilibria, in general, and the Clausius-Clapeyron equation could be applied to phase equilibria, in general. … We came from that angle, and we are going to look at something more in detail for the specific case of vapour liquid equilibrium in what follows now.

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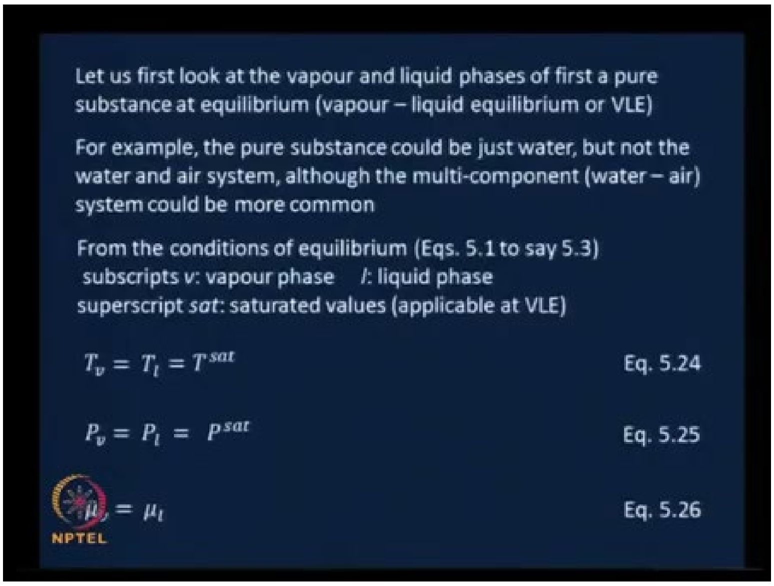

Let us first look at the vapour and liquid phases of first a pure substance at equilibrium (vapour – liquid equilibrium or VLE)

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

Let us first look at the vapour and liquid phases of a pure substance at equilibrium. This we had said earlier – I would like to reemphasize, because I see a lot of confusions when students approach this. So, I will let me state this again … just repeat, whatever I said earlier. For example, the pure substance could be just water, but not the water and air system. It is easy to confuse between the two because water and air is what we come across very commonly. Whereas, we are talking of a pure substance here which could be just water, although the multi component water-air system could be more common as just mentioned. This is the vapour liquid equilibrium, and as we have seen earlier the conditions of equilibrium need to be valid. The conditions of equilibrium as we said were the temperatures need to be equal across phases, the pressures need to be equal across phases, and the chemical potential of a species needs to be equal across phases, and of every species need to equal across phases.

So, the conditions of equilibrium 5.1 to . 3 say exactly, what I just said. Also, we are going to use subscripts V for the vapour phase and L for the liquid phase, and also we are going to use sat for representing saturated values of temperature, pressure, and so on, which is applicable at the vapour liquid equilibrium conditions. So, this is the first condition, temperature of the vapour phase must equal the temperature of the liquid phase. And, this is the saturated condition. Therefore, we can say, it must be equal to … say, T^{sat};

$$T_v = T_l = T^{sat}$$

This is equation 5 24.

The pressure of the vapour phase, the second condition, must equal the pressure of the liquid phase and say that is equal to P^{sat};

$$P_v = P_l = P^{sat}$$

Equation 5.25.

The chemical potential – in this case, only water is present. Therefore, the chemical potential of water in the vapour phase must equal the chemical potential of water in the liquid phase. That is the only substance present in either the liquid phase or the vapour phase. There is no other substance present.

$$\mu_v = \mu_l$$

That is equation 5.26.

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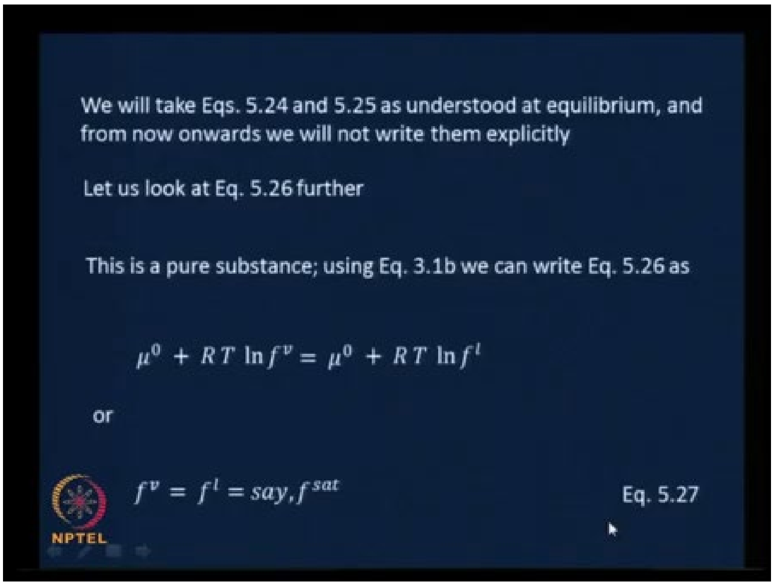

We will take Eqs. 5.24 and 5.25 as understood at equilibrium, and from now onwards we will not write them explicitly

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

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

Now, what we are going to do is we are going to take equation 5.24 and 5.25, which is the equality of temperatures and the equality of a pressures, to be a given whenever we talk of equilibrium. In other words, we are not going to explicitly state this every time. This is understood every time that we mention it. Therefore, we will be only concentrating on this particular equation from now onwards, whenever we talk of vapour liquid equilibrium.

This is a pure substance, and we know that from the condition of equilibrium equation 5.26, mu of the pure substance in the vapour phase equals mu of the pure substance in the liquid phase. Therefore, we can use this equation 3.1 b, which is the expression for the chemical potential, and expand that as

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

Recall this in from module 3 – mu equals mu naught plus R T ln f – that is what we have written here; this is for a pure substance. Therefore, it is quite easy to see mu naught mu naught cancels; RT cancels later. Therefore, ln f V equals ln f L. Therefore, f V equals f L – the fugacity of the pure substance in the vapour phase must equal the fugacity of the pure substance in the liquid phase. And let us say that we are going to call it as … the saturated fugacity value.

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

We will call this equation 5.27.

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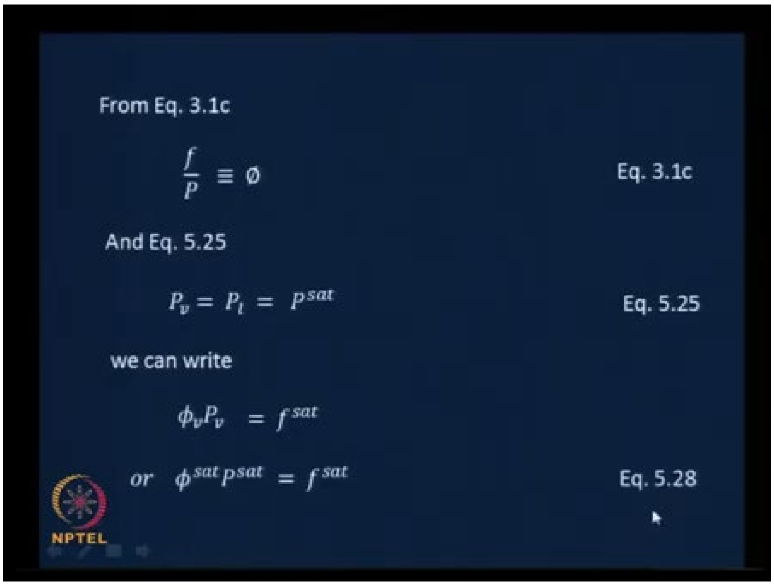

From Eq. 3.1c

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

And Eq. 5.25

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

we can write

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

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

Now, from equation 3.1 c – you can go back and take a look at it what … it exactly says. I am going to restate it here, anyway. It said that

$$\frac{f}{P} \equiv \emptyset$$

Equation 5.25 is

$$P_v = P_l = P^{sat}$$

Therefore, we can write

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

phi V … is the phi value under the saturated conditions in this particular system, which is vapour liquid equilibrium P is P^{sat}. And therefore,

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

We will call this equation 5.28.

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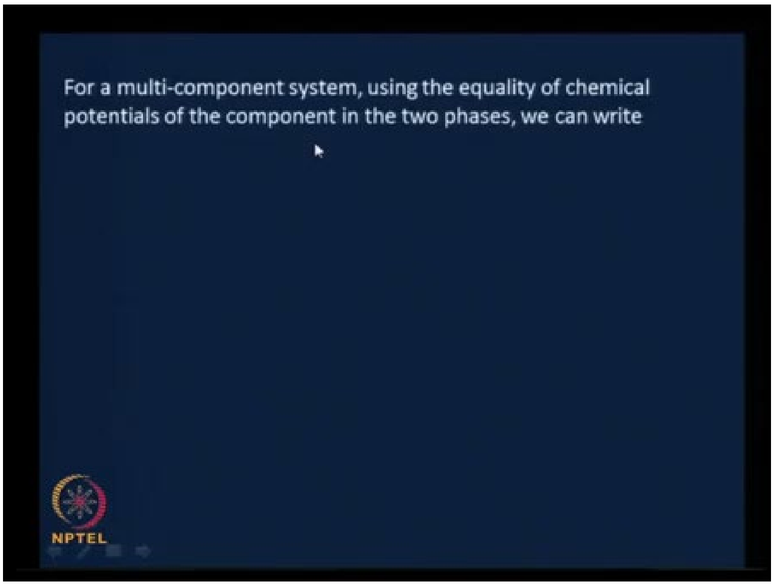

For a multi-component system, using the equality of chemical potentials of the component in the two phases, we can write

The previous development you know, f by P equals phi and therefore, since f V equals f L. We had expressed the fugacity in terms of phi and P here and got f sat. And finally, express it everything in terms of the saturated value and all this was for a pure substance.

Now, let us go and look at a mixture of pure substances – for a multi-component system that is. For a multi-component system, the equality of chemical potentials of the components in the two phases, is the condition. What I would like you to do in the remaining part of this lecture, and you can take this as home work, is to do the same development. This is a good exercise; do the same development and come up with useful relationships, the same way as we did for a pure component system. But you need to do it for a multi-component system. Can you go ahead and do it? I will give you the rest of the class, which is about 3 minutes left, and as homework. When we come back, I will show you how to go about doing it. Go ahead, please.