Course on Phase Equilibrium Thermodynamics
By Professor Gargi Das
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Lecture 28
Estimation of Fugacity Coefficients

Well, so in this class we are going to discuss the estimation of fugacity coefficient for real gases. Now here again I would like to mention we are first going to discuss the estimation of fugacity or fugacity coefficients whatever it is, for real gases and then we are going to do it for the condensed phase it's same for the liquid as well as the solid. After that we go for the, for discussing the fugacity coefficient for one particular component in a mixture of gases.

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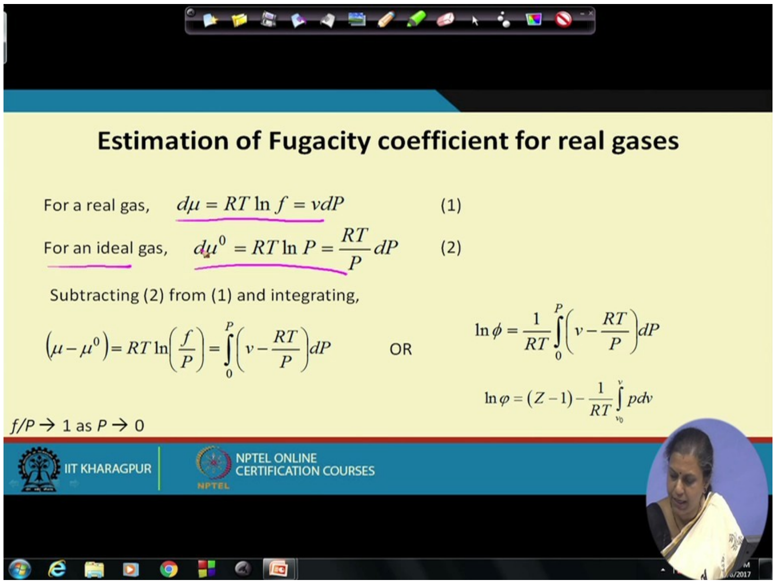

Estimation of Fugacity coefficient for real gases

For a real gas, $\underline{d\mu = RT \ln f = vdP}$ (1)

For an ideal gas, $\underline{d\mu^0 = RT \ln P = \frac{RT}{P} dP}$ (2)

Subtracting (2) from (1) and integrating,

$$\left(\mu - \mu^0\right) = RT \ln\left(\frac{f}{P}\right) = \int_0^P \left(v - \frac{RT}{P}\right) dP$$

OR

$$\ln \phi = \frac{1}{RT} \int_0^P \left(v - \frac{RT}{P}\right) dP$$

$$\ln \varphi = (Z - 1) - \frac{1}{RT} \int_{v_0}^{v} pdv$$

f/P → 1 as P → 0

Now whenever we do, we start from the same 2 equation for a real gas this is this, for an ideal gas the equation is this because every time my standard for all particular system that I use my standard is going to be an ideal gas. Now I subtract one from the other, so on subtraction what do I get?

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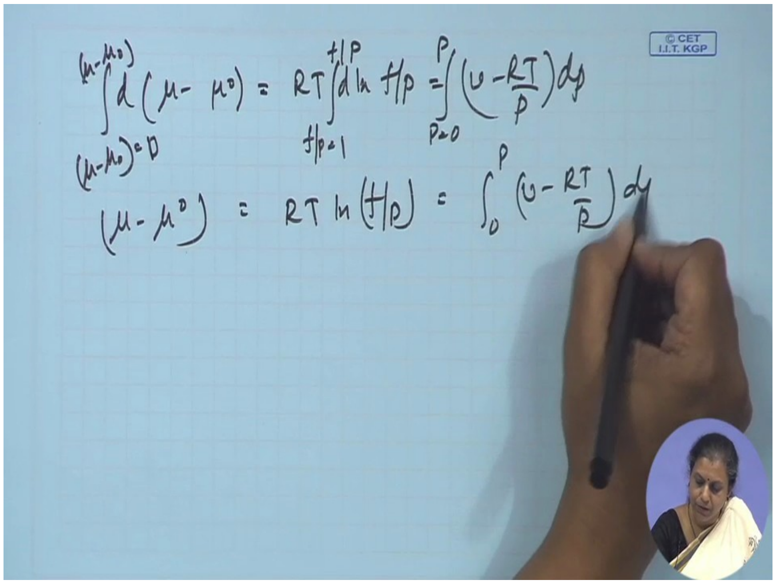

$$\int_{(\mu-\mu_0)=0}^{(\mu-\mu_0)} d(\mu-\mu^0) = RT\int_{f/p=1}^{f/P} d\ln f/p = \int_{P=0}^{P}\left(v-\frac{RT}{P}\right)dp$$

$$(\mu-\mu^0) = RT\ln(f/p) = \int_0^P \left(v-\frac{RT}{P}\right)dp$$

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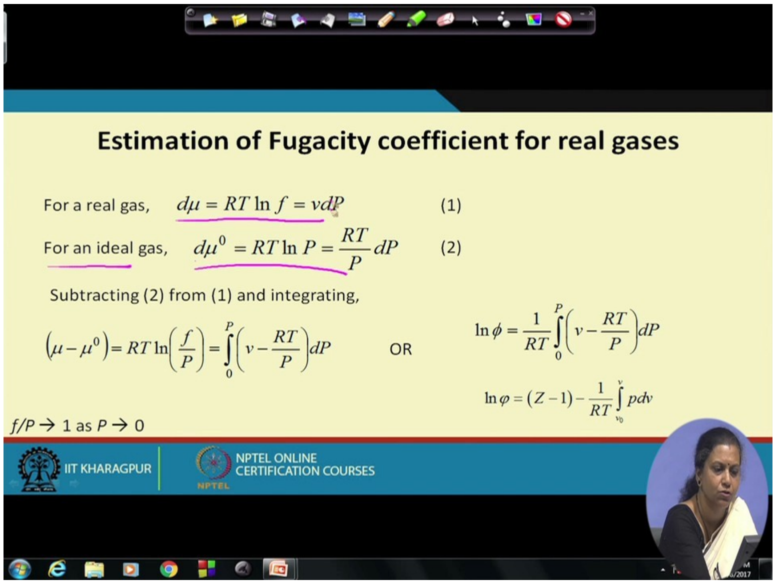

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f/P → 1 as P → 0

I get d of mu minus mu0 equals to each and every term I subtract these 2 terms I subtract these 2 terms I subtract these 2 terms, right? So therefore this gives us RT d ln f by P which is nothing but equal to phi and this is equals to v minus RT by P dp then I can integrate each one of them, what should be my integration? I should be integrating it from a condition where I know the fugacity or in other words I should be integrating it from the ideal gas state which is applicable at P equals to 0 again I recall that ideal all gases for all substances exhibit ideal gas behavior at high-temperature low-pressures since the temperature is constant here, the only way to approach the ideal gas state is by starting from a very low pressure.

So therefore at that particular low pressure say it is P equals to 0 to P equals to P, at P equals to 0 fugacity equals to pressure so therefore this is equals to 1 to f by P and her mu minus mu0 this should be equal to one here and then it should have a value of mu minus mu0 here. So on integration what do I get?

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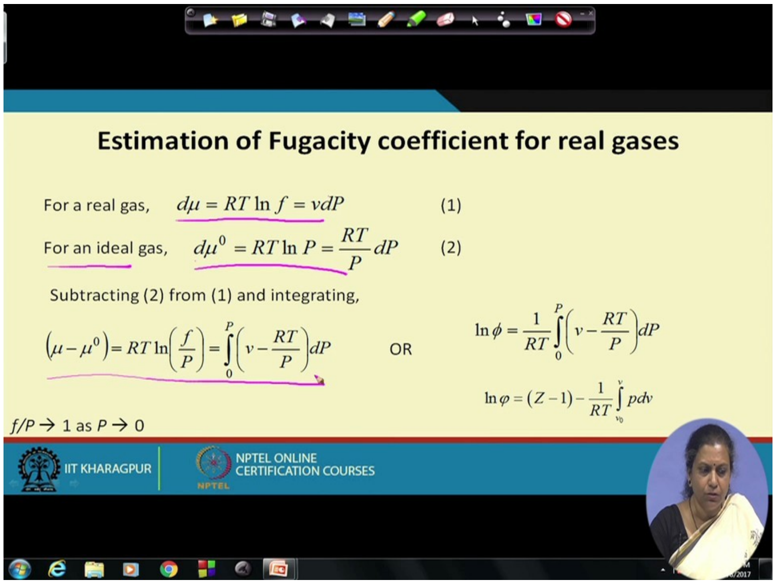

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$f/P \rightarrow 1$ as $P \rightarrow 0$

I get mu minus mu0, sorry it is not one its 0 here because mu equals to mu0 here, mu minus mu 0 this is equals to RT ln f by P which is equal to integral 0 to P, v minus RT by P dp this is the standard equation which I have also mentioned here this is the standard equation which I used in order to find the fugacity of the gases.

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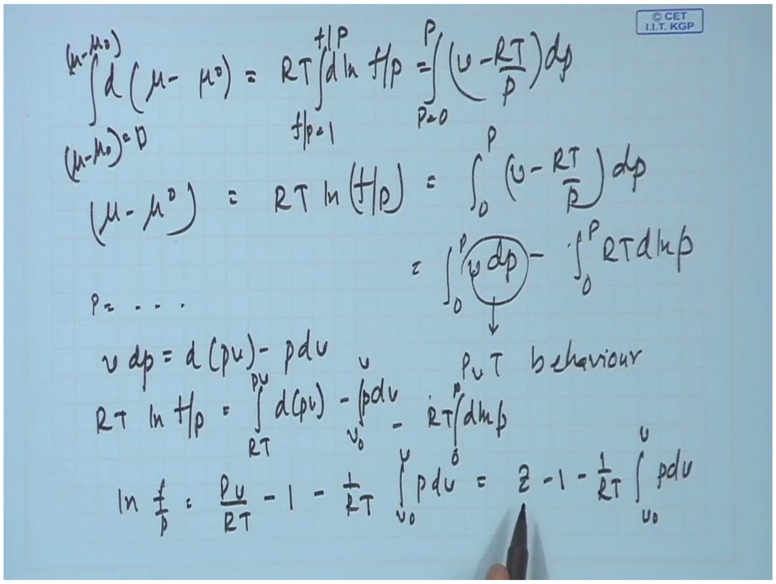

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$$(\mu-\mu^0) = RT\ln(f/p) = \int_0^P\left(v-\frac{RT}{p}\right)dp$$

$$= \int_0^P \boxed{v\,dp} - \int_0^P RT\,d\ln p$$

$$\downarrow$$

PvT behaviour

$p = \dots$

$$v\,dp = d(pv) - p\,dv$$

$$RT\ln f/p = \int_{RT}^{pv} d(pv) - \int_{v_0}^{v} p\,dv - RT\int_0^p d\ln p$$

$$\ln\frac{f}{p} = \frac{pv}{RT} - 1 - \frac{1}{RT}\int_{v_0}^{v} p\,dv = z - 1 - \frac{1}{RT}\int_{v_0}^{v} p\,dv$$

Now the first thing which appears is, this can also be written down as vdp minus 0 to P RT d ln P integrating this is not difficult, for integrating this we have to use the PvT behavior of gas. We have PvT Behavior or the equations of states relating the PV and T of real gases. We have already discussed those equations and as we have found out there are several types of equations, the cubic equations of state, the virial equations of state etc.

We can use any of those equations the only thing that we need to remember in this particular case is the same thing which had happened when we were trying to derive the departure functions for enthalpy and entropy that all these equations they are in terms of pressure explicit form. For example P equals to something whereas in this particular case we would like to express v in terms of P. So therefore in order to perform that again I would like to remind you what do we need to do for that particular case?

We have already done it, for those particular case we can write it down vdp is nothing but equal to dpv minus pdv, so therefore when we write down RT ln f by P then instead of vdp, we can write it down as dpv minus pdv minus RT d ln p integral 0 to P this should be equal to v 0 to v and here what p equals to 0 it is RT this is going to be pv, right? So therefore for such particular conditions we find that ln f by P will be equal to Pv by RT minus1, minus1 by RT integral v0 to v pdv where else we know Pv by RT is equals to Z.

So therefore this is z minus1, minus 1 by RT v0 to v pdv. So therefore in this particular form if we use then in that case we can use any particular equation the cubic equations of state

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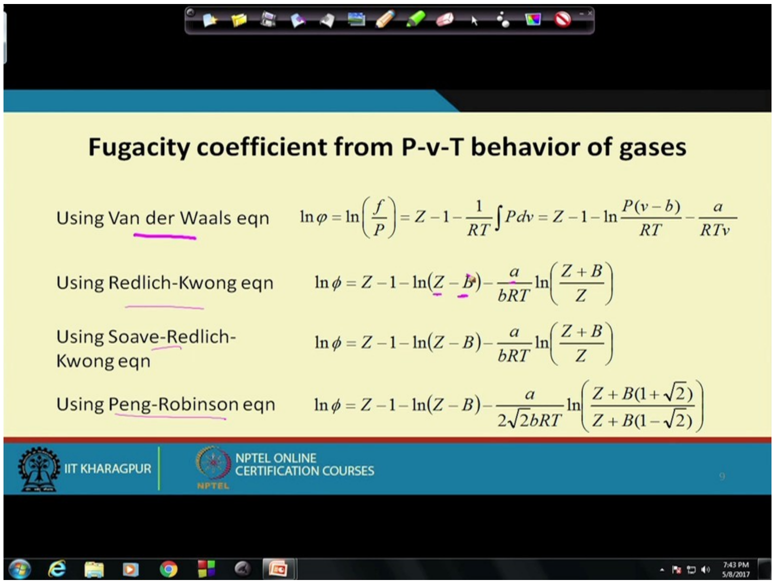

Fugacity coefficient from P-v-T behavior of gases

Using Van der Waals eqn $\ln\varphi = \ln\left(\frac{f}{P}\right) = Z - 1 - \frac{1}{RT}\int P dv = Z - 1 - \ln\frac{P(v-b)}{RT} - \frac{a}{RTv}$

Using Redlich-Kwong eqn $\ln\phi = Z - 1 - \ln(Z - B) - \frac{a}{bRT}\ln\left(\frac{Z+B}{Z}\right)$

Using Soave-Redlich-Kwong eqn $\ln\phi = Z - 1 - \ln(Z - B) - \frac{a}{bRT}\ln\left(\frac{Z+B}{Z}\right)$

Using Peng-Robinson eqn $\ln\phi = Z - 1 - \ln(Z - B) - \frac{a}{2\sqrt{2}bRT}\ln\left(\frac{Z+B(1+\sqrt{2})}{Z+B(1-\sqrt{2})}\right)$

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And in this particular slide what I have done is, I have mentioned the different cubic equations of state which we have already discussed and using this cubic equations of states I have also written down the final forms of the fugacity or the final forms of the fugacity coefficient in terms of z the 2 constants a and b where usually the constant b it refers to the correction due to the non-negligible volume of the molecules as compared to the volume of the gas and a arises due to the interaction between the different molecules.

Well, here there is one but particular thing which I had forgotten to mention in the last class, which I would just like to mention here when we are dealing with the standard states we say that it is the at very low pressure then in that case you must remember that under the standard state conditions we neglect the interactions between the molecules and therefore for all the gases the standard states are different due to the structure and the molecular nature of the different gases and not the way that the gases interact.

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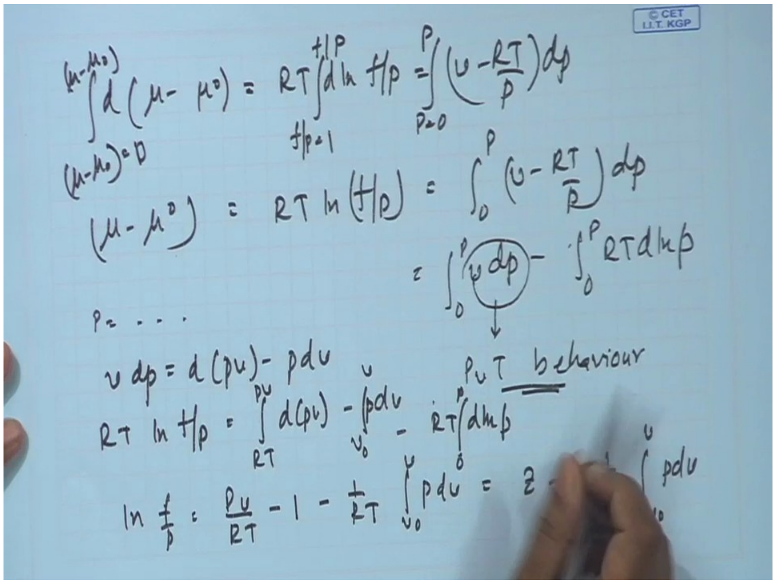

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$\downarrow$ PvT behaviour

$p = \ldots$

$$v\,dp = d(pv) - p\,dv$$

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$$\ln\frac{f}{p} = \frac{pv}{RT} - 1 - \frac{1}{RT}\int_{v_0}^{v} p\,dv = z \ldots \int_{v_0}^{v} p\,dv$$

Well, so therefore this is the first way of determining the fugacity coefficient of the gases that is by the PvT Behavior. Now apart from the PvT Behavior this particular approach is similar to the way we had defined the ways of estimating the departure functions from entropy and enthalpy, we should also be in a position to determine fugacity or fugacity coefficient from compressibility factor as well, isn't it?

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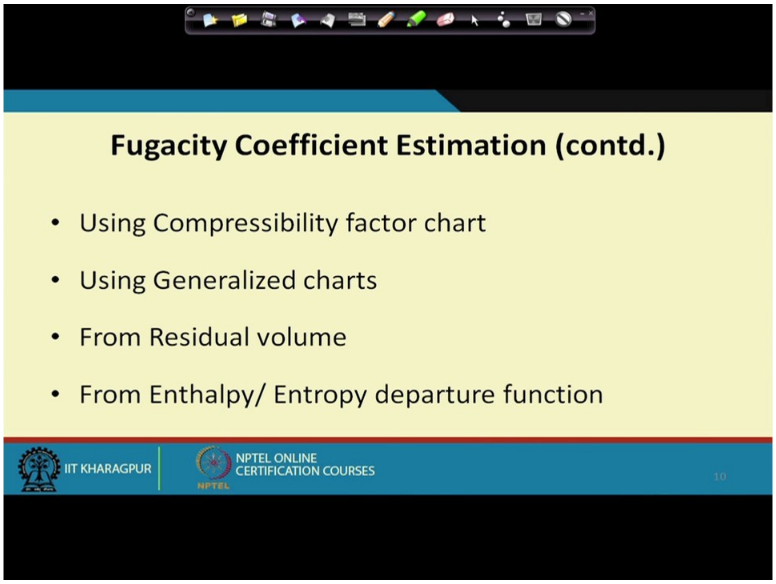

Fugacity Coefficient Estimation (contd.)

- Using Compressibility factor chart
- Using Generalized charts
- From Residual volume
- From Enthalpy/ Entropy departure function

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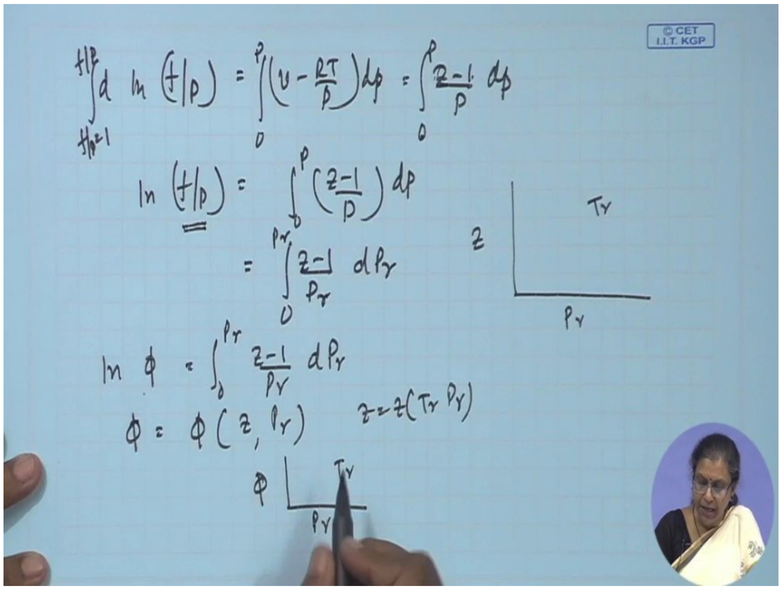

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$$\int_{f/p=1}^{f/p} d\ln\left(f/p\right) = \int_0^P \left(v - \frac{RT}{P}\right)dp = \int_0^P \frac{Z-1}{P}\,dp$$

$$\ln\left(f/p\right) = \int_0^P \left(\frac{Z-1}{P}\right)dp$$

$$= \int_0^{P_r} \frac{Z-1}{P_r}\,dP_r$$

$$\ln\phi = \int_0^{P_r} \frac{Z-1}{P_r}\,dP_r$$

$$\phi = \phi(Z, P_r) \qquad Z = Z(T_r\,P_r)$$

From the compressibility factor also we should be able to able to define it for that in what way should be expressing this particular equation? We can express it as d ln f by P this is equal to v minus RT by P dp this is the same thing which I have written which is nothing but equals to Z minus 1 by P dp. Now here if I integrate it from 0 to P, in this particular case we are going to integrate it from f by P equals to 1 to f by P and this equation also we can define it from 0 to P.

Now in this case we need to remember that Z becomes equal to one for the limiting condition. So therefore in this particular case we can write ln f by P is nothing but equal to integral 0 to P, Z minus 1 by P dp, right? And we can also write this down as z minus 1 by Pr d Pr integral 0 to Pr, can we not write it down in this particular form? And then I have also displayed to you that the different compressibility factor charts which gives z as a function of Pr with Tr as parameter. We have already discussed those particular charts.

So therefore using those particular compressibility factor charts you can find out Z we can substitute Z here and we can find out the value of fugacity coefficient if you observe this equation very closely this and the interesting thing that you find, we find that when you are writing this equation in the form of integral 0 to Pr Z minus 1 by Pr d Pr, if you observe we find that from this particular equation phi it is a function of Z Pr or in other words what do I mean?

And we know Z is a function of Tr Pr, so from here does it suggest that just like entropy and enthalpy departure functions phi also obeys the 2 parameter law of corresponding states or in other words we should be able to generate curves like phi versus Pr with Tr as parameter and from these particular curves in absence of any other data we should be able to find out phi from the this particular charts.

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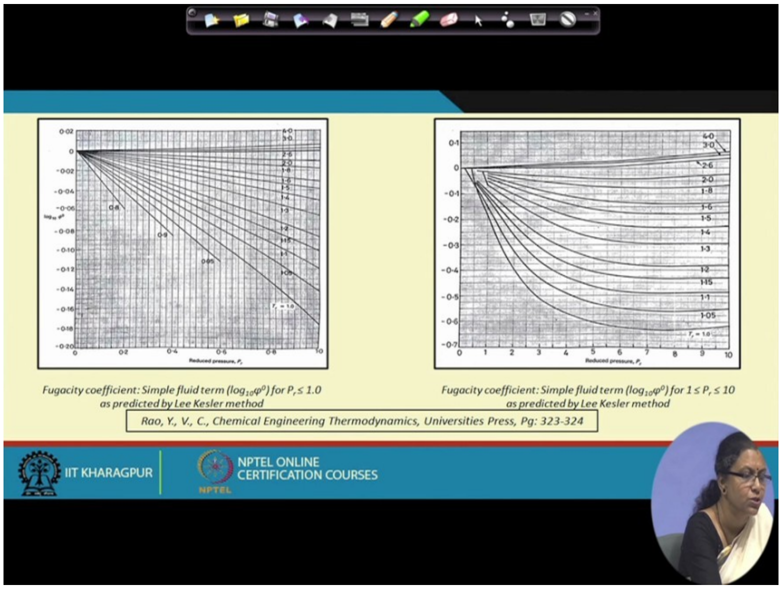

Fugacity coefficient: Simple fluid term ($\log_{10}\varphi^0$) for $P_r \le 1.0$ as predicted by Lee Kesler method

Fugacity coefficient: Simple fluid term ($\log_{10}\varphi^0$) for $1 \le P_r \le 10$ as predicted by Lee Kesler method

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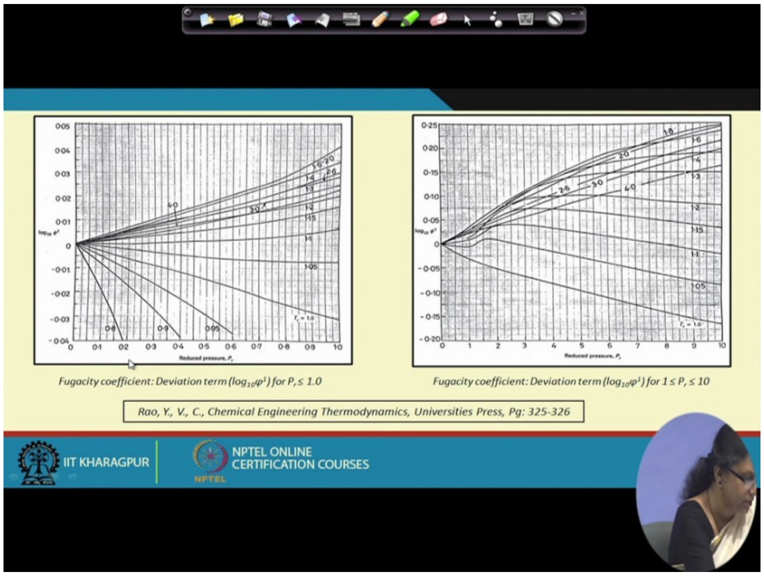

Fugacity coefficient: Deviation term ($\log_{10}\varphi^1$) for $P_r \le 1.0$

Fugacity coefficient: Deviation term ($\log_{10}\varphi^1$) for $1 \le P_r \le 10$

Rao, Y., V., C., Chemical Engineering Thermodynamics, Universities Press, Pg: 325-326

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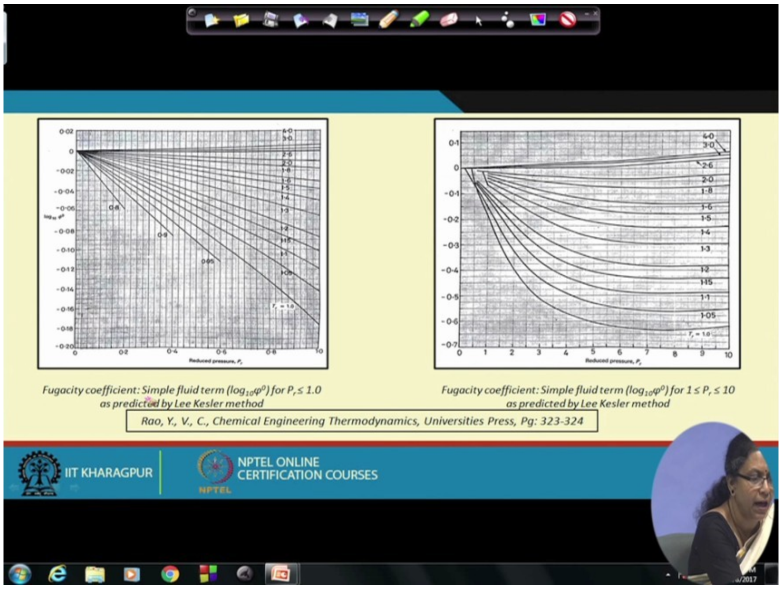
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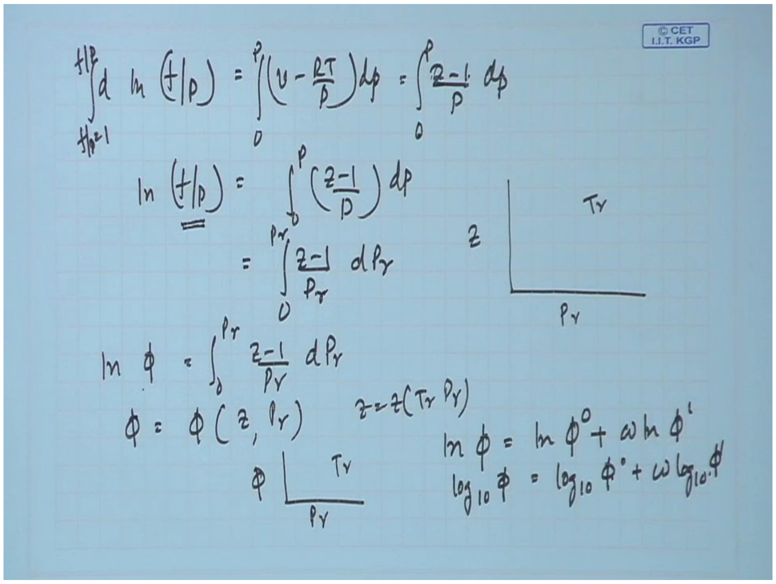

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$$\ln\phi = \int_0^{P_r} \frac{z-1}{P_r}\,dP_r$$

$$\phi = \phi(z, P_r) \qquad z = z(T_r\, P_r)$$

$$\ln\phi = \ln\phi^0 + \omega\ln\phi^1$$

$$\log_{10}\phi = \log_{10}\phi^0 + \omega\log_{10}\phi^1$$

Let us see whether this is, such charts they are available for different types of fluids they are available in several thermodynamic books and we find that these, this particular chart it is applicable both of these charts they are they are there for different values of PR for lower values and higher values of PR and it is also important to note that from this particular equation we can also use the 3 parameter law of corresponding states for greater accuracy where we can define the 3 parameter law in terms of the acentric factor proposed by Pitzer.

We can write it in this particle form or in the log base 10 form which gives the equation as which gives this particular equation and once we know this particular equation then or rather once we know how phi0 and phi1varies with Tr and Pr? We should be in a position to find out phi.

So therefore these graphs they show us the variation of phi 0 with TrPr and also the next graphs they show us the variation of Phi1 with TrPr. So using these curves also we should be in a position to find out the fugacity coefficient from this generalized compressibility factor charts. What is the next technique by which we can find it out?

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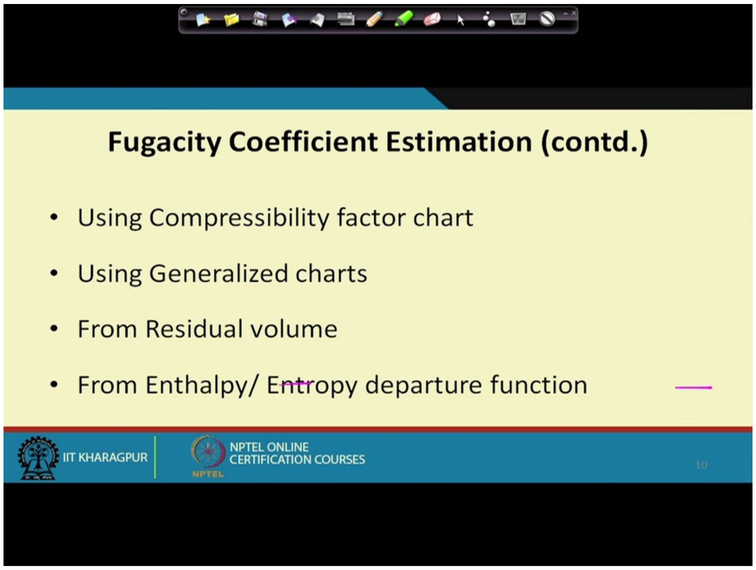

Fugacity Coefficient Estimation (contd.)

- Using Compressibility factor chart
- Using Generalized charts
- From Residual volume
- From Enthalpy/ Entropy departure function

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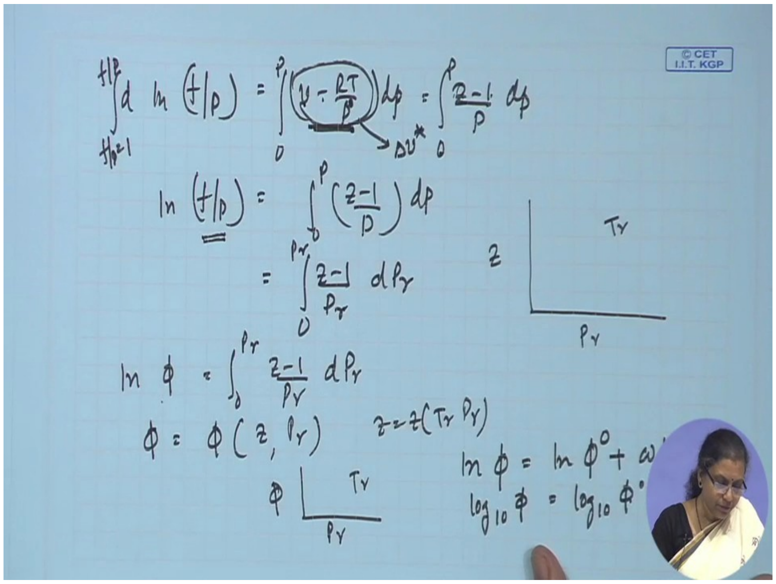

$$\int_{f/p=1}^{f/p} d\ln(f/p) = \int_0^p \underbrace{\left(v - \frac{RT}{p}\right)}_{\Delta v^*} dp = \int_0^p \frac{z-1}{p}\, dp$$

$$\ln(f/p) = \int_0^p \left(\frac{z-1}{p}\right) dp$$

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$$\ln\phi = \int_0^{p_r} \frac{z-1}{p_r}\, dp_r$$

$$\phi = \phi(z, p_r) \qquad z = z(T_r\, p_r)$$

$$\ln\phi = \ln\phi^0 + \omega$$

$$\log_{10}\phi = \log_{10}\phi^0$$

We should also be in a position to find it out from residual volume. We should in a position to find it out from residual volumes and this is very evident if you look at this particular, what is this particular expression? This is nothing but the volume of a gas minus the volume of the same gas one mole of the same gas provided it was behaving ideally under the same conditions of temperature and pressure. So this particular term it is nothing but equal to Delta v star, right?

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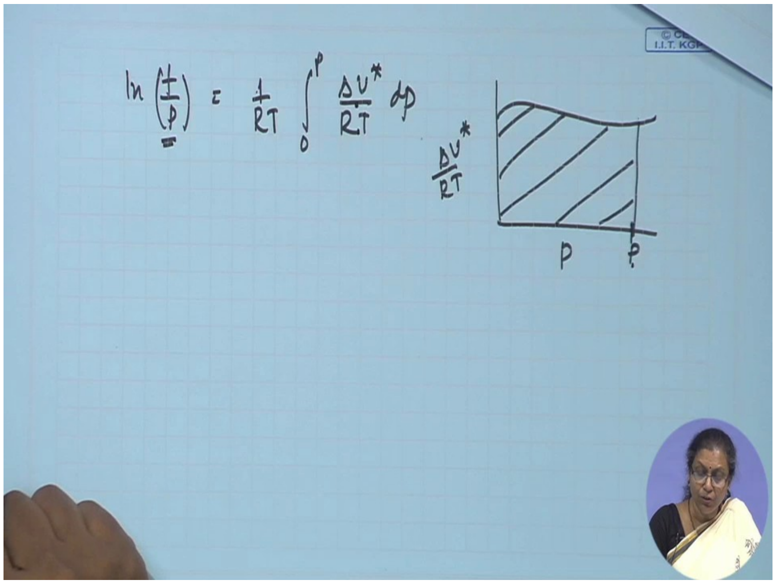

$$\ln\left(\frac{f}{P}\right) = \frac{1}{RT}\int_0^P \frac{\Delta v^*}{RT}\,dp$$

So if we have data on Delta v star then we can directly write ln f by P it is nothing but equals to 1 by RT 0 to P delta v star by RT dp but for this what do we need to know? We need to know how Delta v star by RT varies with P. So therefore we need to, suppose it varies in some particular way and we would like to find out the fugacity at some particular pressure P then the area of the curve starting from P equals to 0 to P equals to P this whole area under the curve that gives us an idea about the fugacity.

Now here I would also like to mention one particular thing, see we can use whatever you have said we can use PV behavior we can use the compressibility factor chart but it is not sufficient to know the Pv behavior or the compressibility factor value at the particular pressure of interest where we want to calculate the fugacity, why?

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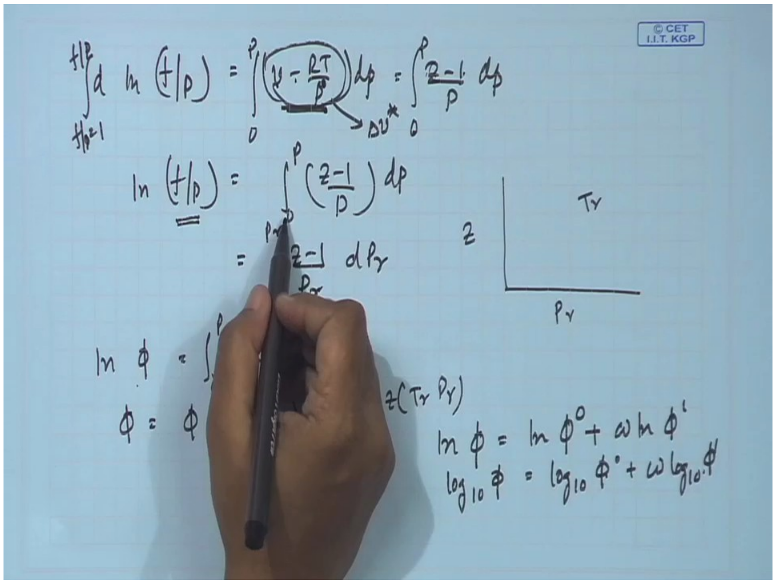

$$\int_{f/P=1}^{f/P} d\ln(f/P) = \int_0^P \underbrace{\left(v - \frac{RT}{P}\right)}_{\Delta v^*} dP = \int_0^P \frac{Z-1}{P}\, dP$$

$$\ln(f/P) = \int_0^P \left(\frac{Z-1}{P}\right) dP$$

$$= \int_0^{P_r} \frac{Z-1}{P_r}\, dP_r$$

$$\ln\phi = \int^P$$

$$\phi = \phi$$

$$Z(T_r\ P_r)$$

$$\ln\phi = \ln\phi^0 + \omega\ln\phi^1$$

$$\log_{10}\phi = \log_{10}\phi^0 + \omega\log_{10}\phi^1$$

Because if you observe all the equations you will find for each of the equations the integration starts from 0 to P. So therefore if I have to integrate over this entire range either this equation or this equation we need to know how volume varies with pressure. How compressibility factor varies with pressure, right from 0 pressure to the pressure of interest? So it is not just sufficient to know the behavior of the gases at the pressure of interest in order to calculate fugacity.

We need to know the behavior of the gases throughout the entire range from the very low pressure almost 0 pressure to the pressure of interest this is one thing which makes the calculation slightly difficult and therefore depending on the availability of the data we have been suggesting the variety of methods which we have proposed.

Now all these methods that we have discussed they are based primarily on PVT Behavior of gases. Suppose we do not have an idea regarding the PVT Behavior then how should we find out the fugacity coefficient?

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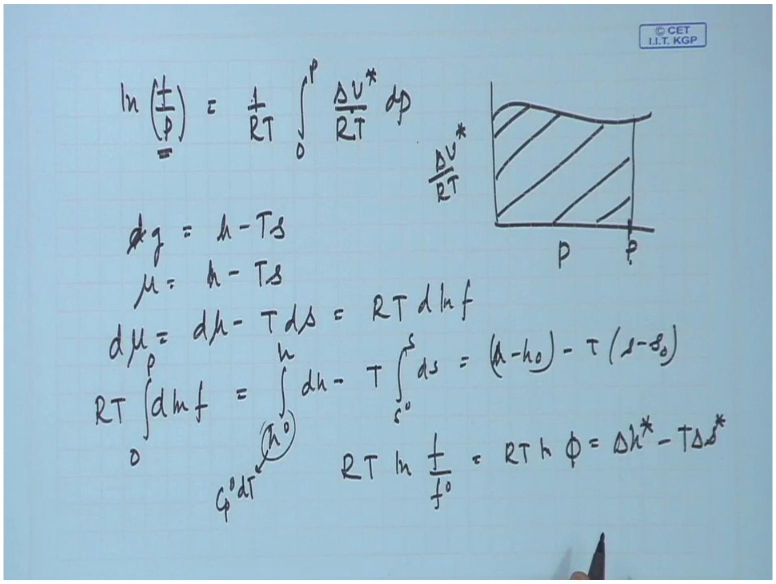

$$\ln\left(\frac{f}{P}\right) = \frac{1}{RT}\int_0^P \frac{\Delta v^*}{RT}\, dP$$

$$\cancel{d}g = h - Ts$$

$$\mu = h - Ts$$

$$d\mu = dh - T\,ds = RT\, d\ln f$$

$$RT\int_0^P d\ln f = \int_{\boxed{h^0}}^{h} dh - T\int_{s^0}^{s} ds = (h-h_0) - T(s-s_0)$$

$$h^0 \rightarrow C_p^0\, dT$$

$$RT\ln\frac{f}{f^0} = RT\ln\phi = \Delta h^* - T\Delta s^*$$

Again we can find out the fugacity coefficient remembering that dg or rather g equals to h minus Ts mu equals to h minus Ts. So therefore at constant temperature d mu equals to dh minus Tds, what is this equal to? This is RT d ln f, so therefore we can also find it out from thermal data as well, right? And this particular case also again the only problem is the identification of the standard states we start from here to here, accordingly h has to be evaluated from very low pressure under which the gas behaves ideally.

So therefore this is equal to Cp0 dT dh minus T s0 to s ds which gives us h minus h0 minus T s minus s0. So from which we can write it down as RT ln f by f0 if f0 equals to P then this can reduce to RT ln phi provided f0 is equals to P and this is nothing but equal to delta h star minus T delta s star.

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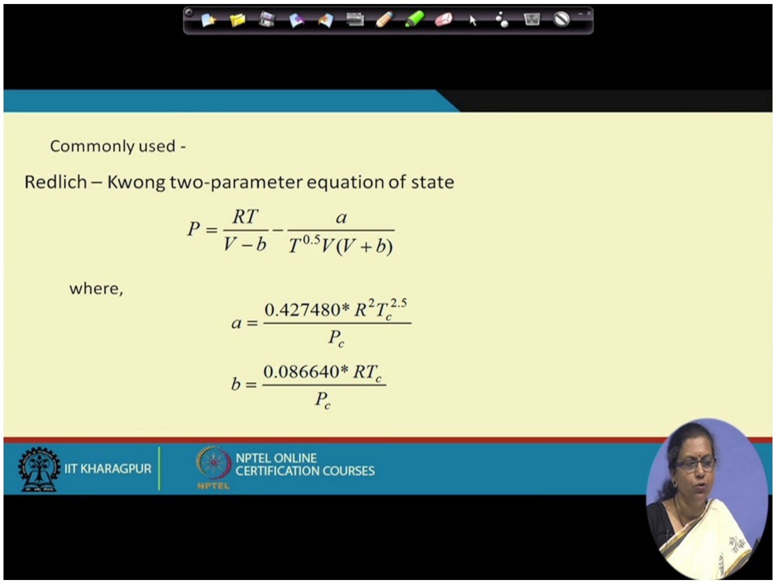

Commonly used -

Redlich – Kwong two-parameter equation of state

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

where,

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

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

And there is one more thing which I would also like to mention that usually what we do is, the other thing what we do is, we usually use the Redlich Kwong 2 parameter equation of state. So in the next class we will be first discussing how to estimate the fugacity? We have discussed how to estimate the fugacity of gases definitely pure gases but real gases single component real gases but if you are dealing with phase equilibrium problems then definitely the most common problems are liquid vapor equilibrium or solid vapor equilibrium.

So therefore if we have to find out the equilibrium we need to have an idea about the fugacity of the gas as well as the fugacity of the condensed phase under any particular condition of temperature and pressure. Regarding fugacity of gases we had a good amount of discussion.

Next class we are going to discuss the fugacity of the condensed phase and then we would like to take up the 2 parameter Redlich Kwong equation of state which is very frequently used for gases as well as for the condensed phase and we are just going to, this is particularly important or it is particularly frequently used for in the hydrocarbon industries. So we are going to end with the discussions on how to use the equation Redlich Kwong equation of state, thank you very much.