Course on Phase Equilibrium Thermodynamics
By Professor Gargi Das
Department of Chemical Engineering
Indian Institute of Technology Kharagpur
Lecture 29
Fugacity of Condensed Phase

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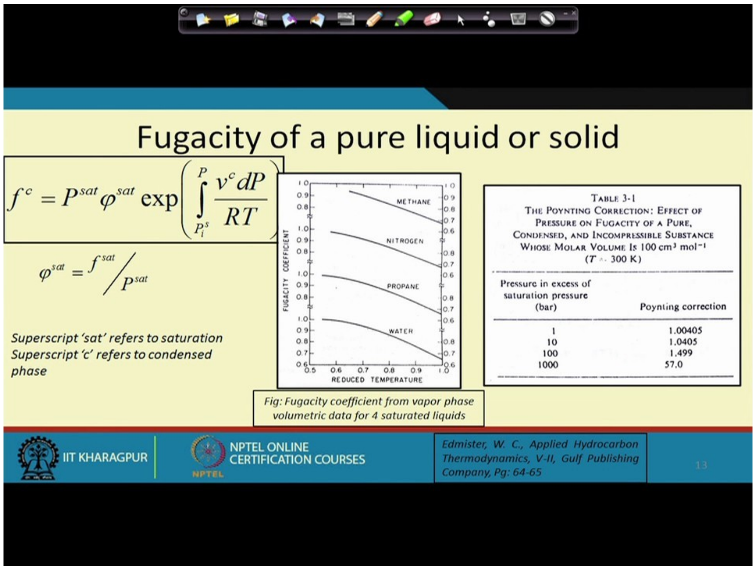

Fugacity of a pure liquid or solid

$$f^c = P^{sat}\varphi^{sat}\exp\left(\int_{P_i^s}^{P}\frac{v^c dP}{RT}\right)$$

$$\varphi^{sat} = f^{sat}/P^{sat}$$

Superscript 'sat' refers to saturation
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Fig: Fugacity coefficient from vapor phase volumetric data for 4 saturated liquids

TABLE 3-1
THE POYNTING CORRECTION: EFFECT OF PRESSURE ON FUGACITY OF A PURE, CONDENSED, AND INCOMPRESSIBLE SUBSTANCE WHOSE MOLAR VOLUME IS 100 $cm^3\ mol^{-1}$
($T \approx 300$ K)

Pressure in excess of saturation pressure (bar)	Poynting correction
1	1.00405
10	1.0405
100	1.499
1000	57.0

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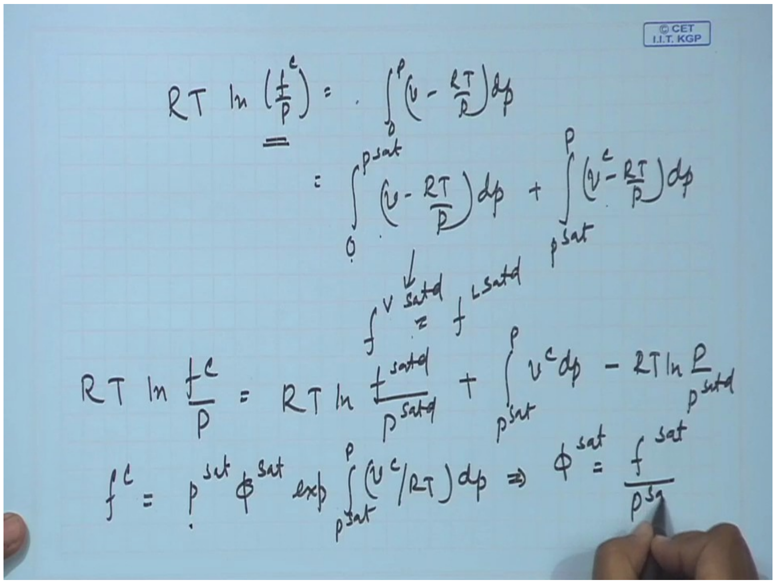

$$RT\ln\left(\frac{f^{\ell}}{P}\right) = \int_0^P \left(v - \frac{RT}{P}\right)dp$$

$$= \int_0^{P^{sat}}\left(v - \frac{RT}{P}\right)dp + \int_{P^{sat}}^{P}\left(v^{\ell} - \frac{RT}{P}\right)dp$$

$$\downarrow$$

$$f^{V\,satd} = f^{L\,satd}$$

$$RT\ln\frac{f^{\ell}}{P} = RT\ln\frac{f^{satd}}{P^{satd}} + \int_{P^{sat}}^{P} v^{\ell}dp - RT\ln\frac{P}{P^{satd}}$$

$$f^{\ell} = P^{sat}\phi^{sat}\exp\int_{P^{sat}}^{P}\left(v^{\ell}/RT\right)dp \Rightarrow \phi^{sat} = \frac{f^{sat}}{P^{s}}$$

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Well, just as I had mentioned in the last class, in this class I am going to discuss fugacity of pure liquid or pure solids, remember one thing the starting equation is the same in this particular case as well, what is the starting equation? The starting equation just I had mentioned several times earlier it is ln f by P equals to integral 0 to P v minus RT by P dp, we start from this particular equation but we must remember that we are dealing with a liquid.

So how to perform the entire integration starting from 0 pressure where usually all substances they exhibit or they are in the gas phase and they exhibit ideal gas behavior from there I would like to reach a pressure where the substance has undergone a phase transition from the vapor phase to the liquid phase and then it remains in the liquid phase from the saturated vapor pressure to the pressure where we would like to find out the fugacity of the pure liquid.

So therefore to calculate and whatever I discuss this same thing is applicable for a pure solid as well. So therefore to calculate the fugacity of liquid or a solid at a given temperature and pressure, what do we do? We breakup this whole thing into 2 parts, the first part it gives us the fugacity of the vapor's phase from 0 pressure to the saturated pressure such that this gives us the fugacity of the vapor phase under saturated conditions, right?

And after that we have another part which extends from P saturated to P which gives us the fugacity of the condensed phase and we need to remember that when we have in this particular integration we get the fugacity of the vapor at the saturated condition. Under this condition we know that the vapor and liquid they are at equilibrium. So therefore this is nothing but equal to fL saturated fine, so therefore what do I do here?

To find out the fugacity of the condensed phase I simply break it up into 2 parts the first part gives us the fugacity of the saturated vapor which is nothing but equal to the fugacity of the condensed phase under the saturated pressure conditions and then if my particular or the condition of interest is far removed from the saturated pressure then we need to calculate the additional fugacity which is generated by compression of the condensed phase from the saturated pressure to the pressure of interest.

So therefore this can be written down as I can write this down as RT ln f saturated by P saturated this part can be written down by f saturated by P saturated and then the other part can be written down as P saturated to P, v condensed phase dp minus RT ln P by P saturated I can write it down very much in this particular form. Now removing all the logarithm of and writing it down we can write it as fC this is nothing but equal to P saturated Phi saturated exponential integral P saturated to P vC by RT into dp, right? Where this is the saturated vapor pressure, this Phi saturated it is nothing but equal to the fugacity of the vapor under the saturated state divided by the pressure under the saturated state.

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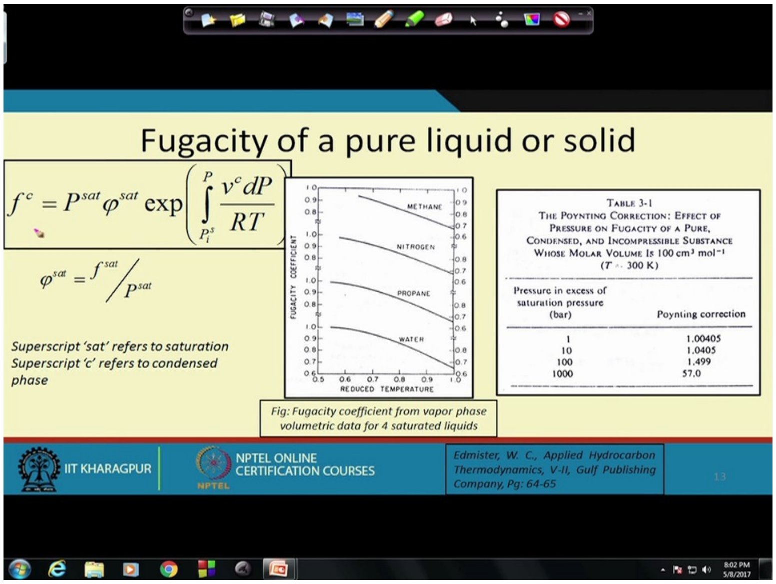

Fugacity of a pure liquid or solid

$$\boxed{f^c = P^{sat}\varphi^{sat}\exp\left(\int_{P_i^s}^{P}\frac{v^c dP}{RT}\right)}$$

$$\varphi^{sat} = f^{sat}/P^{sat}$$

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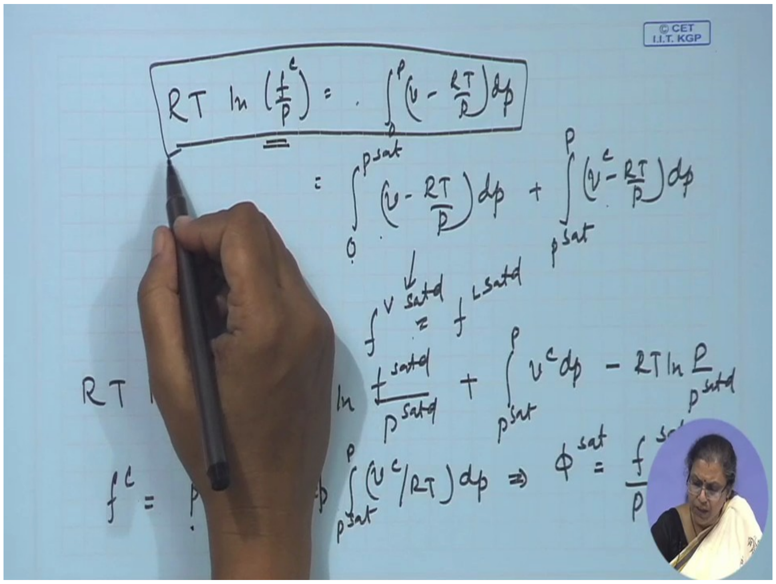

$$\boxed{RT\ln\left(\frac{f^c}{P}\right) = \int_0^P\left(v - \frac{RT}{P}\right)dp}$$

$$= \int_0^{P^{sat}}\left(v - \frac{RT}{P}\right)dp + \int_{P^{sat}}^{P}\left(v^c - \frac{RT}{P}\right)dp$$

$$f^{V\,satd} = f^{L\,satd}$$

$$RT \quad \ln\frac{f^{satd}}{P^{satd}} + \int_{P^{sat}}^{P} v^c dp - RT\ln\frac{P}{P^{satd}}$$

$$f^c = P \quad \int_{P^{sat}}^{P}\left(v^c/RT\right)dp \Rightarrow \phi^{sat} = \frac{f}{P}$$

Well, this is the equation that I have mentioned here. So this is the fugacity of the condensed phase and I would like to recall that this particular expression has been derived starting from the same equation the defining equation of fugacity with the supposition that the fugacity is equal to the pressure for very low pressure.

So we have started from very low pressures and we have assumed that under this condition the gas the substance is in the gaseous state and the gas is an ideal gas. So therefore what we did? What is the path of integration? The path of integration is compressing the ideal gas from 0 pressure to the saturated pressure where it becomes a saturated vapor under this condition the saturated vapor and the saturated liquid states have got the same fugacity and so therefore whatever fugacity value I get in compressing the gas from 0 pressure to the saturated pressure is the fugacity of the liquid under same conditions then there is an additional fugacity generated because the liquid has to be compressed from the saturated state to the state of interest.

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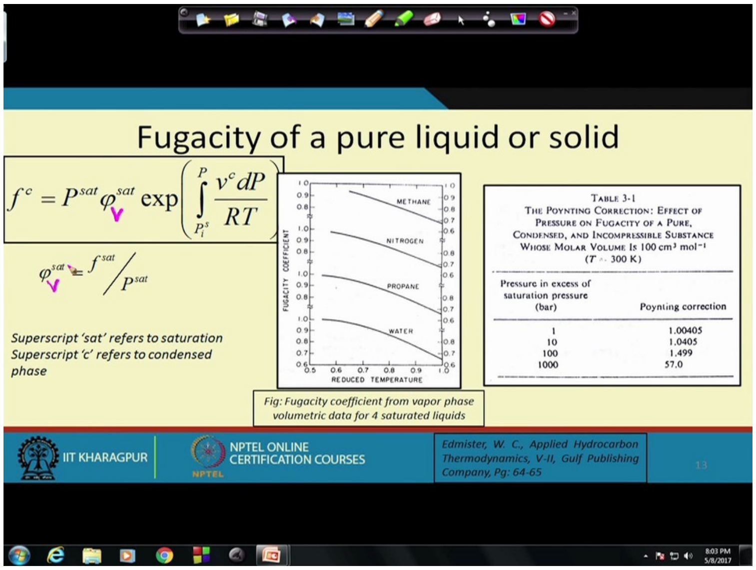

Fugacity of a pure liquid or solid

$$f^{c} = P^{sat}\varphi^{sat}_{V}\exp\left(\int_{P_i^s}^{P}\frac{v^{c}dP}{RT}\right)$$

$$\varphi^{sat}_{V} = f^{sat}/P^{sat}$$

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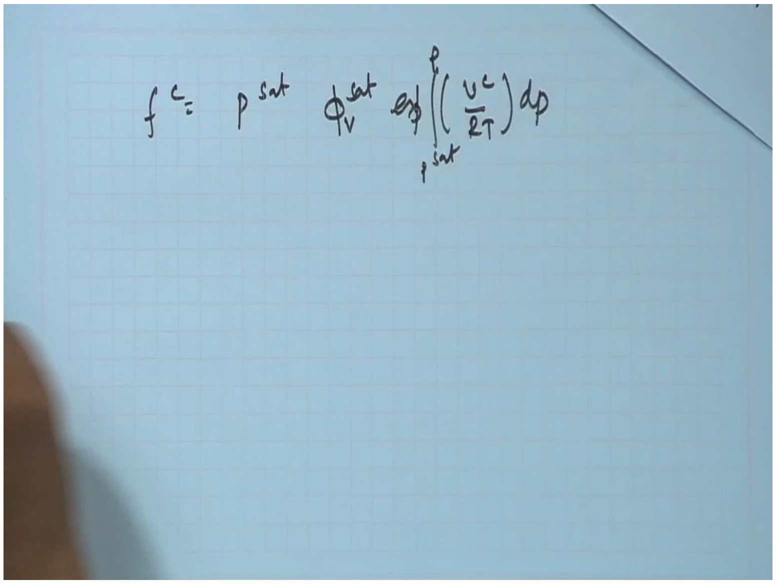

$$f^c = P^{sat} \phi_v^{sat} \exp \int_{P^{sat}}^{P} \left(\frac{v^c}{RT} \right) dp$$

Now here I would like to say that suppose we are dealing with very low pressures, now let me write it down in the next page and then it is going to be easier for me fC equals to P saturated Phi vapor saturated it's better written as phi v saturated exponential P saturated to P v condensed phase by RT into dp, here also I would like to make the correction this is phi v saturated this is also the vapor phase saturated, right? Now try to observe this particular equation what do we get?

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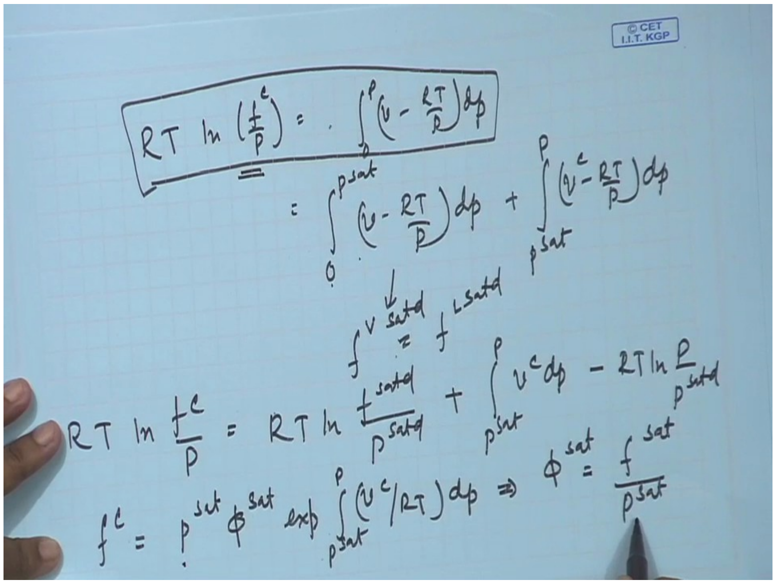
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$$f^c = P^{sat}\phi^{sat}\exp\int_{P^{sat}}^{P}(v^c/RT)\,dp \Rightarrow \phi^{sat} = \frac{f^{sat}}{P^{sat}}$$

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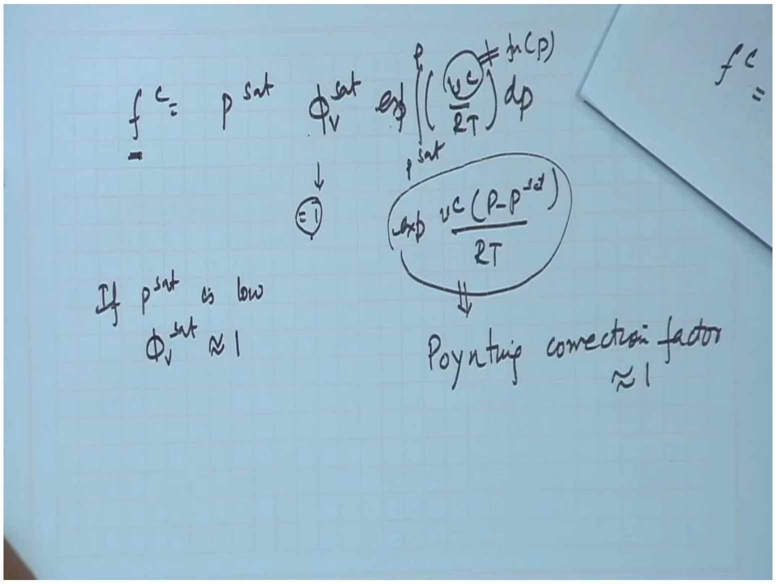

$$f^c = P^{sat}\,\underset{\downarrow\ (=1)}{\phi_v^{sat}}\,\exp\int_{P^{sat}}^{P}\left(\frac{\overset{\neq fn(p)}{v^c}}{RT}\right)dp$$

$$\boxed{\exp\frac{v^c(P-P^{sat})}{RT}}$$

$$\Downarrow$$

Poynting correction factor ≈ 1

If P^{sat} is low
$\phi_v^{sat} \approx 1$

$f^c =$

The first thing we get is fugacity of a pure component at temperature and pressure, suppose the temperature and the pressure is not very high then in that case the gas can be assumed to behave ideally when the gas is assume to behave ideally then in that case its fugacity and pressure are equal under saturated conditions, as a result of which this term it becomes equal to one, right? So therefore this is basically it is a deviation of saturated vapor from the ideal gas behavior.

Next we look at this exponential term, this exponential term arises because the liquid or the solid for that matter with whatever we are dealing that is at a pressure P far removed from the saturated pressure. Now at conditions which are much remote from the critical very frequently a condensed phase can be regarded as incompressible as a result of which vC it is not a function of P, under that condition the exponential term can be written down as vC P minus P saturated by RT, we can write it down in this particular form.

The other thing which is important is that usually but not always these 2 correction terms they are negligible because unless P is not far removed from P saturated this particular correction term which is usually known as the poynting correction factor, this correction factor it is not very high if provided the temperature is such that P saturated is low under that condition if P saturated is low then phi v saturated is almost equal to one.

And we find that if the pressure is not very high then poynting correction factor can also be taken as one.

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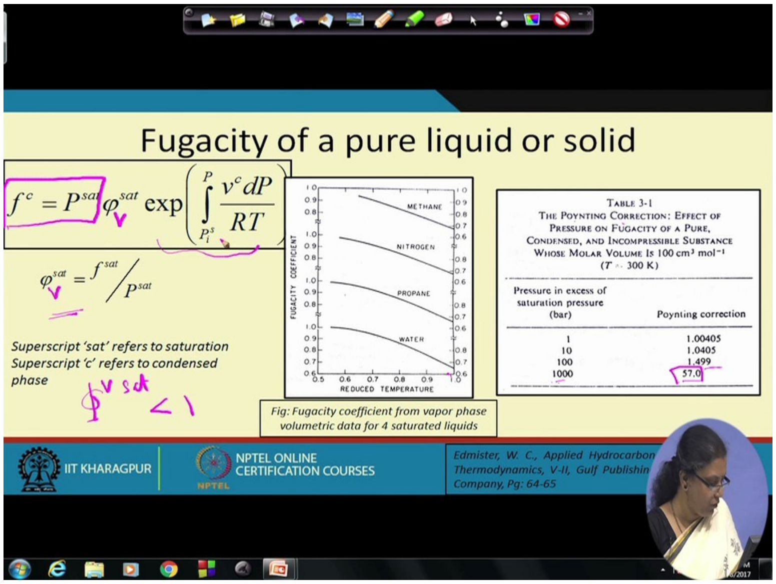

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$$\varphi_v^{sat} = f^{sat}/P^{sat}$$

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$\phi^{v\,sat} < 1$

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Just to give you an idea regarding these 2 correction factors, I have a table and a graph with if you if you observe this particular table what do we see? Here I have taken it from the book of Prausnitz and there we have found out that the poynting correction factor for the condensed and incompressible substances in this particular case. We find that for 1 bar pressure even for 100 bar pressure also its not high but if you are dealing with thousand bar pressure then it becomes really high. So therefore this implies that the poynting correction factor, it becomes important when we are dealing with condensed phases at very high pressure.

So under that condtion this particular term this term is important otherwise it is not very important even if we observe the variation of the fugacity coefficients with reduced temperature, what do we find? We find that at conditions closed to the critical for those particular conditions the fugacity coefficient differs remarkably from unity and we find that as go for lower and lower reduced temperatures the fugacity coefficient almost approaches one.

So therefore this implies there are 2 things which are important one is phi v saturated it differs considerately from unity as the critical temperature is approached. So under this condition we cannot neglect Phi v saturated the other thing is if you observe phi v saturated is always less than one this particular term phi v saturated it is always less than one which implies that this correction term it tends to decrease the condensed phase fugacity and usually we find that the poynting correction factor is the exponential function of pressure this is low at small values of pressure but it may be very large for large values of pressure or at low-temperature.

We also find that the phi v saturated that is also for conditions far removed from the critical this is also one. So therefore for low to moderate pressures we can safely assume that the fugacity of the condensed phase is equal to the saturated vapor pressure and when we are dealing with conditions like high pressure or very low temperature or for conditions close to the critical then we need to incorporate the corrections to the saturated vapor pressure in order to obtain the fugacity of the condensed phase and these 2 corrections they arise primarily because of the non-ideality of the vapor phase and the fugacity generated due to the compression of the liquid of the liquid phase from the saturated pressure to the pressure far removed from the saturated.

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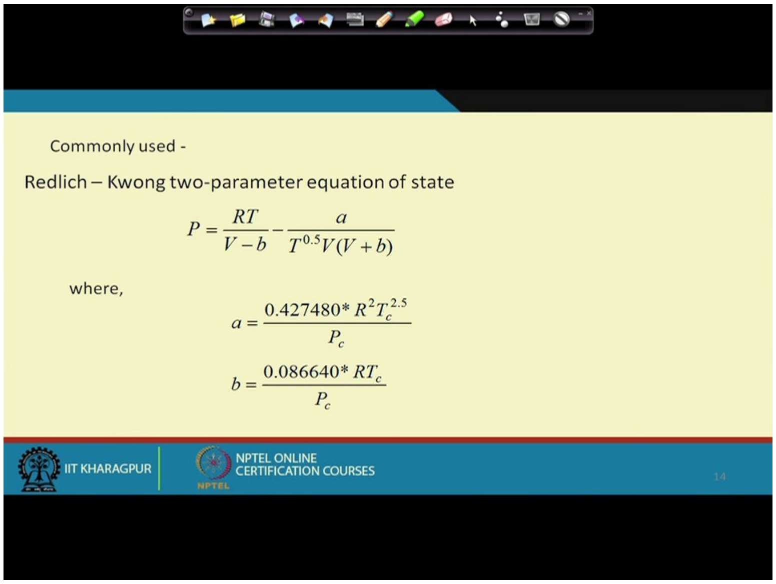

Commonly used -

Redlich – Kwong two-parameter equation of state

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

where,

$$a = \frac{0.427480^* R^2 T_c^{2.5}}{P_c}$$

$$b = \frac{0.086640^* RT_c}{P_c}$$

Now before ending fugacity there is one more thing that I would just like to mention, this is very commonly used for the for predicting the fugacity's of hydrocarbons and therefore I have used this particular equation or rather I have discussed this particular equation usually we use the Redlich Kwong equation of state which is given here, you already know it with the constant value is given in this particular equation.

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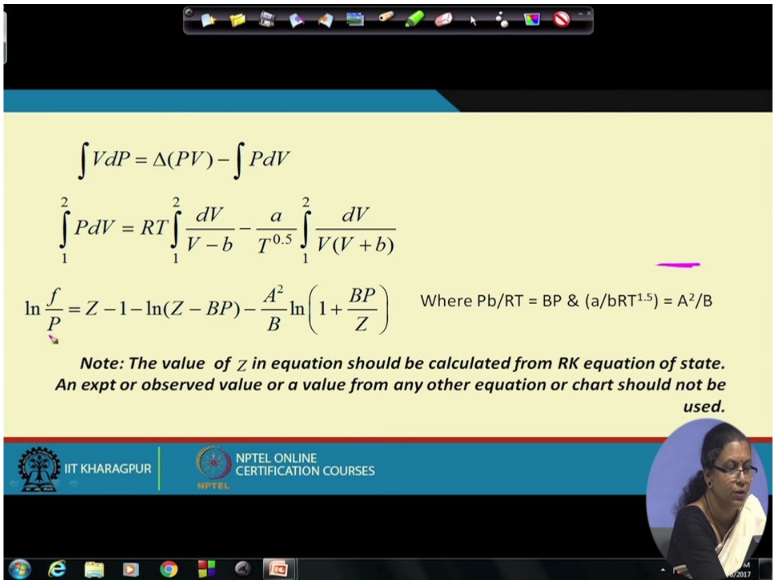

$$\int VdP = \Delta(PV) - \int PdV$$

$$\int_1^2 PdV = RT\int_1^2 \frac{dV}{V-b} - \frac{a}{T^{0.5}}\int_1^2 \frac{dV}{V(V+b)}$$

$$\ln\frac{f}{P} = Z - 1 - \ln(Z - BP) - \frac{A^2}{B}\ln\left(1 + \frac{BP}{Z}\right)$$

Where $Pb/RT = BP$ & $(a/bRT^{1.5}) = A^2/B$

Note: The value of Z in equation should be calculated from RK equation of state. An expt or observed value or a value from any other equation or chart should not be used.

Now when we use this particular equation we find that the expression of fugacity is given by this equation where we find that fugacity coefficient it's a function of Z it is a function of BP and it is a function of A square by B. So therefore if we know these 3 quantities we would be in a position to find out f by P. Now usually we can use this analytical form to find it out but there is one note of caution which we should remember for using this equation that is the value of Z that we are using here that should be calculated from the Redlich Kwong equation of state which I have already mentioned here.

It should be used with the Redlich Kwong we should be calculating Z from here and we should not be using any particular experimentally observed value of Z or we should not take Z from any other equation or chart in this equation if we want to get a correct value of the fugacity coefficient using Redlich Kwong equation of state.

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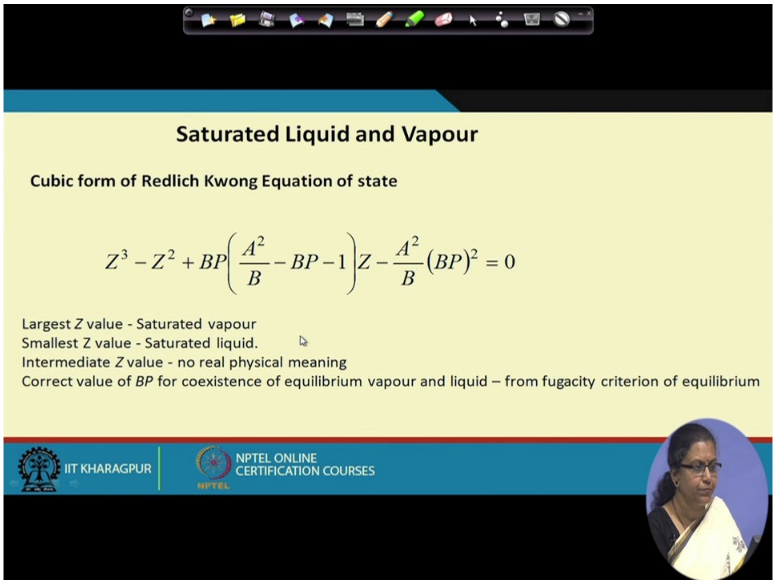

Saturated Liquid and Vapour

Cubic form of Redlich Kwong Equation of state

$$Z^3 - Z^2 + BP\left(\frac{A^2}{B} - BP - 1\right)Z - \frac{A^2}{B}(BP)^2 = 0$$

Largest *Z* value - Saturated vapour
Smallest Z value - Saturated liquid.
Intermediate *Z* value - no real physical meaning
Correct value of *BP* for coexistence of equilibrium vapour and liquid – from fugacity criterion of equilibrium

The other interesting thing is this also I had discussed earlier since we know that Redlich Kwong equation of state is a cubic form, so therefore it can be used to predict the fugacities of a saturated liquid as well as a saturated vapor.

If you are solving this particular equation we know that we get a cubic value of or rather we get 3 routes of Z out of these 3 roots the largest value that corresponds the saturated vapor the smallest value that corresponds to the saturated liquid and intermediate value that we get that has no real physical meaning. The only problem of finding out the fugacities of saturated liquid and vapor using this cubic form of Redlich equation of state is that in this particular case usually the BP that is an unknown.

So therefore how to find out BP from this particular equation, for this we use the concept that the vapor and liquid are in equilibrium under the saturated conditions. So how do we go about doing it? What we do in this particular case is, first what we do is we use this particular equation, in this particular equation we try to find out BP by rather we assume different values of pressure and we try to find out the BP value such that we use it to find out the fugacity of the liquid phase, we use it to find the fugacity of the vapor phase and then we choose that particular pressure as the actual pressure in which we use that particular pressure under which the fugacity calculated for the liquid phase and the vapor phases are the same.

Once we have identified the pressure under which the liquid phase and the vapor phase pressures are the same then we know that the Z corresponding to that pressure should be used here or in other words the BP value which we have obtained from this particular equation is then used in this equation and then we obtained the roots of Z and then the higher value is taken as a saturated vapor and the lower value is taken as the saturated liquid.

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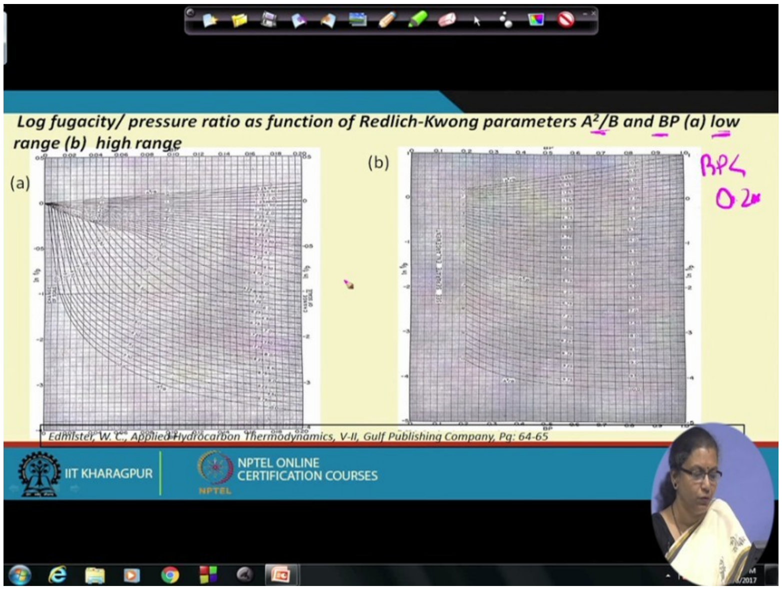

Log fugacity/ pressure ratio as function of Redlich-Kwong parameters A^2/B and BP (a) low range (b) high range

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Now other than that just like I had shown you the Lee Kesler plots we find that solving this particular equation and equation for Z we can generate a set of curves which can give us the fugacity the coefficient in terms of the Redlich Kwong parameters which are A square by B and BP and we know that that these 2 curves have been plotted under 2 conditions one is the low range of BP for which in this particular graph we have shown the fugacities of both the liquid and the vapor and this is for the high range of BP under which condition we have shown for only the vapor phase.

For this particular low range of BP this is applicable for BP less than 0.20, for this condition this graph is drawn and then this is primarily for coexisting vapor and liquid regions and this is ffor higher values. Now in this particular case using the chart are must simpler as compared to using the equations.

For using the charts it is very easy we first have to evaluate the 2 parameters A square by B and BP. Once we have evaluated this from the temperature, pressure and the criticals of the system once these are evaluated then we read the charts and we use and we using the aforementioned values and we try to find out the fugacity coefficient for the condition of interest we can use this for finding out the fugacity coefficients for both the condensed phase as well as for the gas phase.

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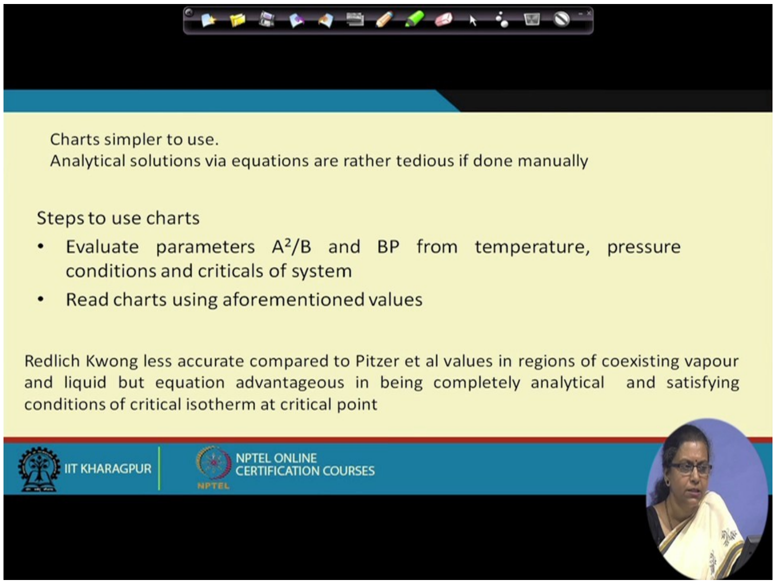

Charts simpler to use.
Analytical solutions via equations are rather tedious if done manually

Steps to use charts

- Evaluate parameters A^2/B and BP from temperature, pressure conditions and criticals of system
- Read charts using aforementioned values

Redlich Kwong less accurate compared to Pitzer et al values in regions of coexisting vapour and liquid but equation advantageous in being completely analytical and satisfying conditions of critical isotherm at critical point

So therefore here I would just like to mention in conclusion. Since Redlich Kwong equation is used very frequently to find the fugacity coefficient in the case of hydrocarbons we can use the analytical equations but they are quite tedious but they are accurate, on the contrary if we use charts, the charts are simpler to use we just need to find out as I have already mentioned we need to find out the parameters A square by B and BP from temperature, pressure, conditions and the critical of the system and then read the charts using this aforementioned values.

Here I would also like to mention that the Redlich Kwong equation is less accurate compared to the Pitzer correlation particular regions of coexisting vapor and liquid but since these equations have an advantage of being completely analytical and they satisfy conditions of critical isotherm at the critical point. So therefore under these conditions these few equations are quite useful with this I end my discussions on the concept of fugacity.

This be the importance of standards states for a correct estimation of fugacity reframing the equilibrium conditions in terms of fugacity estimating fugacities for gases estimating fugacities for liquid, a practical method of estimating fugacity for hydrocarbons and after this we go to discuss mixtures their properties, fugacity of a component in a mixture and after that we go for discussing the ideal solutions and the non-ideal solutions.

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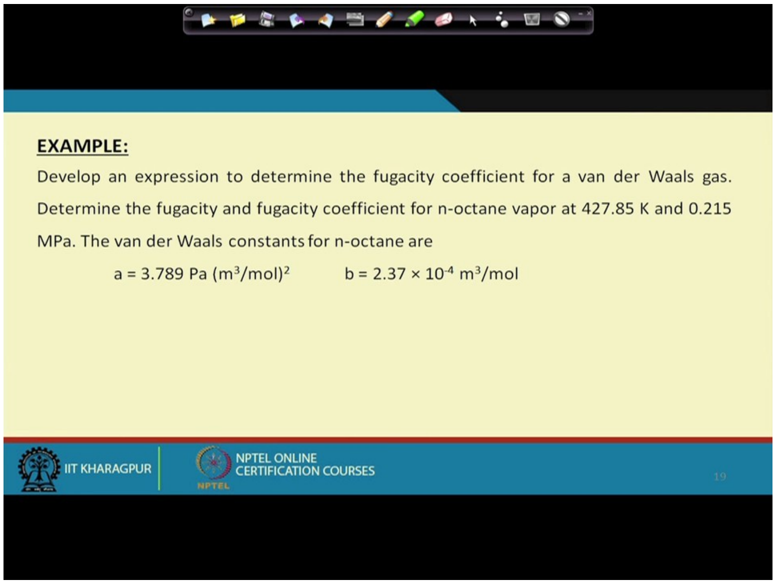

EXAMPLE:

Develop an expression to determine the fugacity coefficient for a van der Waals gas. Determine the fugacity and fugacity coefficient for n-octane vapor at 427.85 K and 0.215 MPa. The van der Waals constants for n-octane are

$a = 3.789$ Pa $(m^3/mol)^2$ $\quad b = 2.37 \times 10^{-4}$ m^3/mol

Well, just one particular example or one particular problem has been provided here to find out the fugacity coefficient for a Van der waal's gas. You can use or rather you can try this problem to find out the value and I think it is pretty straightforward you will not get stuck up in this but in case you are stuck up we are there with you, thank you very much.