Upstream LNG Technology
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Lecture – 09
Problems on Vapor Pressure, Gibb's Phase Rule, Dew Point Bubble Point Temperatures

Welcome, after learning about the Gibbs phase rule, Dew point bubble point and Vapor pressure, let us now take a few example problems to implement all those theories we have learned so far.

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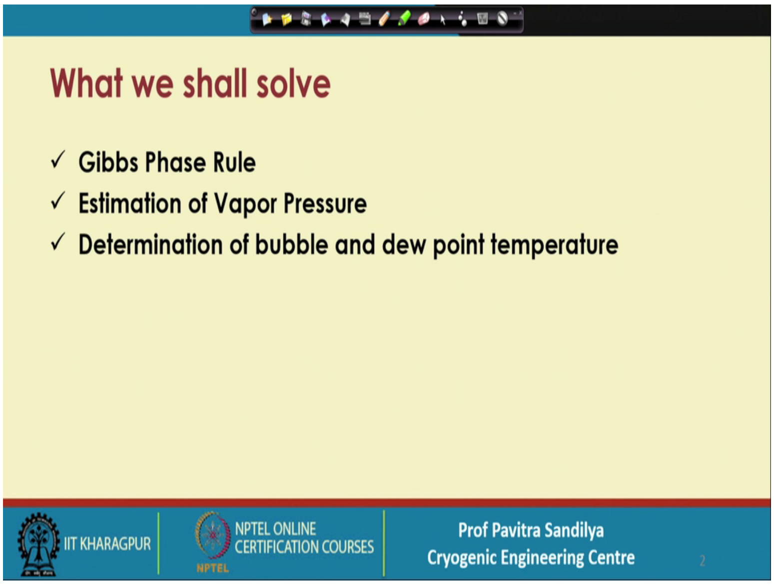

What we shall solve

- ✓ Gibbs Phase Rule
- ✓ Estimation of Vapor Pressure
- ✓ Determination of bubble and dew point temperature

So, first we go to solve a Gibbs phase rule problem, then we go to a vapor pressure estimation problem and lastly, we shall see, how we find out the dew point and bubble point temperature.

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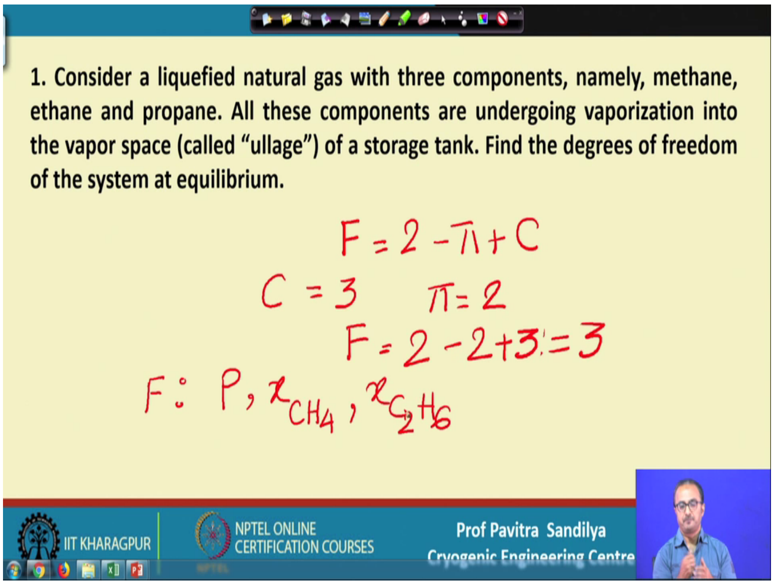

1. Consider a liquefied natural gas with three components, namely, methane, ethane and propane. All these components are undergoing vaporization into the vapor space (called "ullage") of a storage tank. Find the degrees of freedom of the system at equilibrium.

$$F = 2 - \pi + C$$

$$C = 3 \qquad \pi = 2$$

$$F = 2 - 2 + 3 = 3$$

$$F : P, x_{CH_4}, x_{C_2H_6}$$

Let us look at the first problem on the application of Gibbs phase rule. In this case, we find that we are given a liquefied natural gas which is in short called LNG and having 3 components like methane, ethane and propane and these are been kept in a storage tank which is covered and all these 3 components are undergoing some kind of vaporization, in the vapor space above the liquid. Please mind it, whenever we are storing any kind of liquid, we never fill it up to the brink that is to the 100 percent filling is never done, why because whenever you are storing a such kind of liquids which are vaporizing very fast, then if we do not keep any kind of free space above the liquid, this vapor will not be able to escape and ultimately what will happen it can lead to explosion.

So, we always keep some vapor space above the liquid. In this case of natural gas also because natural gas is very volatile liquid with all these methane, ethane, propane, etcetera, they propagate very easily. So, this evaporation takes place because there is heat in leak from the ambient into the system, despite the insulations being used. So, this 3 components, for example, undergoing evaporation; evaporation into the vapor space above the liquid and during this process we assuming that certain at certain temperature has been reached a pressure has been reached; that means, the total system has come to an equilibrium.

So, with this assumption in reality, the equilibrium may not be reached because as the evaporation takes place the pressure in the vapor phase will keep on rising. So, for the sake of simplicity, we assume that the total system has come to an equilibrium that is the temperature of the liquid and the vapor are the same pressure in the liquid and the vapor are the same and the components have redistributed themselves in the liquid and in the vapor. So, that the chemical potential of each of the components in the liquid and vapor phase equalize.

So, with these assumptions, what we are doing? We are trying to apply the Gibbs phase rule to find out the degrees of freedom or the minimum number of properties which we must prescribed to characterize the whole system. So, to find this what we do we go back to the Gibbs phase rule and we know that is F is equal to 2 minus pi plus C. Now, in this case, C is the 3 because we have methane ethane and propane and we have 2 phases that is pi is equal to 2. So, F is equal to 2 minus 2 plus C that is sorry, we put directly 3 here that is equal to 3.

So, now we find that the number the degrees of freedom is 3; that means, we must specify 3 intensive variables to describe the system. Now, we can extend this particular problem to know, what are the possibilities, we can have for prescribing F 1 possibility may be that I can take F to be prescription, I can specify see the pressure and say, suppose, the liquid phase mole fraction of say methane and liquid phase mole fraction of say ethane. So, this may be one set of prescriptions. Now, this is counts to 1, 2 and 3.

Similarly, I would suggest you, you also think of that what are other possibilities to prescribe this degrees of freedom according to that we will have different sets of problems after this what we do. Now, we go to next problem.

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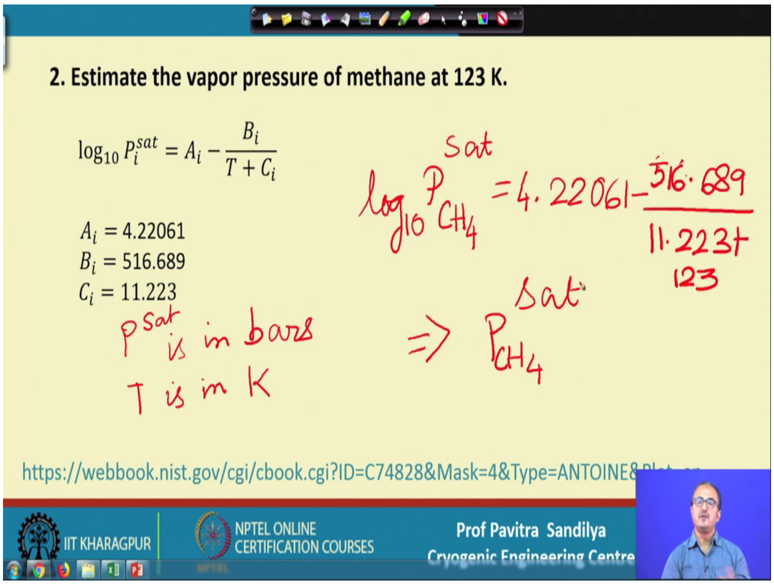

2. Estimate the vapor pressure of methane at 123 K.

$$\log_{10} P_i^{sat} = A_i - \frac{B_i}{T + C_i}$$

$A_i = 4.22061$
$B_i = 516.689$
$C_i = 11.223$

P^{sat} is in bars
T is in K

$$\log_{10} P_{CH_4}^{sat} = 4.22061 - \frac{516.689}{11.223 + 123}$$

$$\Rightarrow P_{CH_4}^{sat}$$

https://webbook.nist.gov/cgi/cbook.cgi?ID=C74828&Mask=4&Type=ANTOINE&

This problem is on the estimation of the vapor pressure in this case, we said we want to know the vapor pressure of methane at some given temperature that is about 123 K for your information, I say that is methane the normal boiling point of methane is about 123 Kelvin, what is normal boiling point that is the boiling point at the one atmospheric pressure, the normal boiling point.

So, with this particular 123 K, we have to see that what is the vapor pressure of methane and we now use this particular entire equation, please note here that in our lecture, we used natural logarithm, but in this case, we are using logarithm base 10 now is it does not make much of difference. Only thing is that these values of this A, B and C will change depending on which scale we are using and these A, B, C values have been taken from this particular reference given at the bottom of this slide.

Now, in this case which has not been mentioned is this P sat this is very important for us to know that P sat is in bars perhaps you know that pressure can be represented in various units like atmosphere bar millimeter of mercury millimeter of water something like this. So, this is one of the unit systems. So, pressure in bars and temperature is in Kelvin, this things is very very important, but otherwise you may land up with wrong answers. So, we must know whenever we are using the correlation, we must know the units in which all the physical variables have been described ok.

So, now after knowing this what we simply do we take this equation log 10 P, I put instead of I put methane CH 4 sat is equal to Ai, Bi, Ci are given here. So, I put 4.22061 minus 51.5; 506; 516; 516.689 divided by 11.223 plus 123. Now please solve this equation and do needful and you get the value of P CH 4 sat.

Now, as I said that this normal boiling point of methane is around 120 to 123 K. So, you may find that this value of P sat should be nearby about one bar that is kind of a cross check to verify that whether your solution is right or wrong, it cannot be too high like 2 atmosphere 2 bar, it cannot be like that or it cannot be going to very very less than the 1 bar means; it cannot be like 0.8 or 0.7, it may be 0.99; 0.98 or something within the numerical errors of our calculations ok. So, this is a problem on vapor pressure calculation.

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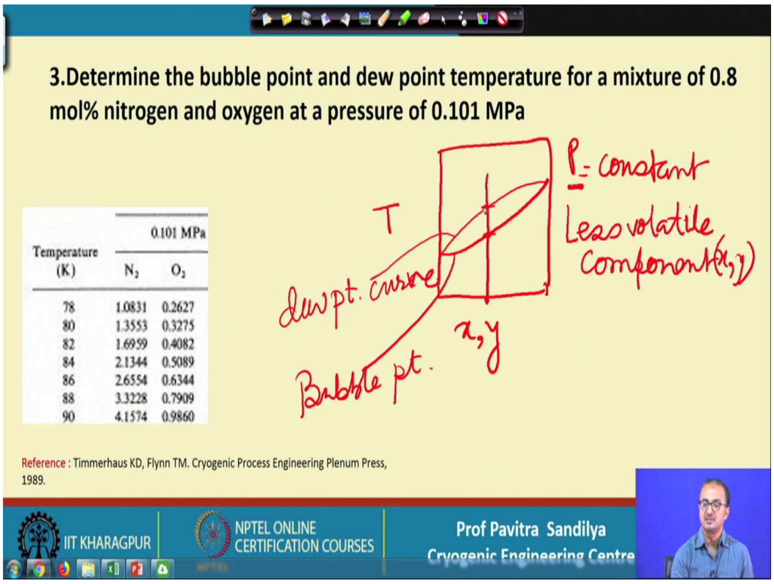

3.Determine the bubble point and dew point temperature for a mixture of 0.8 mol% nitrogen and oxygen at a pressure of 0.101 MPa

Temperature (K)	0.101 MPa	
	N_2	O_2
78	1.0831	0.2627
80	1.3553	0.3275
82	1.6959	0.4082
84	2.1344	0.5089
86	2.6554	0.6344
88	3.3228	0.7909
90	4.1574	0.9860

Reference : Timmerhaus KD, Flynn TM. Cryogenic Process Engineering Plenum Press, 1989.

Next we go to a problem on the dew point and bubble point calculation. Now please understand, we can get the dew point and bubble point for a given composition ok, if you go back to our fundamentals we described in the other lecture that how the dew point and bubble point curve looks on a T xy diagram for a given pressure that it looks like something like this if this means that this is for the less volatile component this xy ok.

So, this in this case for a at any given composition, see this is the dew point curve dew point curve and this is the bubble point curve. So, we find that for a given composition for a given pressure, I can always find the dew point temperature and the bubble point temperature. So, in this; what we are going to do in this particular problem, it has been asked to determine the bubble point temperature and the dew point temperature for a given mixture; mixture composition is given and for a given pressure the pressure is this P value is prescribed and this composition is prescribed. So, we have to find out basically this value that is the bubble point temperature and this value that is the dew point temperature.

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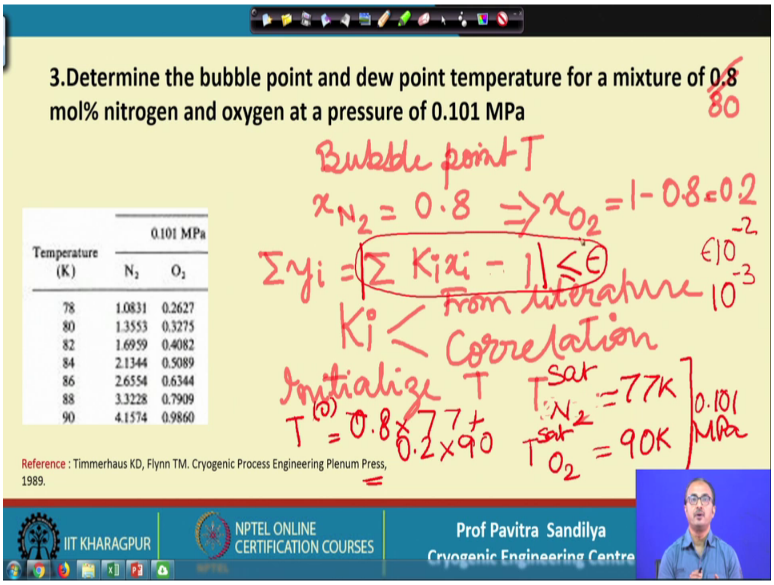

3.Determine the bubble point and dew point temperature for a mixture of ~~0.8~~ 80 mol% nitrogen and oxygen at a pressure of 0.101 MPa

Temperature (K)	0.101 MPa	
	N_2	O_2
78	1.0831	0.2627
80	1.3553	0.3275
82	1.6959	0.4082
84	2.1344	0.5089
86	2.6554	0.6344
88	3.3228	0.7909
90	4.1574	0.9860

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Bubble point T

$$x_{N_2} = 0.8 \Rightarrow x_{O_2} = 1 - 0.8 = 0.2$$

$$\Sigma y_i = \boxed{\left|\Sigma K_i x_i - 1\right| \le \epsilon} \quad \epsilon\ 10^{-2}\quad 10^{-3}$$

K_i < From literature / Correlation

Initialize T

$$T^{(0)} = 0.8 \times 77 + 0.2 \times 90$$

$$\left.\begin{aligned} T^{sat}_{N_2} &= 77K \\ T^{sat}_{O_2} &= 90K \end{aligned}\right]\ 0.101\ \text{MPa}$$

So, now let us see how we do this calculation. So, first let us go with the bubble point calculation bubble point temperature ok. Now in this, we shall see that again, we go to the think that in this case, this particular composition 0.8 bubble point means a liquid is forming the bubble; that means, the liquid composition is given as x into is given as 0.8.

So, it means x O 2 is equal to 1 minus 0.8 is equal to 0.2 and for bubble point calculation our thing was that yi summation is equal to summation equal to yi is given in terms of Ki into xi is equal to 1, here I must make some correction here this value of this composition is not very nice value, let me make correction this is not 0.8 mole percent, it is 80; 80 percent. So, 80 percent translates to 0.8 mole fraction, it is 80 mole percent. So, that 0.8 is wrong. So, this is like this.

So, yi is equal to Ki xi and here we find now this Ki; this Ki may be found from different places, it may be given directly from literature from literature, I can get it or I can have it from some correlation now in this particular case what we find that we have taken the K values from a book on cryogenic process engineering by Timmerhaus and Flynn and these books gives the value of the K for nitrogen oxygen system at one atmosphere.

So, we can take the value of K directly from this particular system and let us see that to do this calculation first I have to know that what value of Ki should I choose and since we have to find the temperature, we do not know the pressure and we know the pressure not the temperature, what we do is this for at this same pressure 0.101 MPa, I go with this particular thing this and nitrogen oxygen form ideal mixture.

In case of ideal mixture we do not need to really bother about this liquid phase activity coefficient we directly go to the K value and to find the K value, what we do that we have to assume the first initialize T initialize T. Now, in this case, I can initialize T like the T set of nitrogen of nitrogen T set of nitrogen is about at this particular pressure is about 77 K, 77 K whereas, T set of oxygen is about 90 Kelvin all that 0.101 Mega Pascal.

This is almost equal to 1 atmosphere ok. So, with this knowledge, I can initialize T that I can say that T 0 is equal to 0.8 into 77 plus 0.2 into 90, whatever the value may be. So, at this particular temperature from this particular table, I find out the value of K for nitrogen oxygen please mind it that I may have to interpolate the values in this particular range to find out the value of the Ki for each of the components.

Once I get the value of Ki, I put the values over here and check that whether it is coming to 1 or not if I find that this particular summation value is coming more than 1; that means, the initial temperature the assumed temperature is more than the actual temperature then what I will do? I will reduce the temperature once I reduce the temperature again I go back to this particular table to find the value of the K of nitrogen and K of oxygen.

Again put the values over here again if I find that this summation is coming more than one I will reduce the temperature and this I will keep doing until unless I find that I gets this particular summation less than one. So, when I go to less than one; that means, the temperature should be more than this last temperature found now we know the bound of the temperatures within which the actual temperature should lie that bound is the last temperature we found where this becomes less than 1 and the last before one temperature at which this was more than 1.

Now, I know 1 temperature at which this is more than 1 and 1 temperature at which this is less than 1; that means, the actual temperature must be lying between these 2 temperatures in this case, we can go to do some numerical standard numerical methods we can use like bisection search to keep on correcting this temperature to go to the actual value of the temperature and we also have to prescribe some convergence criterion epsilon because whenever we are carrying out any kind of numerical method because of due to truncation error due to the round off error we will never reach this particular right hand side exactly.

So, we have been deviating from that value maybe we can give some criterion like 10 to the power minus 2, 10 to the power minus 3, this kind of epsilon value we can get give. So, that we can see that this minus this particular thing this particular thing we say that this absolute value should be less than equal to this prescribed epsilon. So, with this, we if we are do this problem with whenever for the whichever temperature this particular thing is satisfied we say that is the bubble point temperature.

Now, similarly we can go for the dew point calculation in case of dew point calculation.

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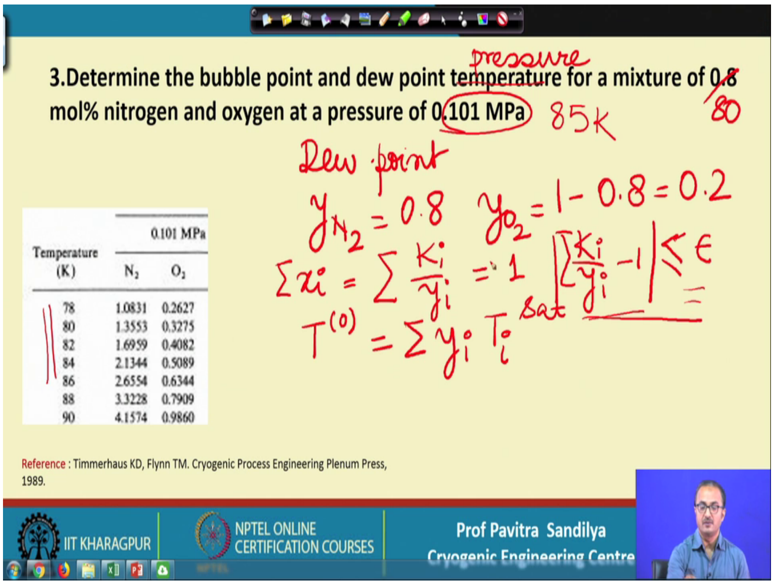

3.Determine the bubble point and dew point ~~temperature~~ pressure for a mixture of ~~0.8~~ 80 mol% nitrogen and oxygen at a pressure of 0.101 MPa 85K

Temperature (K)	0.101 MPa	
	N_2	O_2
78	1.0831	0.2627
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86	2.6554	0.6344
88	3.3228	0.7909
90	4.1574	0.9860

Dew point

$y_{N_2} = 0.8 \quad y_{O_2} = 1 - 0.8 = 0.2$

$\sum x_i = \sum \frac{K_i}{y_i} = 1 \quad \left| \sum \frac{K_i}{y_i} - 1 \right| \leq \epsilon$

$T^{(0)} = \sum y_i T_i^{sat}$

Reference : Timmerhaus KD, Flynn TM. Cryogenic Process Engineering Plenum Press, 1989.

Now, what we will do this particular value will be dew point means I am given the vapor phase composition which is going to condense and form the due. So, in this case, I will say that y in 2 is equal to 0.8 and y o 2 is equal to 1 minus 0.8 is equal to 0.2. Now with this knowledge, now we go to the again the dew point equation that is summation of xi which is unknown to us these are unknown to us is equal to Ky by y, i is equal to 1 or for our convergence, we should see summation Ki by yi minus 1 should be less than equal to some epsilon ok.

Again, what we do now in this case we find the initialize the temperature as before by taking this same yi ti sat and we find out the initialized temperature at this temperature again we go back to this particular table and from this table we find out appropriate value of the K by interpolation put those value of K here in this particular equation and check that whether we are getting this absolute value of this particular expression less than equal to epsilon naught.

If it is so, it generally does not happen, but if it is. So, that is the solution if it is not again we have to take whether this particular expression is more than or equal to one if more than that is we have to reduce the temperature it is less than then to increase the temperature. So, by doing these adjustments we can slowly and slowly approach the solution and once this particular criterion is satisfied whatever temperature, we are obtaining at that particular criterion, we take that temperature to be the dew point temperature.

The same problem may be given to find out the dew point pressure and the bubble point pressure in that case what we will do instead of this pressure, we will prescribe some temperature for example, I can say that temperature is 85 K and I say that not temperature. Now, I have to find out the dew point and bubble point pressure. So, this way we can modify the same problem to find out the dew point temperature bubble point temperature dew point pressure and bubble point pressure ok, only thing is this.

In this case, the iterative variable was temperature and in case of pressure calculation the iteration will be done with the pressure and that is how we can get the value of the dew point temperature bubble point temperature dew point pressure and bubble point pressure with this, we come to the end of this lecture.

Thank you.