Thermodynamics for Biological Systems:
Classical and Statistical Aspects

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Lecture – 25
Review Module 3

Welcome!

Over the past eight to nine lectures we have seen many aspects related to thermodynamic properties of pure fluids. It might be worthwhile reviewing whatever we have seen so far, so that the learning is better. Let us spend today in reviewing the thermodynamic properties of pure fluids that we have covered so far.

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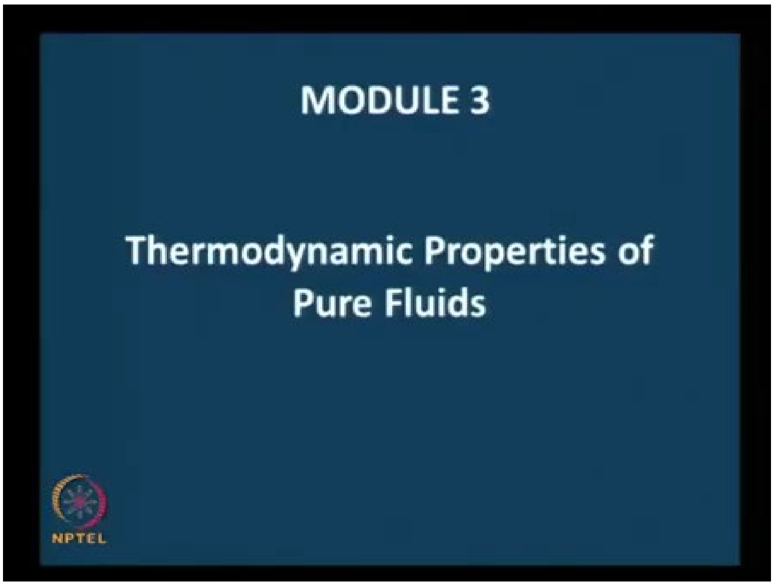

MODULE 3

Thermodynamic Properties of Pure Fluids

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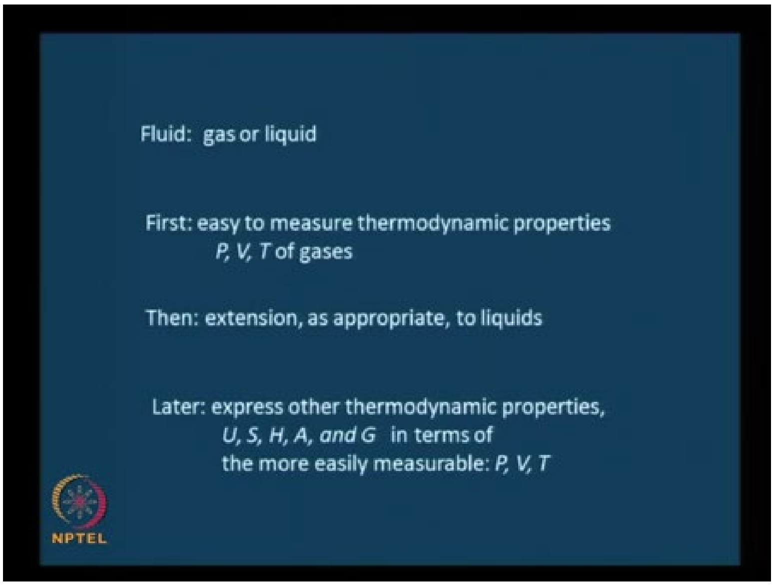

Fluid: gas or liquid

First: easy to measure thermodynamic properties
P, V, T of gases

Then: extension, as appropriate, to liquids

Later: express other thermodynamic properties,
$U, S, H, A,$ and G in terms of
the more easily measurable: P, V, T

We first looked at what a fluid was – it is either a gas or a liquid that we all know. And then we said, we were going to look at easy to measure thermodynamic properties, which are essentially P V T, of gases. Then we said, we would extend it, as appropriate, to liquids; first gases and then to liquids. And then we said that, we would express the other thermodynamic properties such as Internal Energy, Entropy, Enthalpy, Helmholtz free energy and Gibbs free energy, as well as, let us say, the fugacity coefficient in terms of the more easily measurable P, V and T. That was the whole scheme of things for this module.

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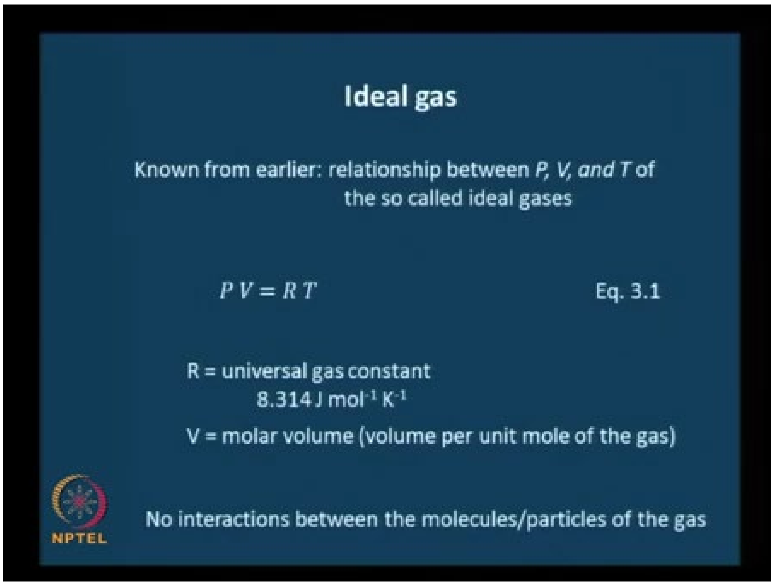

Ideal gas

Known from earlier: relationship between $P, V,$ and T of
the so called ideal gases

$$P V = R T \qquad \text{Eq. 3.1}$$

R = universal gas constant
$8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}$
V = molar volume (volume per unit mole of the gas)

No interactions between the molecules/particles of the gas

And we first looked at an ideal gas, which you are already familiar with from your earlier classes. So, we will not spend much time on that. We know that the relationship between P V and T for an ideal gas is

$$P\,V = R\,T$$

for 1 mole of an ideal gas, or molar volume considered here. And these results, when there are no interactions between the molecules of the gas – that is when a gas would be ideal. And so, it happens that some gases, some noble gases do follow the equation of state for ideal gas. This is called an equation of state. Any relationship between P, V and T is an equation of state. And this is where we brought in things specific to our course.

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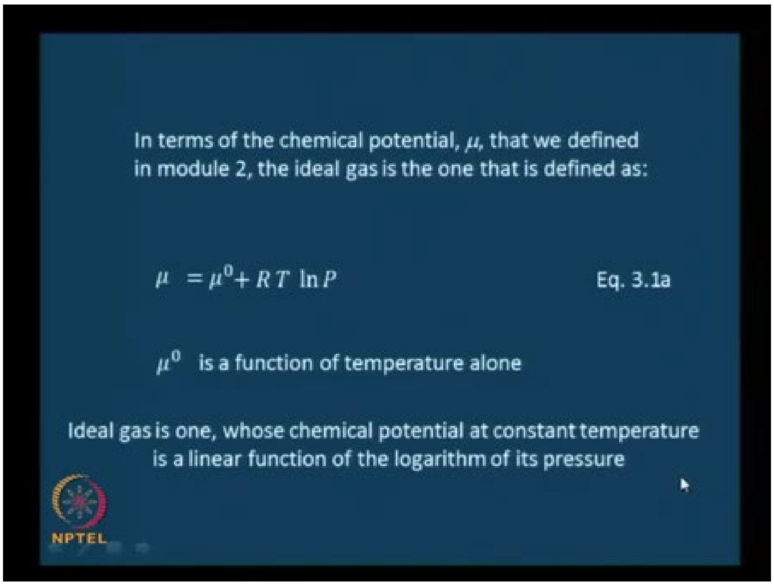

In terms of the chemical potential, μ, that we defined in module 2, the ideal gas is the one that is defined as:

$$\mu = \mu^0 + R\,T\,\ln P \qquad \text{Eq. 3.1a}$$

μ^0 is a function of temperature alone

Ideal gas is one, whose chemical potential at constant temperature is a linear function of the logarithm of its pressure

We said it in terms of the chemical potential, we will define or we have already defined the ideal gas as something that follows

$$\mu = \mu^0 + R\,T\,ln\,P$$

In fact, we have defined, what a chemical potential is earlier. We are defining what an ideal gas is? In terms of the chemical potential in this module, we said

$$\mu = \mu^0 + R\,T\,ln\,P$$

that satisfies this equation is an ideal gas, where μ^0 is a function of temperature alone. It is quite easy to see here, you know this can be considered of the form

$$y = mx + c$$

straight line equation. Therefore, if you plot y, which is μ here, versus $ln\, P$, which is x here, then you should get a straight line with this as the intercept.

Therefore, the ideal gas is one whose chemical potential at constant temperature is a linear function of the logarithm. The natural logarithm or whatever logarithm that one takes of it is pressure.

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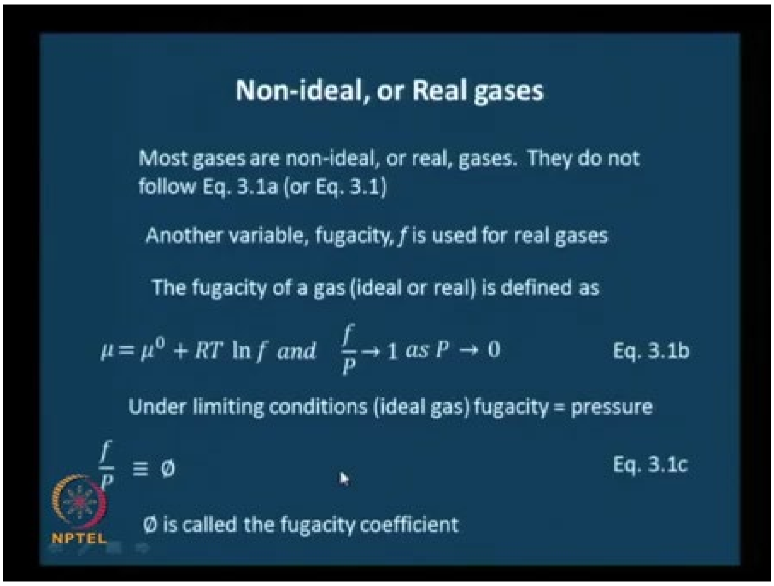

Non-ideal, or Real gases

Most gases are non-ideal, or real, gases. They do not follow Eq. 3.1a (or Eq. 3.1)

Another variable, fugacity, f is used for real gases

The fugacity of a gas (ideal or real) is defined as

$\mu = \mu^0 + RT \ln f$ *and* $\frac{f}{P} \to 1$ *as* $P \to 0$ Eq. 3.1b

Under limiting conditions (ideal gas) fugacity = pressure

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

$\emptyset$ is called the fugacity coefficient

Then, we started looking at non-ideal or real gases which of course, most gases are real or non-ideal. Or in other words they do not follow the equation of the state P V equals R T. And to describe them, we brought in the variable fugacity in terms of the chemical potential that, we have seen fugacity can be given as

$$\mu = \mu^0 + R\,T\, ln\, f \qquad \frac{f}{P} \rightarrow 1 \quad as\, P \rightarrow 0$$

This is for a real gas or all gases, you know when it is a real gas, it should also include ideal gases or a real gas formulation should include an ideal gas formulation. Therefore,

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

instead of RT ln P should be able to define all gases that is what we said. And this is not complete without stating that f by P will tend to 1 as the pressure goes to 0.

Therefore, quite easy to see under limiting conditions, when f by P goes to 1, the fugacity is actually equal to the pressure. So, it is fine for ideal gases also. We defined something called a fugacity coefficient,

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

which is unique to a particular pure substance. It is quite easy to realize that, we need more mathematical, more accurate mathematical representations, because PV = RT is not going to the job anymore.

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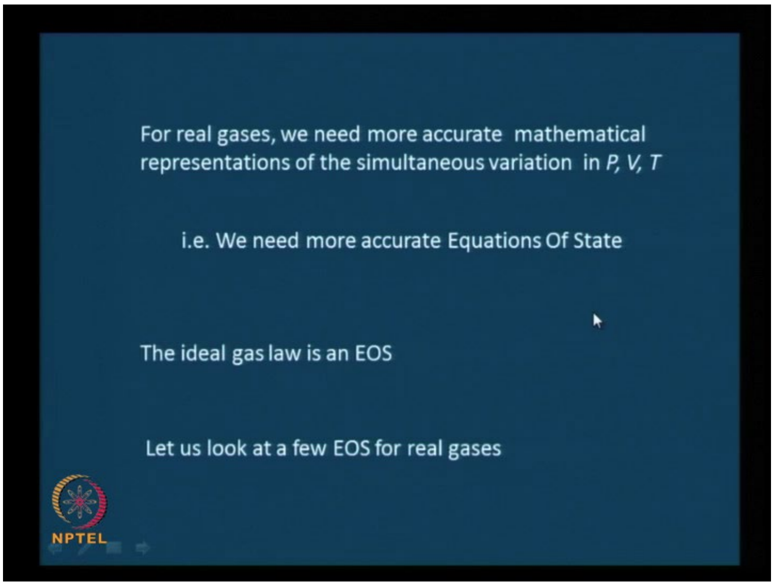
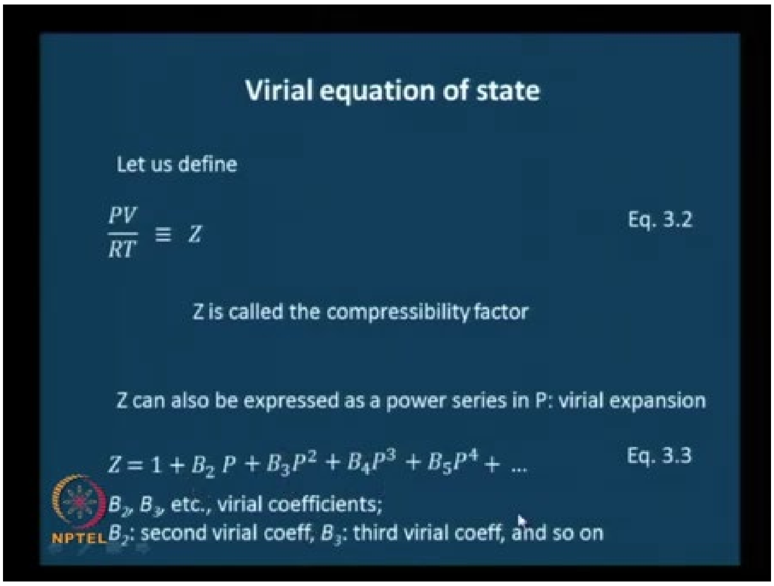


For real gases, we need more accurate mathematical representations of the simultaneous variation in P, V, T

i.e. We need more accurate Equations Of State

The ideal gas law is an EOS

Let us look at a few EOS for real gases



Virial equation of state

Let us define

$$\frac{PV}{RT} \equiv Z \qquad \text{Eq. 3.2}$$

Z is called the compressibility factor

Z can also be expressed as a power series in P: virial expansion

$$Z = 1 + B_2 P + B_3P^2 + B_4P^3 + B_5P^4 + \ldots \qquad \text{Eq. 3.3}$$

B_2, B_3, etc., virial coefficients;

B_2: second virial coeff, B_3: third virial coeff, and so on

The first complication that we saw, or the first improvement that we saw in the equation of state to represent real gases is the virial equation of state. It is to know what are virial equation of state is which is written in terms of what is called the compressibility factor, compressibility factor is nothing but,

$$\frac{PV}{RT} \equiv Z$$

Z can be expressed in terms of a power series in P and that is called a virial expansion. For example,

$$Z = 1 + B_2 P + B_3P^2 + B_4P^3 + B_5P^4 + \ldots$$

This is a virial expansion in pressure for the gas. Here B_2, B_3 are called the virial coefficients, the second virial coefficient B_2, third virial coefficient B_3 and so on.

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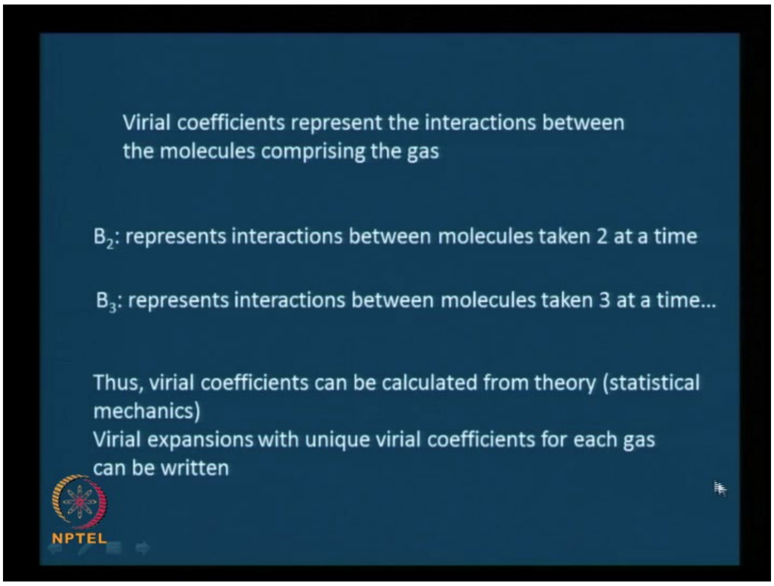
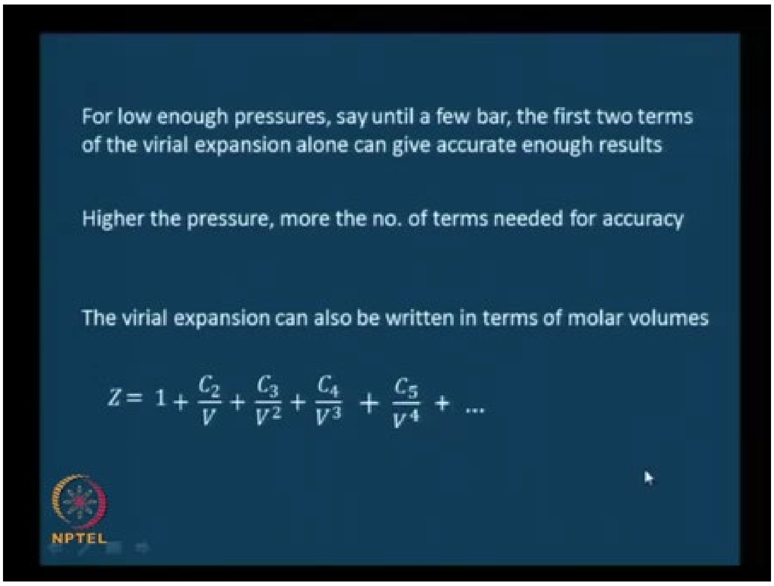


Virial coefficients represent the interactions between the molecules comprising the gas

B_2: represents interactions between molecules taken 2 at a time

B_3: represents interactions between molecules taken 3 at a time…

Thus, virial coefficients can be calculated from theory (statistical mechanics)
Virial expansions with unique virial coefficients for each gas can be written



For low enough pressures, say until a few bar, the first two terms of the virial expansion alone can give accurate enough results

Higher the pressure, more the no. of terms needed for accuracy

The virial expansion can also be written in terms of molar volumes

$$Z = 1 + \frac{C_2}{V} + \frac{C_3}{V^2} + \frac{C_4}{V^3} + \frac{C_5}{V^4} + \dots$$

And we also said that, Virial coefficients are actually they represent the interactions between the molecules comprising the gas and therefore, they can actually be found from theory statistical mechanics. For example, B_2 represents interactions between molecules taken 2 at a time; B_3 represents interactions between molecules taken three at a time and so on.

Also for low enough pressures say about a few bar, just the first two or three terms of the Virial expansion is good enough to give an acceptably accurate representation of the gas behaviour. But higher the pressure, more terms are needed to accurately represent the behaviour and we also saw that the Virial expansion can be written in terms of molar volumes. Of course, since it is direct function of pressure, this has to be an inverse function of volume. Therefore,

$$Z = 1 + \frac{C_2}{V} + \frac{C_3}{V^2} + \frac{C_4}{V^3} + \frac{C_5}{V^4} + \cdots$$

And C_2, C_3 can also be calculated from theory.

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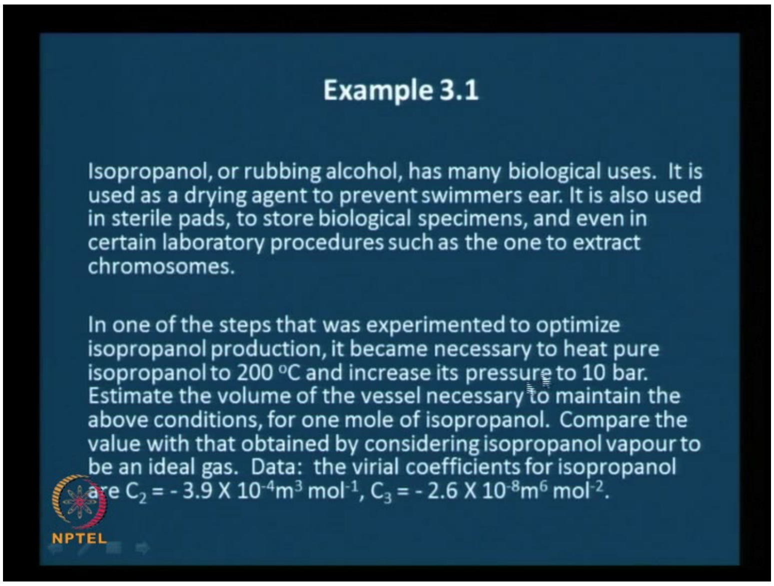
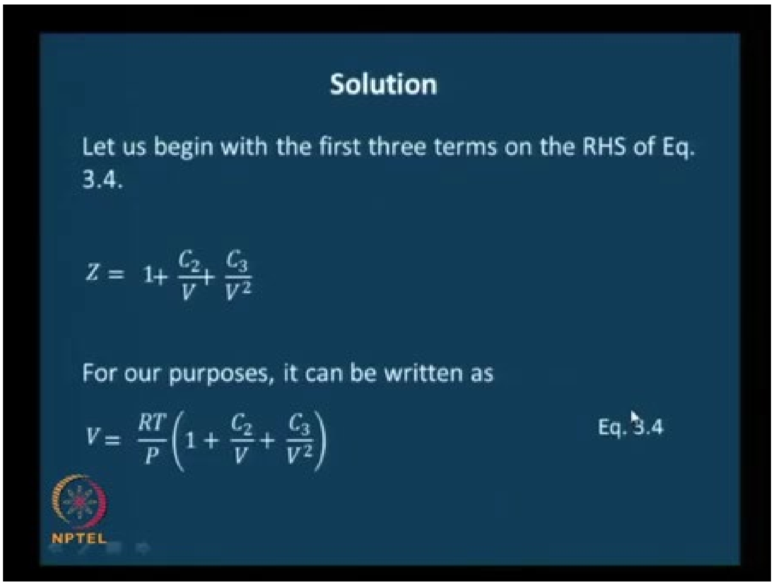


Example 3.1

Isopropanol, or rubbing alcohol, has many biological uses. It is used as a drying agent to prevent swimmers ear. It is also used in sterile pads, to store biological specimens, and even in certain laboratory procedures such as the one to extract chromosomes.

In one of the steps that was experimented to optimize isopropanol production, it became necessary to heat pure isopropanol to 200 °C and increase its pressure to 10 bar. Estimate the volume of the vessel necessary to maintain the above conditions, for one mole of isopropanol. Compare the value with that obtained by considering isopropanol vapour to be an ideal gas. Data: the virial coefficients for isopropanol are $C_2 = -3.9 \times 10^{-4} m^3 mol^{-1}$, $C_3 = -2.6 \times 10^{-8} m^6 mol^{-2}$.



Solution

Let us begin with the first three terms on the RHS of Eq. 3.4.

$$Z = 1 + \frac{C_2}{V} + \frac{C_3}{V^2}$$

For our purposes, it can be written as

$$V = \frac{RT}{P}\left(1 + \frac{C_2}{V} + \frac{C_3}{V^2}\right) \qquad \text{Eq. 3.4}$$

We did an example, where we looked at how to use the virial equation. To calculate some properties of interest in this case I think, we did the volume of the vessel. We will not go through the example again.

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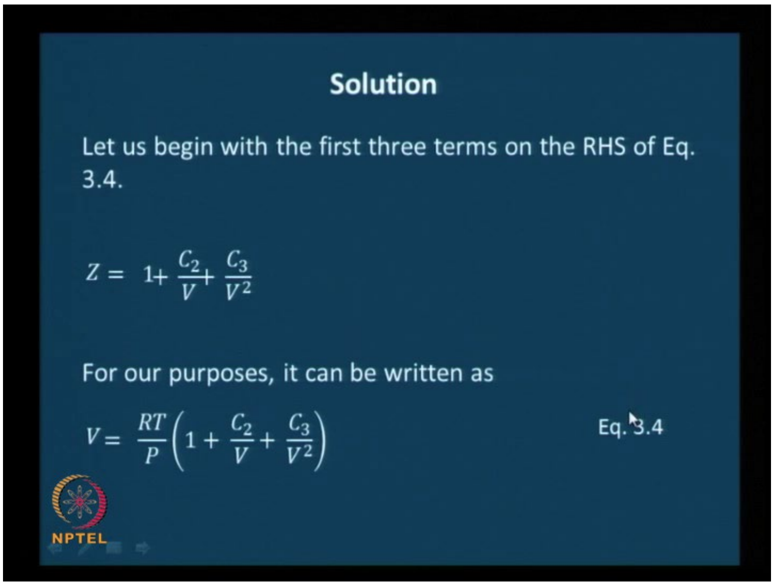

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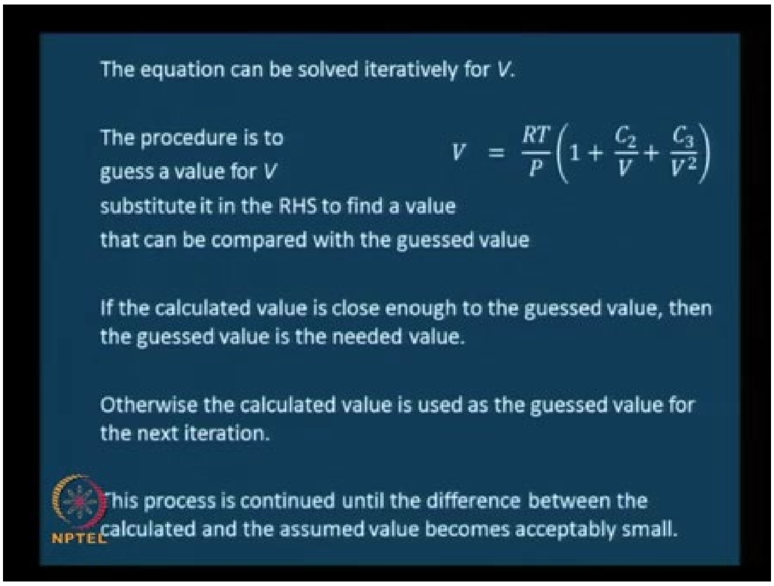

The equation can be solved iteratively for *V*.

The procedure is to
guess a value for *V*
substitute it in the RHS to find a value
that can be compared with the guessed value

$$V = \frac{RT}{P}\left(1 + \frac{C_2}{V} + \frac{C_3}{V^2}\right)$$

If the calculated value is close enough to the guessed value, then the guessed value is the needed value.

Otherwise the calculated value is used as the guessed value for the next iteration.

This process is continued until the difference between the calculated and the assumed value becomes acceptably small.

If you are interested, you can go back to the part of lecture and look at it again.

Since, some of you may have looked at an iterative solution for the first time let we, let me just run through it again here. An iterative solution comes about, when especially, when you have higher order equations polynomial expressions here, we had a cubic equation. Therefore, we set it up of the form you know we had

$$Z = 1 + \frac{C_2}{V} + \frac{C_3}{V^2}$$

but we knew that we were looking for V.

Therefore, if we set up the equations as set, we have V on the left hand side and V on the right hand side. You can do an iterative process to get at the solution and to do that, we replaced Z by P V by R T. Which is the definition of Z and thus, we got V on the left hand side and this on the right hand side.

$$V = \frac{RT}{P}\left(1 + \frac{C_2}{V} + \frac{C_3}{V^2}\right)$$

To solve iteratively for V the procedure was to guess a certain value of V and substitute it into the right hand side to find the value of the right hand side. Then compare that value to the guessed value or in other words take the difference. If the calculated value was close enough to the guessed value, you know close enough is I said was the operator word here, close enough to the guessed value. Then the guessed value was the needed value.

Otherwise the calculated value is put back into the right hand side; rather it is used as the second guess that is put back into the right hand side to calculate third value. Then, that is compared with the second value; this process is continued till a certain convergence. As it is called in other words, the difference between the calculated value and guessed value is small enough compared to the value of V itself. For example, in this particular case, if it is less than, let us say about 1 or 2 percent it should be acceptable for most of our needs. These are the details of the solution; we will not get into that and the review.

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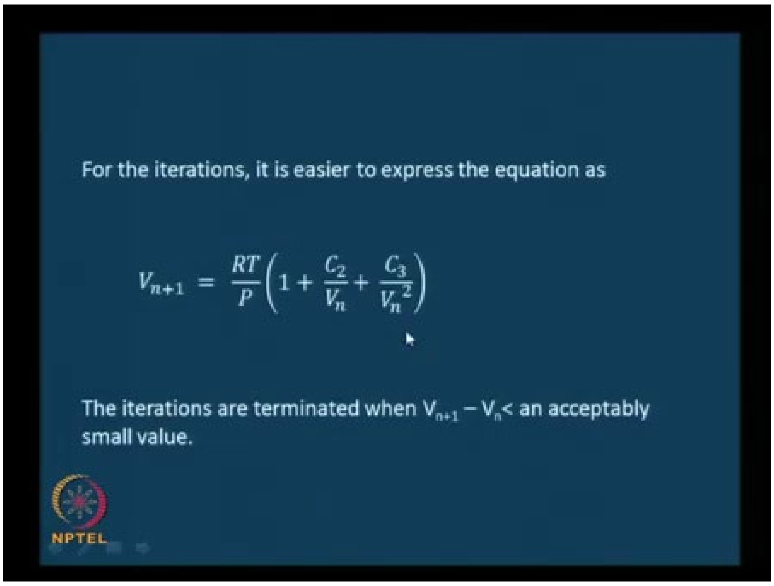

For the iterations, it is easier to express the equation as

$$V_{n+1} = \frac{RT}{P}\left(1 + \frac{C_2}{V_n} + \frac{C_3}{V_n^{\,2}}\right)$$

The iterations are terminated when $V_{n+1} - V_n <$ an acceptably small value.

Let me also mention this, that it is easiest to do these iterations, iterative calculations by using a program and to write it in a form, that can be converted into a program for easy calculations. We write it as

$$V_{n+1} = \frac{RT}{P}\left(1 + \frac{C_2}{V_n} + \frac{C_3}{{V_n}^2}\right)$$

Therefore, V_0 could be the guess value and V_0 would result in V_1, then if $(V_1 - V_0)$ is small enough then, we stop the iterations there, otherwise V_1 is substituted here to get V_2 then the comparison is made. And, if it is small if the error is small enough the difference is small enough, we terminated their otherwise keep, we keep going on.

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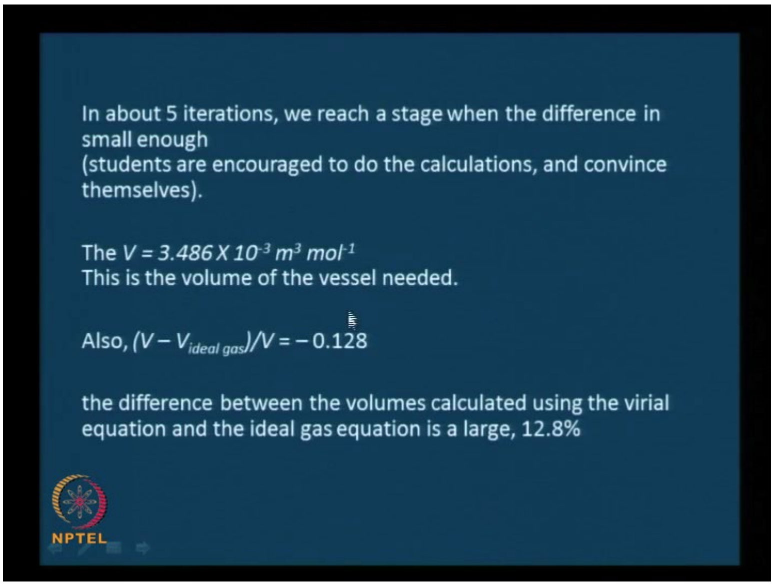
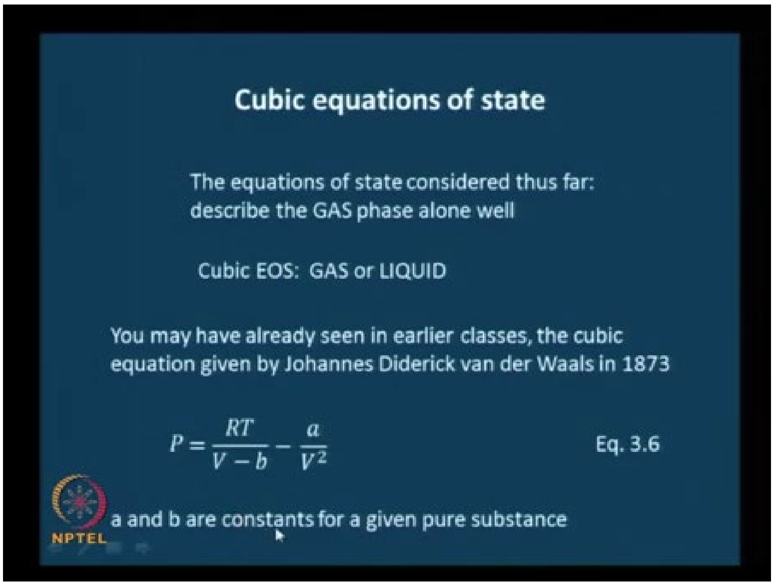


In about 5 iterations, we reach a stage when the difference in small enough
(students are encouraged to do the calculations, and convince themselves).

The $V = 3.486 X 10^{-3}\ m^3\ mol^{-1}$
This is the volume of the vessel needed.

Also, $(V - V_{ideal\ gas})/V = -0.128$

the difference between the volumes calculated using the virial equation and the ideal gas equation is a large, 12.8%



Cubic equations of state

The equations of state considered thus far:
describe the GAS phase alone well

Cubic EOS: GAS or LIQUID

You may have already seen in earlier classes, the cubic equation given by Johannes Diderick van der Waals in 1873

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \qquad \text{Eq. 3.6}$$

a and b are constants for a given pure substance

So, it is easy to write a program, if we represent the equation in this form and I think I will mention it here itself. It is the ideal gas volume is a good first guess value, for the gas volume usually.

Then we looked at cubic equations of state before that, we considered whatever we did till then, we said that, we considered equations that describe the gas phase alone well. Then, we looked at the rather, we will be looking at cubic equation of state, which would represent both the gas and the liquid behaviour reasonably well. One of the cubic equations you may have already encountered in your higher second years class or in your first year courses, which is the Van der waals equation of state. It goes as

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

a and b are constants for a given pure substance.

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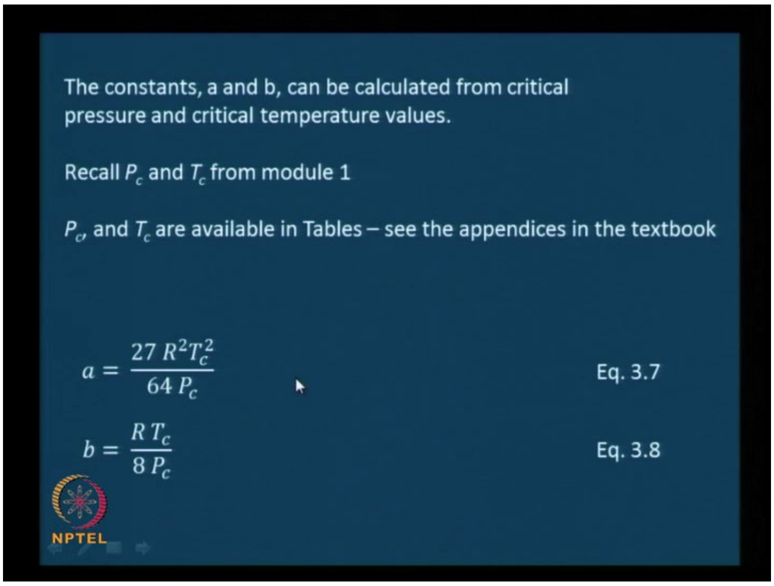

The constants, a and b, can be calculated from critical pressure and critical temperature values.

Recall P_c and T_c from module 1

P_c, and T_c are available in Tables – see the appendices in the textbook

$$a = \frac{27\, R^2 T_c^2}{64\, P_c} \qquad \text{Eq. 3.7}$$

$$b = \frac{R\, T_c}{8\, P_c} \qquad \text{Eq. 3.8}$$

We said that the a and b can be calculated from critical pressure and critical temperature values.

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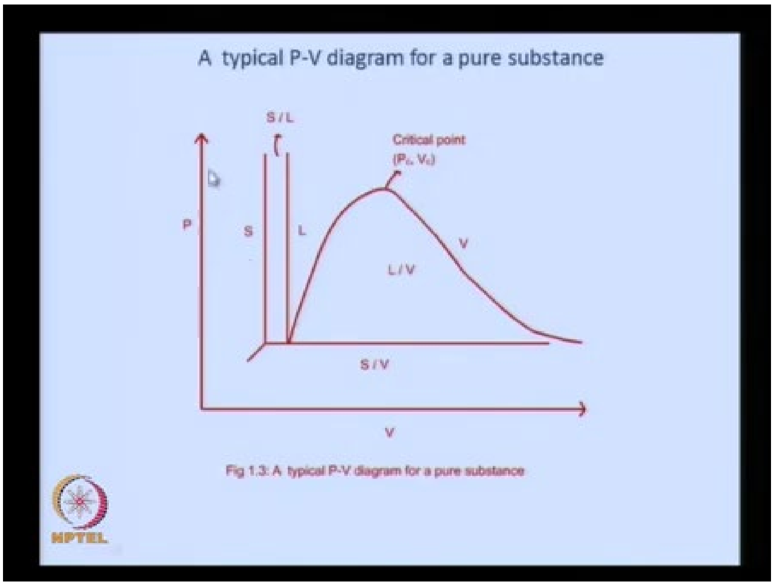

A typical P-V diagram for a pure substance

Fig 1.3: A typical P-V diagram for a pure substance

This might be worthwhile. Let me recall our P V diagram here, you know P V the variation between pressure and specific volume for a pure substance. Let us focus on this curve alone, there are many many parts to this diagram. In other words these are pressure specific volume combinations or specific volume pressure combinations, where the different phases exist. We said under this dome you have the saturated phase, which is the mixture of liquid and vapour. And the top point of this is the critical point beyond this, you have critical behaviour where the properties are very different, we said that we are not going to look at the properties of the critical phase in this particular course. So, this is the critical point just to recall.

And from that critical point, which is tabulated for pure substances and that tabulation is available in the appendix of your text book. We could get the values of a and b by these expressions

$$a = \frac{27\, R^2 T_C^2}{64\, P_C}$$

$$b = \frac{R\, T_C}{8\, P_C}$$

This is for the Van der Waals equation of state.

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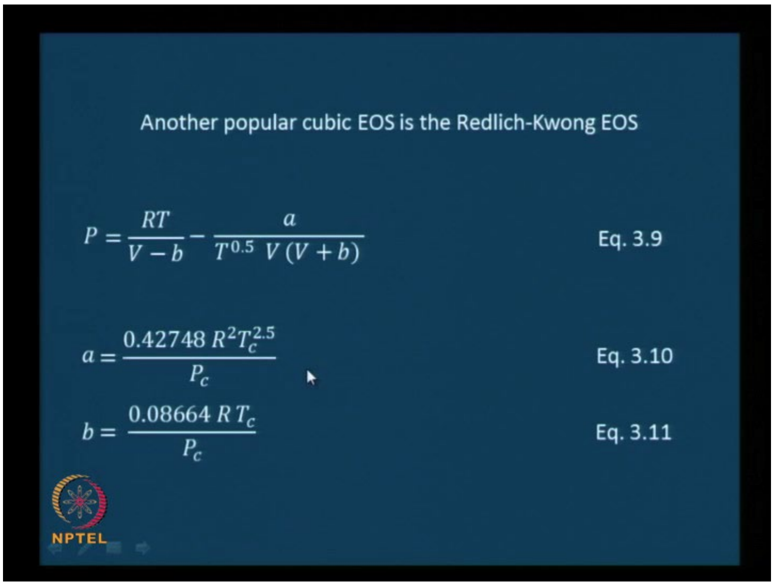
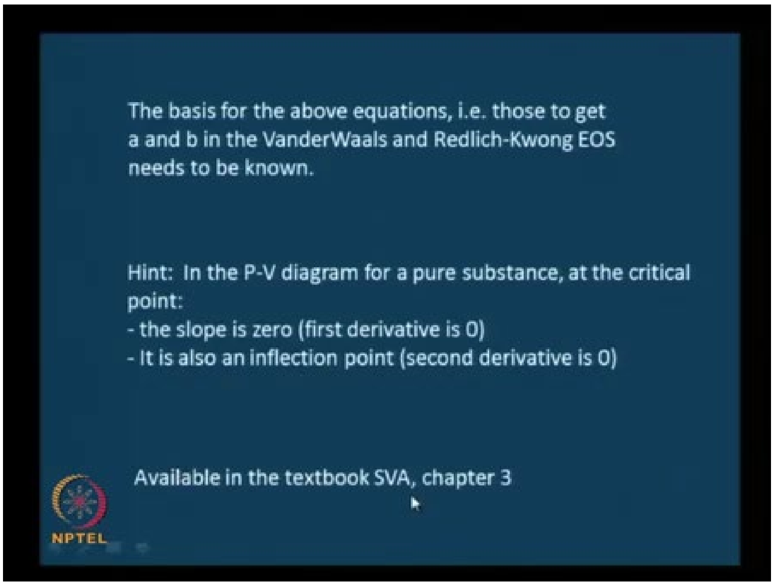


Another popular cubic EOS is the Redlich-Kwong EOS

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}\ V\,(V+b)} \qquad \text{Eq. 3.9}$$

$$a = \frac{0.42748\ R^2 T_c^{2.5}}{P_c} \qquad \text{Eq. 3.10}$$

$$b = \frac{0.08664\ R\,T_c}{P_c} \qquad \text{Eq. 3.11}$$



The basis for the above equations, i.e. those to get a and b in the VanderWaals and Redlich-Kwong EOS needs to be known.

Hint: In the P-V diagram for a pure substance, at the critical point:
- the slope is zero (first derivative is 0)
- It is also an inflection point (second derivative is 0)

Available in the textbook SVA, chapter 3

Then another popular cubic equation of state, we saw as the Redlich-Kwong equation of state.

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

We said the a and b in the Redlich-Kwong equation of state are can also be calculated from the critical properties,

$$a = \frac{0.42748\ R^2 T_c^{2.5}}{P_c}$$

$$b = \frac{0.08664\ R\,T_c}{P_c}$$

Then, we also saw the basis for writing these a and b values in terms of Tc Pc and so on. We have equivalent expressions for the Vander Waals equation of state also.

This was given as a home work and the basis for that is as follows. Let us go back to our P versus V diagram again, if you look at this point here at this point you have a 0 slope, you know the slope changes sign. Therefore, $\frac{\partial P}{\partial V}$ at a particular temperature. Therefore, $\left(\frac{\partial P}{\partial V}\right)_T = 0$ at the critical point, not just that the sign it is also an inflection point which means, if you look at the derivative the sign of the derivative also changes at this point. Therefore, this becomes a inflection point and therefore, the second derivative $\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$.

We said we could use these two criteria or these two relationships that have been that become apparent to calculate the a and b values in terms of the critical constants. This is actually available in your text book chapter 3, if you want you can look at that.

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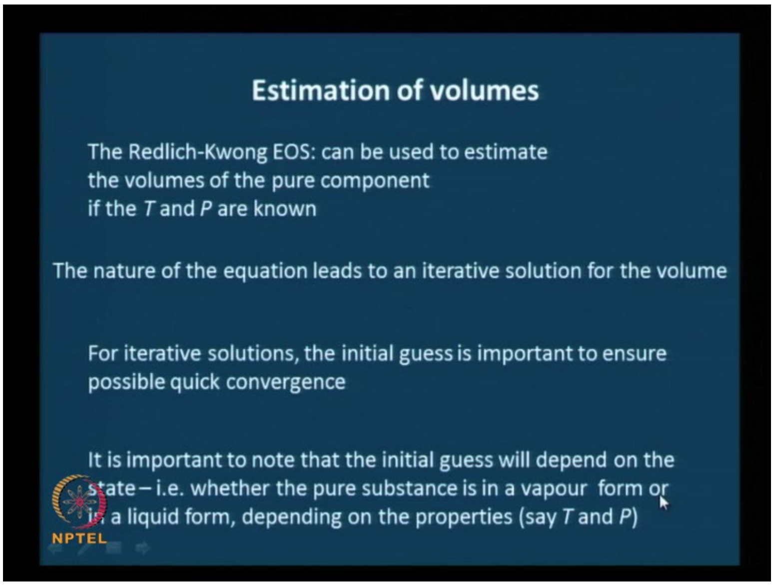

Estimation of volumes

The Redlich-Kwong EOS: can be used to estimate
the volumes of the pure component
if the *T* and *P* are known

The nature of the equation leads to an iterative solution for the volume

For iterative solutions, the initial guess is important to ensure
possible quick convergence

It is important to note that the initial guess will depend on the
state – i.e. whether the pure substance is in a vapour form or
in a liquid form, depending on the properties (say *T* and *P*)

And then, we went to the estimation of volumes using the equations of state. We said that the Redlich-Kwong equation can be used to estimate volumes of pure component. And since it is a cubic equation we need an iterative solution, the initial gas of course, is important and So on, we said.

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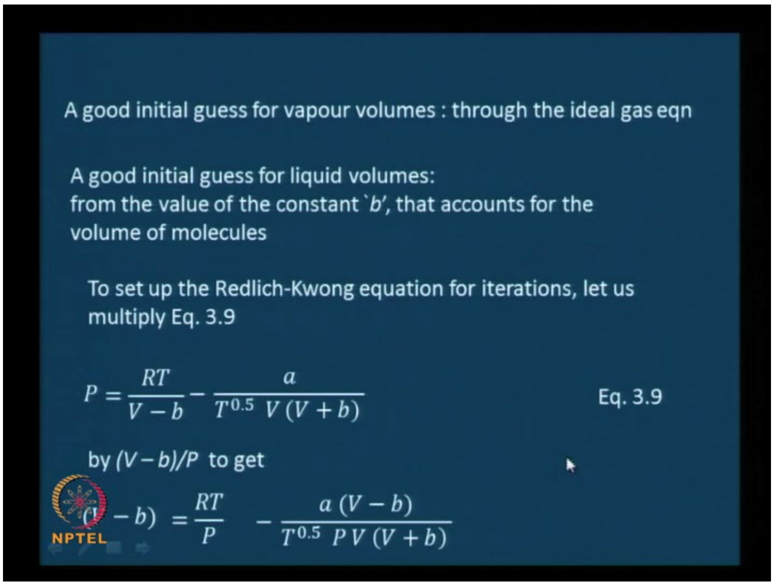

A good initial guess for vapour volumes : through the ideal gas eqn

A good initial guess for liquid volumes:
from the value of the constant `b', that accounts for the volume of molecules

To set up the Redlich-Kwong equation for iterations, let us multiply Eq. 3.9

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}\, V\,(V+b)} \qquad \text{Eq. 3.9}$$

by $(V-b)/P$ to get

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

The good initial gas for vapour volumes is through the ideal gas equation a good initial gas for the liquid volumes is from the constant b. Because remember that V minus b term either in the Vander Waals equation or in the Redlich-Kwong equation of state. Therefore, that gives you an idea that b represents the volume that is occupied by the molecules. When it is a gas the molecules are further apart and therefore, the fraction of volume that is occupied by the molecules is less. Whereas, in the liquid they are all close together and this value of b could be the first guess that one could make. When one is looking at liquid volumes, it is quite easy to see that, you put all the molecules together and you choose the total volume of the molecules. That should give you some value of the volume in the ball park of the liquid volume that is idea with which these are chosen. And to set up the Redlich-Kwong equation for the iterations itself, we went through a strategy, we multiplied the Redlich-Kwong equation by V minus b by P, to get it of this form.

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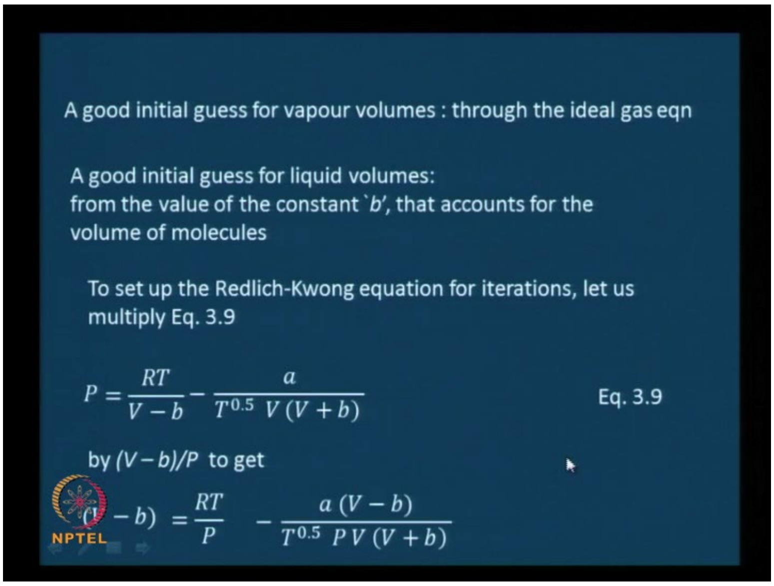

A good initial guess for vapour volumes : through the ideal gas eqn

A good initial guess for liquid volumes:
from the value of the constant `b', that accounts for the volume of molecules

To set up the Redlich-Kwong equation for iterations, let us multiply Eq. 3.9

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}\ V(V+b)} \qquad \text{Eq. 3.9}$$

by $(V-b)/P$ to get

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

And to facilitate for vapour volumes, we had written it as

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

Therefore, you could do iterations with this for the vapour volumes. Whereas, we have a problem, if we consider the same form to do liquid volumes, why we said our initial gas was going to be b. Therefore, initial gas is going to be b you substituted here this entire term will go to 0. Therefore, we loose the information that is given by this term all together and may be the either the values that we get will not be realistic or they may not be convergence at all.

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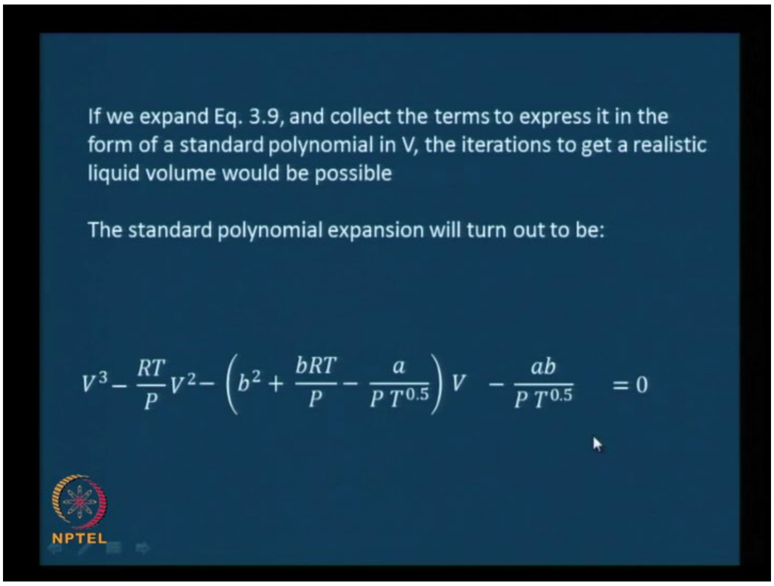

If we expand Eq. 3.9, and collect the terms to express it in the form of a standard polynomial in V, the iterations to get a realistic liquid volume would be possible

The standard polynomial expansion will turn out to be:

$$V^3 - \frac{RT}{P}V^2 - \left(b^2 + \frac{bRT}{P} - \frac{a}{P\,T^{0.5}}\right)V - \frac{ab}{P\,T^{0.5}} = 0$$

Therefore, we need another form of the Redlich-Kwong equation, to estimate liquid volumes and that was obtained by writing the Redlich-Kwong equation. Expanding, you know multiplying taking out common terms multiplying, cross multiplying and representing it as a polynomial expression in V. So, that was

$$V^3 - \frac{RT}{P}V^2 - \left(b^2 + \frac{bRT}{P} - \frac{a}{P\,T^{0.5}}\right)V - \frac{ab}{P\,T^{0.5}} = 0$$

This does not pose the problem of the any term vanishing completely and thereby not contributing to the solution or a meaningful solution of the volume.

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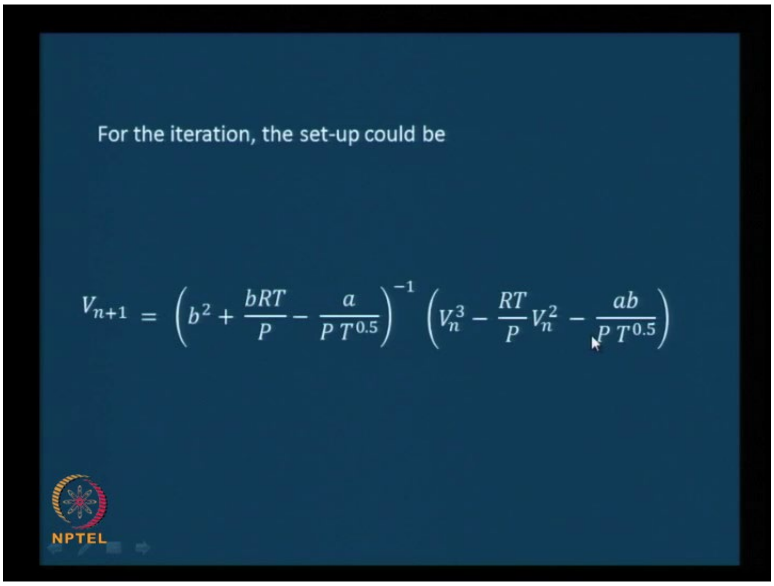

For the iteration, the set-up could be

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

So, this form can be used to iterate for liquid volumes and to do that iteration, we had to transpose that equation as

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

In other words, we are dividing both sides by this two to get rid of the term here. Therefore, this is to the power of minus 1 into the remaining terms that was there in the previous equation V n cubed minus R T by P V n squared minus a b by P T power 0.5.

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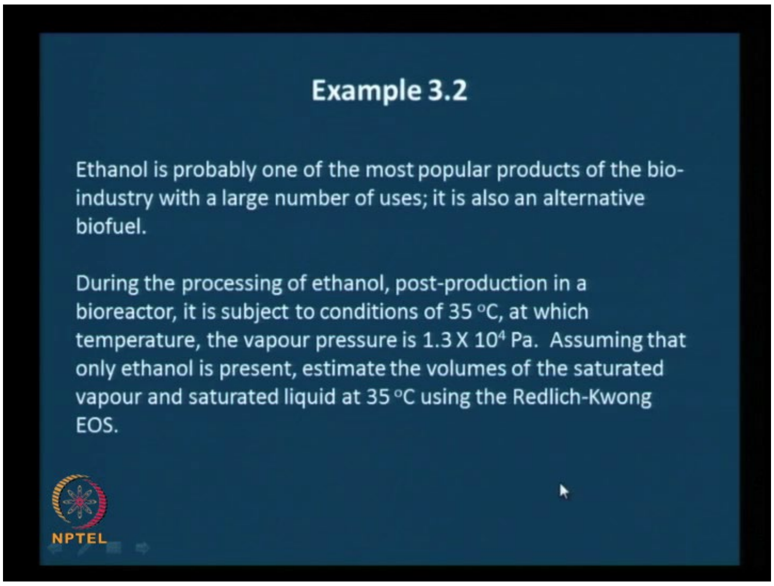

Example 3.2

Ethanol is probably one of the most popular products of the bio-industry with a large number of uses; it is also an alternative biofuel.

During the processing of ethanol, post-production in a bioreactor, it is subject to conditions of 35 °C, at which temperature, the vapour pressure is 1.3 X 10^4 Pa. Assuming that only ethanol is present, estimate the volumes of the saturated vapour and saturated liquid at 35 °C using the Redlich-Kwong EOS.

We again worked out an example, where we had used that Redlich-Kwong equation to estimate the volumes of the saturated vapour and the saturated liquid of a very popular biological substance ethanol. (No audio from 21:05 to 21:13)

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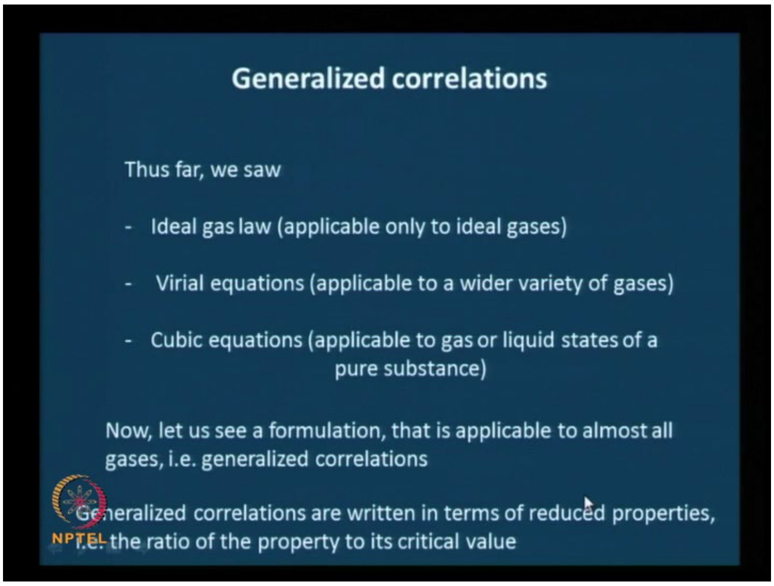

Generalized correlations

Thus far, we saw

- Ideal gas law (applicable only to ideal gases)
- Virial equations (applicable to a wider variety of gases)
- Cubic equations (applicable to gas or liquid states of a pure substance)

Now, let us see a formulation, that is applicable to almost all gases, i.e. generalized correlations

Generalized correlations are written in terms of reduced properties, i.e. the ratio of the property to its critical value

Then we said that, we had seen ideal gas law, the equation of state applicable only to ideal gases. The Virial equations those were applicable to a wider variety of gases and cubic equations that are applicable either to a gas or the liquid states of the pure substance. And then we said that, we are going to come up with a formulation that is applicable to almost all gases.

So, this part of the module focussed on the P V T relationships in increasing degree of generality in a certain sense. An ideal gas, ideal gas law a very narrow range of application Virial equations, a very wide variety of gases from some small number of gases. Then cubic equations could do both gas and a liquid and the generalized formulation could do a larger variety of gases, with lower input essentially. The data that you need is only the critical constants; you do not need pure substance specific constants. That was the, that is the advantage while using generalized correlations as we had seen, we will see again here.

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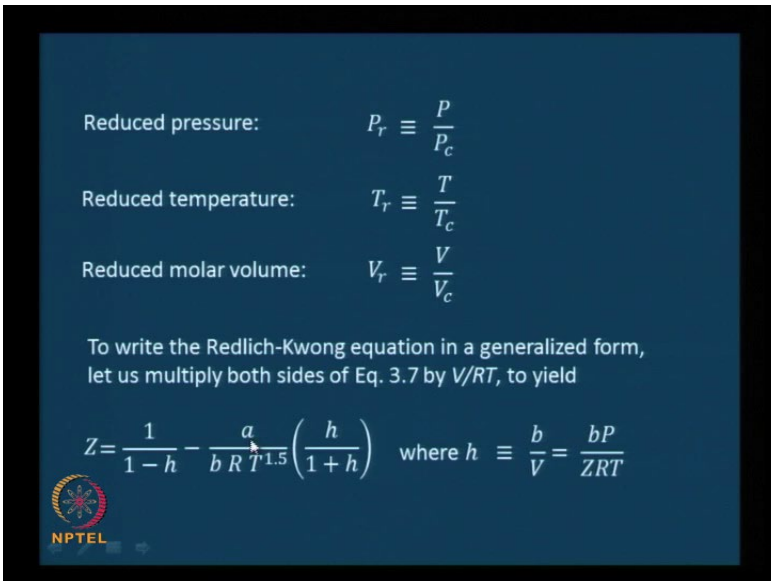

Reduced pressure: $P_r \equiv \frac{P}{P_c}$

Reduced temperature: $T_r \equiv \frac{T}{T_c}$

Reduced molar volume: $V_r \equiv \frac{V}{V_c}$

To write the Redlich-Kwong equation in a generalized form, let us multiply both sides of Eq. 3.7 by *V/RT*, to yield

$$Z = \frac{1}{1-h} - \frac{a}{b\,R\,T^{1.5}}\left(\frac{h}{1+h}\right) \quad \text{where } h \equiv \frac{b}{V} = \frac{bP}{ZRT}$$

So, the generalized correlations are written in terms of the reduced properties and the reduced property was nothing, but the ratio of the property to it is critical value. For example, reduced pressure

$$P_r \equiv \frac{P}{P_c}$$

Similarly, reduced temperature and the reduced molar volume and to write the Redlich-Kwong equation in a generalized form, we did some manipulations to get rid of this form

$$Z = \frac{1}{1-h} - \frac{a}{b\,R\,T^{1.5}}\left(\frac{h}{1+h}\right)$$

Then we could express a and b in terms of the critical constants, that we have already seen earlier and therefore, if you put in substitute those expressions here for a by a and b.

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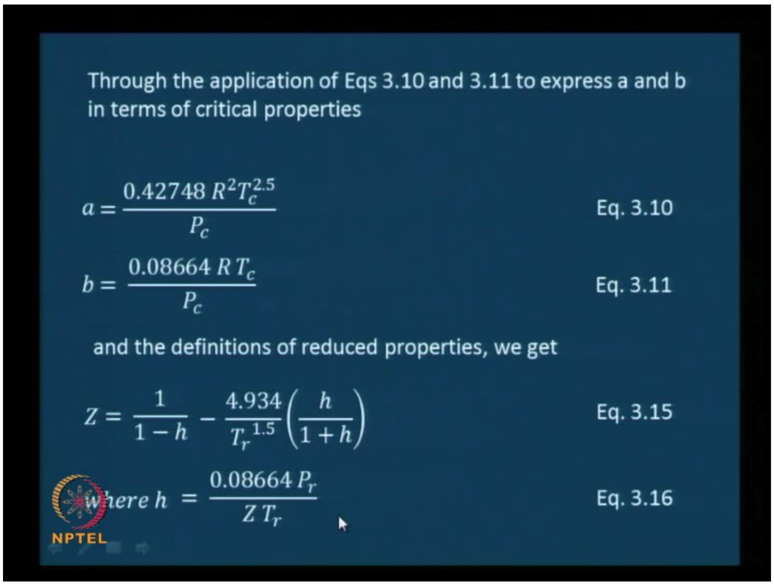

Through the application of Eqs 3.10 and 3.11 to express a and b in terms of critical properties

$$a = \frac{0.42748\, R^2 T_c^{2.5}}{P_c} \qquad \text{Eq. 3.10}$$

$$b = \frac{0.08664\, R\, T_c}{P_c} \qquad \text{Eq. 3.11}$$

and the definitions of reduced properties, we get

$$Z = \frac{1}{1-h} - \frac{4.934}{{T_r}^{1.5}}\left(\frac{h}{1+h}\right) \qquad \text{Eq. 3.15}$$

$$\text{where } h = \frac{0.08664\, P_r}{Z\, T_r} \qquad \text{Eq. 3.16}$$

Then which are these I had already seen, then the generalized Redlich-Kwong expression turns out to be

$$Z = \frac{1}{1-h} - \frac{4.934}{{T_r}^{1.5}}\left(\frac{h}{1+h}\right)$$

That is the Redlich-Kwong equation written in terms of reduced properties, the advantage here is that you have only T_r the reduced temperature and h of course, is given in terms of Pr and Tr. So, Pr and Tr relationships would be applicable in general and therefore, this expression it is applicability becomes a lot more general, not just that.

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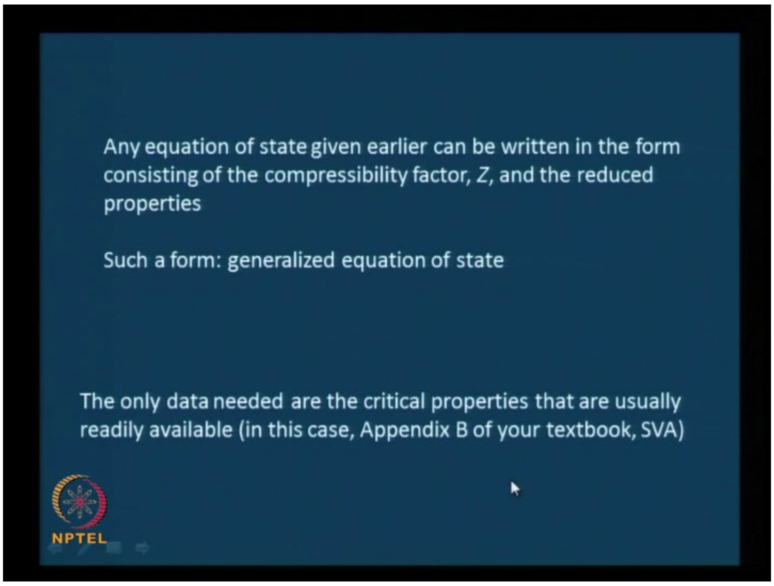

Any equation of state given earlier can be written in the form consisting of the compressibility factor, Z, and the reduced properties

Such a form: generalized equation of state

The only data needed are the critical properties that are usually readily available (in this case, Appendix B of your textbook, SVA)

Any equation of state can be written in terms of the reduced form or the generalized form if it is written in terms of the compressibility factor and reduced properties. And to reemphasize only data that is needed when, we use the generalized equation of state are the critical properties that are readily available for example, in the appendix of your text book.

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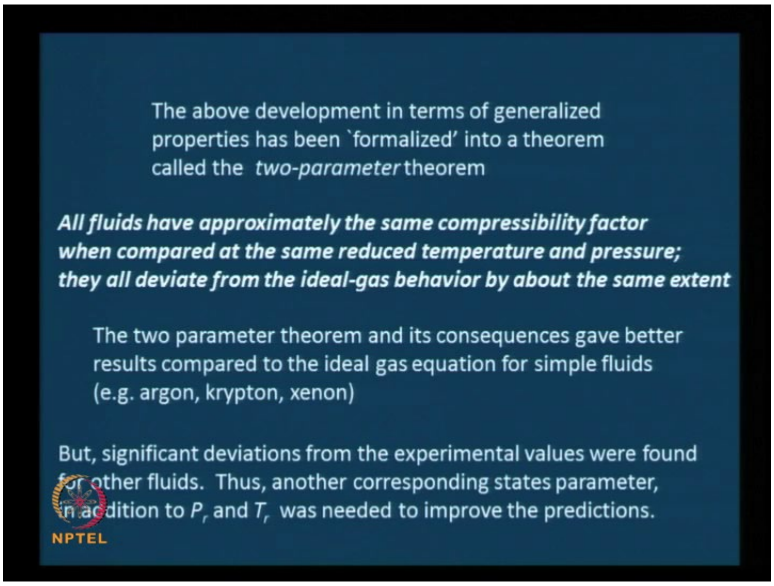

The above development in terms of generalized properties has been 'formalized' into a theorem called the *two-parameter* theorem

All fluids have approximately the same compressibility factor when compared at the same reduced temperature and pressure; they all deviate from the ideal-gas behavior by about the same extent

The two parameter theorem and its consequences gave better results compared to the ideal gas equation for simple fluids (e.g. argon, krypton, xenon)

But, significant deviations from the experimental values were found for other fluids. Thus, another corresponding states parameter, in addition to P_r and T_r was needed to improve the predictions.

So, then we looked at a slightly abstract concept, which was the two parameter theorem. Theorem has a lot of power to it, you have tremendous confidence when you have it in a theorem form you could apply it in many different situations. And the above development in fact, was formalized into a two parameter theorem, which said that all fluids have a approximately the same compressibility factor when compared at the same reduced temperature and pressure. In other words they all deviate from the ideal gas behaviour by the same extent. It was found that the two parameter theorems applicability was somewhat limited, it could give good results for simple fluids whereas, there were significant deviations for many other fluids.

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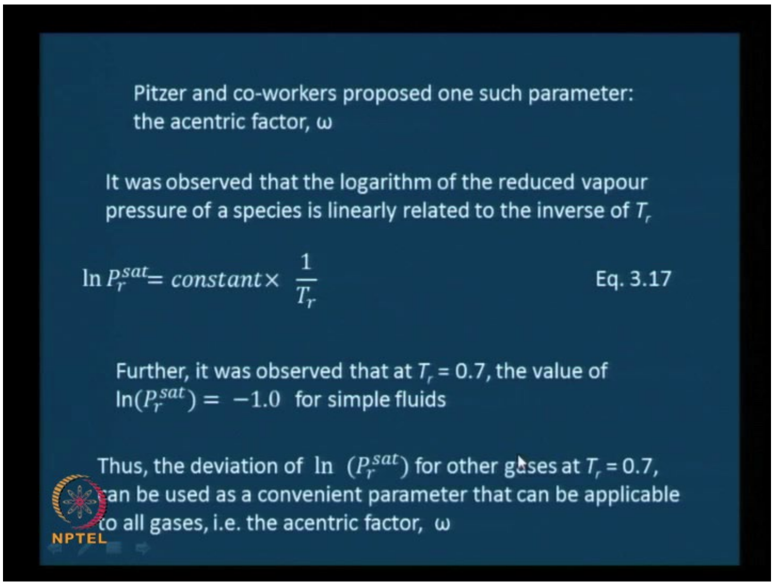

Pitzer and co-workers proposed one such parameter:
the acentric factor, ω

It was observed that the logarithm of the reduced vapour pressure of a species is linearly related to the inverse of T_r

$$\ln P_r^{sat} = constant \times \frac{1}{T_r} \qquad \text{Eq. 3.17}$$

Further, it was observed that at $T_r = 0.7$, the value of $\ln(P_r^{sat}) = -1.0$ for simple fluids

Thus, the deviation of $\ln(P_r^{sat})$ for other gases at $T_r = 0.7$, can be used as a convenient parameter that can be applicable to all gases, i.e. the acentric factor, ω

To account for that, Pitzer and co-workers brought in the acentric factor. Which was essentially I will not go through the development. Here you can look at the notes or the presentation, these appropriates, these slides in the presentation later.

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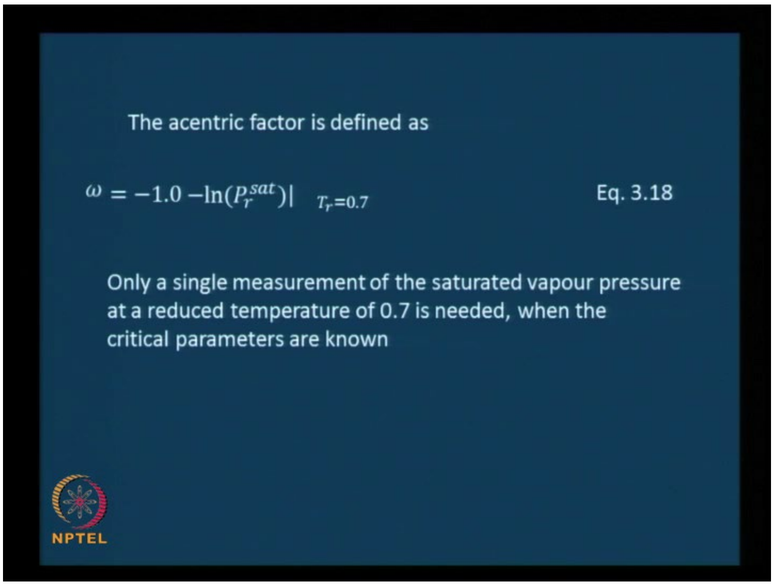

The acentric factor is defined as

$$\omega = -1.0 - \ln(P_r^{sat})|_{T_r=0.7} \qquad \text{Eq. 3.18}$$

Only a single measurement of the saturated vapour pressure at a reduced temperature of 0.7 is needed, when the critical parameters are known

The acentric factor is essentially the difference between the logarithm of the Pr sat value at Tr value of 0.7 and that value for simple fluids, which happens to be minus 1. Therefore, this in essence gives the deviation from the simple fluid behaviour of the other fluids. Therefore, this is taken as a single parameter and this also is attractive, because it involves only one measurement at Tr equals 0.7 the vapour pressure. It is a very simple measurement to find out the acentric factor. We do not have to do all that the values of the acentric factors of most substances that, we would need is available in tables. Of course, one if and when one needs to generate that data, then you know how to the basis for generating that data.

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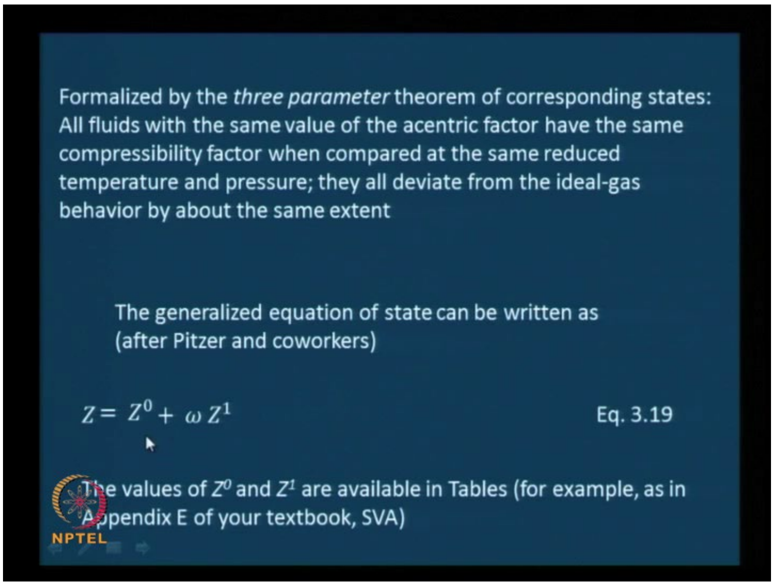

Formalized by the *three parameter* theorem of corresponding states: All fluids with the same value of the acentric factor have the same compressibility factor when compared at the same reduced temperature and pressure; they all deviate from the ideal-gas behavior by about the same extent

The generalized equation of state can be written as (after Pitzer and coworkers)

$$Z = Z^0 + \omega Z^1 \qquad \text{Eq. 3.19}$$

The values of Z^0 and Z^1 are available in Tables (for example, as in Appendix E of your textbook, SVA)

And this led to the three parameter theorem of corresponding states, which said that all fluids with the same value of the acentric factor have the same compressibility factor when compared with the same reduced temperature and pressure. In other words they all deviate from the ideal gas behaviour to the same extent. This was applicable to a wide variety of gases and the kind of equation of state that can be written in terms of. That can be a consequence of the three parameter theorem is

$$Z = Z^0 + \omega Z^1$$

It so happens that the value of Z^0 and Z^1 are available in tables. In fact, that is the reason why we write in this form. So, that we can rather it was we would use this form as written here, because the values are available to us.

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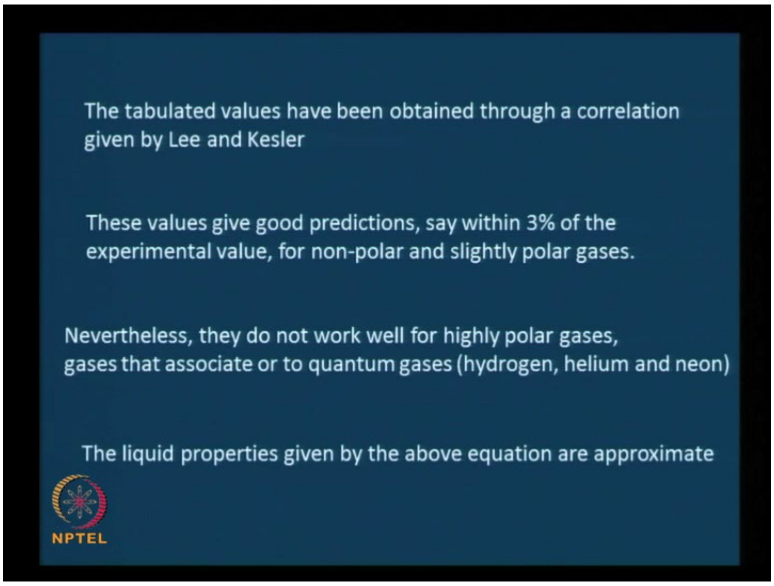

The tabulated values have been obtained through a correlation given by Lee and Kesler

These values give good predictions, say within 3% of the experimental value, for non-polar and slightly polar gases.

Nevertheless, they do not work well for highly polar gases, gases that associate or to quantum gases (hydrogen, helium and neon)

The liquid properties given by the above equation are approximate

They work well for most cases, when we use the $Z = Z^0 + \omega Z^1$ formulation. The predictions are within 3 percent of the experimental value for highly non polar and slightly polar gases. Well they do not work as well for highly polar gases or gases that associate or quantum gases, such as hydrogen, helium and neon. You could also get liquid properties from the generalized correlation nevertheless, the importance that you that one would associate to those values are needed to be a little less. The values are approximate the liquid values are approximate; the gas values are very good.

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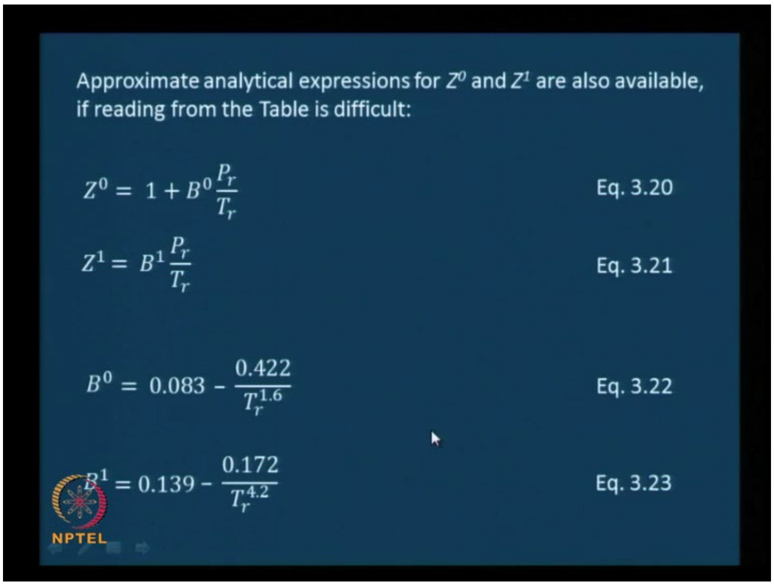

Approximate analytical expressions for Z^0 and Z^1 are also available, if reading from the Table is difficult:

$$Z^0 = 1 + B^0 \frac{P_r}{T_r} \qquad \text{Eq. 3.20}$$

$$Z^1 = B^1 \frac{P_r}{T_r} \qquad \text{Eq. 3.21}$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \qquad \text{Eq. 3.22}$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \qquad \text{Eq. 3.23}$$

Apart from the tables there are analytical expressions for Z^0 and Z^1 that are also available if the table is not available to somebody, one can use these expressions which are reasonably accurate. Z^0 is given in terms of B^0 the virial coefficient and B^0 is given in terms of Tr, B^0 and B^1 are given in terms of Tr.

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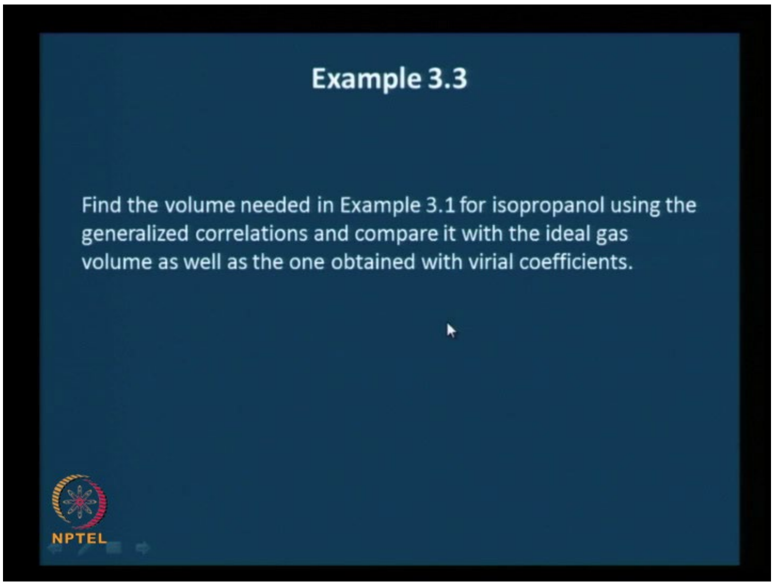

Example 3.3

Find the volume needed in Example 3.1 for isopropanol using the generalized correlations and compare it with the ideal gas volume as well as the one obtained with virial coefficients.

Then we worked out an example where we applied the generalized correlation and also compared it with the ideal gas and the virial correlations. So, the values obtained from those.

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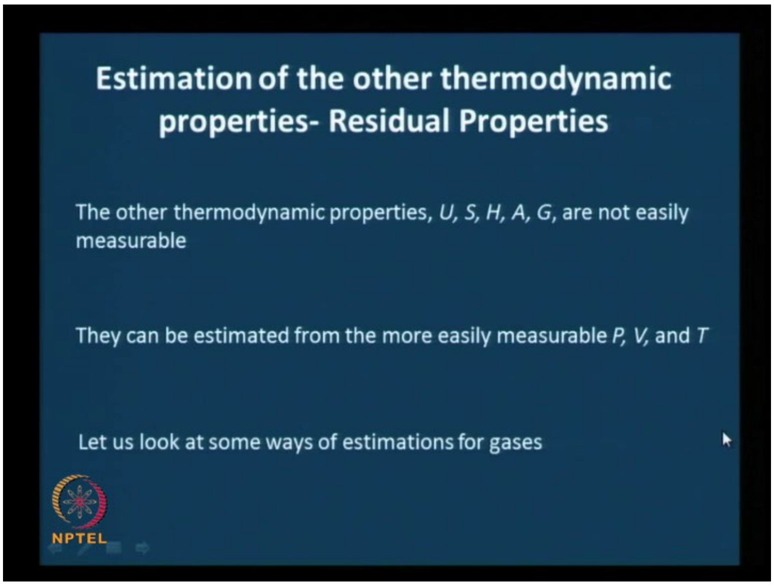

Estimation of the other thermodynamic properties- Residual Properties

The other thermodynamic properties, *U, S, H, A, G*, are not easily measurable

They can be estimated from the more easily measurable *P, V*, and *T*

Let us look at some ways of estimations for gases

So, that was one major part of the module, then we went into the second major part of the module, which was estimation of the other thermodynamic properties are more difficult to measure thermodynamic properties in terms of P V T. For that, we needed a formulation and that formulation required.

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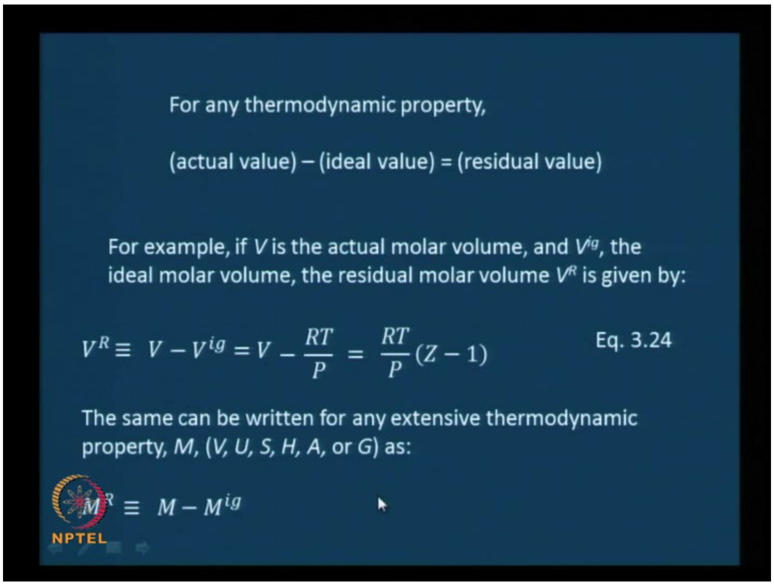

For any thermodynamic property,

(actual value) – (ideal value) = (residual value)

For example, if *V* is the actual molar volume, and V^{ig}, the ideal molar volume, the residual molar volume V^R is given by:

$$V^R \equiv V - V^{ig} = V - \frac{RT}{P} = \frac{RT}{P}(Z-1) \qquad \text{Eq. 3.24}$$

The same can be written for any extensive thermodynamic property, *M*, (*V, U, S, H, A*, or *G*) as:

$$M^R \equiv M - M^{ig}$$

What are called residual properties? Residual property is nothing but the difference between the actual value and the ideal gas value. For example, the residual volume V^R is nothing but the actual volume minus the ideal gas volume, which was written in terms of the compressibility factor for ease of use. It will turn out to be

$$V^R \equiv V - V^{ig} = V - \frac{RT}{P} = \frac{RT}{P}(Z-1)$$

Then, we said that we could write any the residual property for any extensive thermodynamic property. To write one for internal energy, for entropy, enthalpy, Helmholtz free energy, or Gibbs free energy and if that is represented as M,

$$M^R \equiv M - M^{ig}$$

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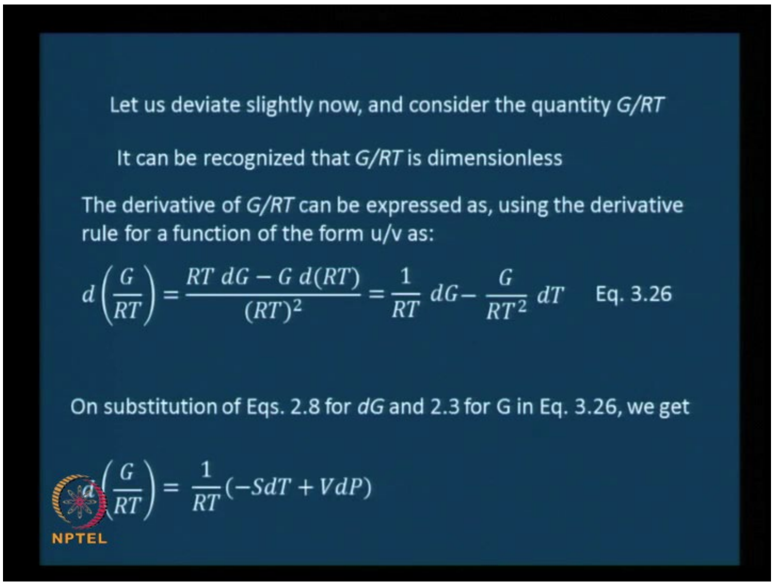

Let us deviate slightly now, and consider the quantity *G/RT*

It can be recognized that *G/RT* is dimensionless

The derivative of *G/RT* can be expressed as, using the derivative rule for a function of the form u/v as:

$$d\left(\frac{G}{RT}\right) = \frac{RT\,dG - G\,d(RT)}{(RT)^2} = \frac{1}{RT}\,dG - \frac{G}{RT^2}\,dT \qquad \text{Eq. 3.26}$$

On substitution of Eqs. 2.8 for *dG* and 2.3 for G in Eq. 3.26, we get

$$d\left(\frac{G}{RT}\right) = \frac{1}{RT}(-SdT + VdP)$$

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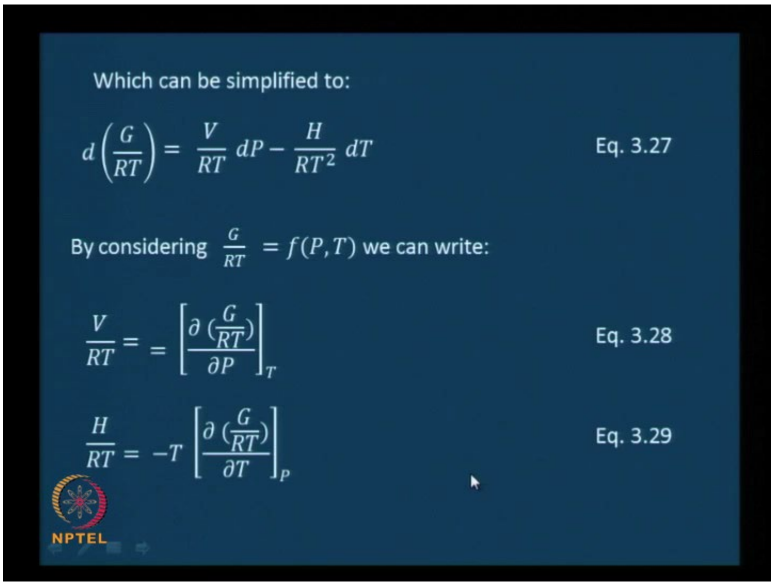

Which can be simplified to:

$$d\left(\frac{G}{RT}\right) = \frac{V}{RT}\,dP - \frac{H}{RT^2}\,dT \qquad \text{Eq. 3.27}$$

By considering $\frac{G}{RT} = f(P,T)$ we can write:

$$\frac{V}{RT} = = \left[\frac{\partial\,(\frac{G}{RT})}{\partial P}\right]_T \qquad \text{Eq. 3.28}$$

$$\frac{H}{RT} = -T\left[\frac{\partial\,(\frac{G}{RT})}{\partial T}\right]_P \qquad \text{Eq. 3.29}$$

And then we showed why $\left(\frac{G}{RT}\right)$ is considered the generating function or G is considered as the generating function, because if we have the value of G you could get other values. Please go through this derivation again it might be interesting here, if we have $\left(\frac{G}{RT}\right)$

$$\frac{V}{RT} = \left[\frac{\partial\,(\frac{G}{RT})}{\partial P}\right]_T$$

$$\frac{H}{RT} = -T\left[\frac{\partial\,(\frac{G}{RT})}{\partial T}\right]_P$$

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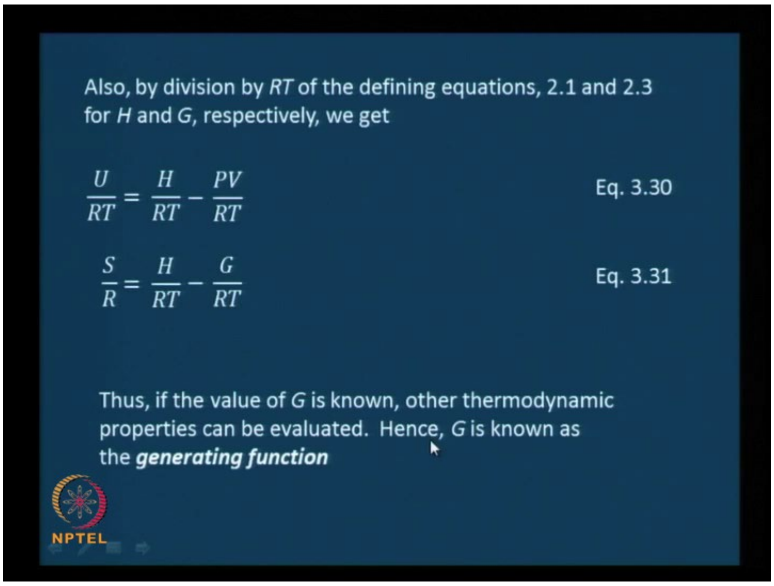

Also, by division by RT of the defining equations, 2.1 and 2.3 for H and G, respectively, we get

$$\frac{U}{RT} = \frac{H}{RT} - \frac{PV}{RT}$$ Eq. 3.30

$$\frac{S}{R} = \frac{H}{RT} - \frac{G}{RT}$$ Eq. 3.31

Thus, if the value of G is known, other thermodynamic properties can be evaluated. Hence, G is known as the ***generating function***

Also

$$\frac{U}{RT} = \frac{H}{RT} - \frac{PV}{RT}$$

$$\frac{S}{R} = \frac{H}{RT} - \frac{G}{RT}$$

We are not looking at A, because we may not need it extensively in this course but of course, you could write A too. It is not a problem.

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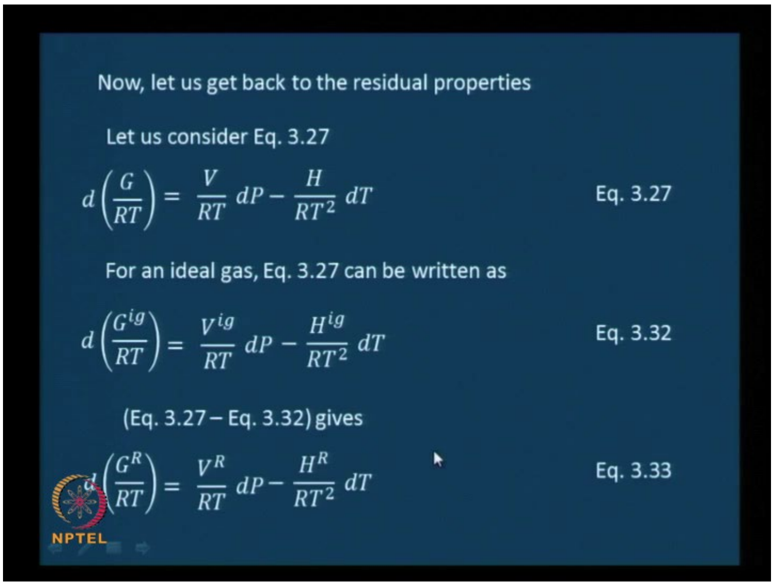

Now, let us get back to the residual properties

Let us consider Eq. 3.27

$$d\left(\frac{G}{RT}\right) = \frac{V}{RT}\,dP - \frac{H}{RT^2}\,dT$$ Eq. 3.27

For an ideal gas, Eq. 3.27 can be written as

$$d\left(\frac{G^{ig}}{RT}\right) = \frac{V^{ig}}{RT}\,dP - \frac{H^{ig}}{RT^2}\,dT$$ Eq. 3.32

(Eq. 3.27 – Eq. 3.32) gives

$$d\left(\frac{G^{R}}{RT}\right) = \frac{V^{R}}{RT}\,dP - \frac{H^{R}}{RT^2}\,dT$$ Eq. 3.33

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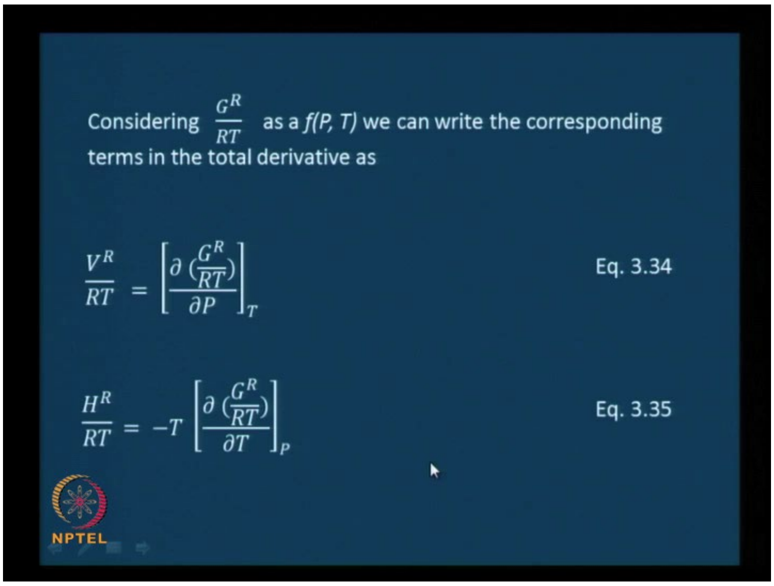

Considering $\frac{G^R}{RT}$ as a *f(P, T)* we can write the corresponding terms in the total derivative as

$$\frac{V^R}{RT} = \left[\frac{\partial\left(\frac{G^R}{RT}\right)}{\partial P}\right]_T \qquad \text{Eq. 3.34}$$

$$\frac{H^R}{RT} = -T\left[\frac{\partial\left(\frac{G^R}{RT}\right)}{\partial T}\right]_P \qquad \text{Eq. 3.35}$$

Then

$$\frac{V^R}{RT} = \left[\frac{\partial\left(\frac{G^R}{RT}\right)}{\partial P}\right]_T$$

$$\frac{H^R}{RT} = -T\left[\frac{\partial\left(\frac{G^R}{RT}\right)}{\partial T}\right]_P$$

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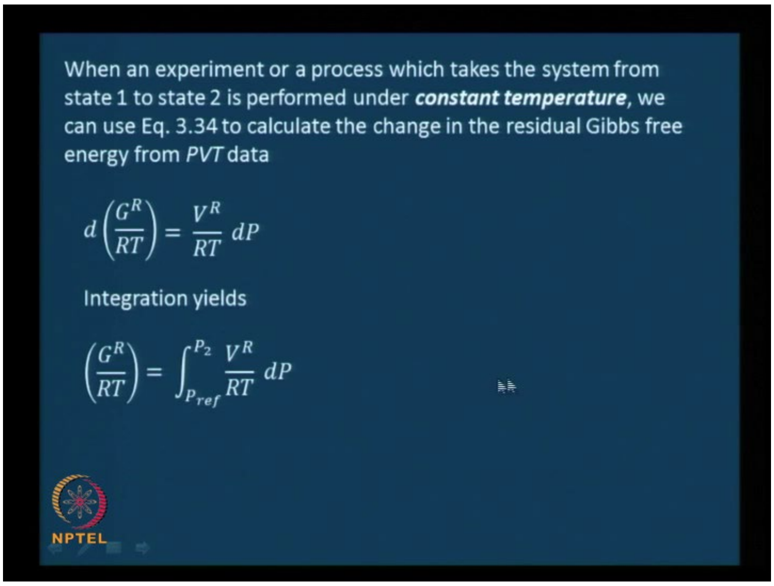

When an experiment or a process which takes the system from state 1 to state 2 is performed under ***constant temperature***, we can use Eq. 3.34 to calculate the change in the residual Gibbs free energy from *PVT* data

$$d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT}\,dP$$

Integration yields

$$\left(\frac{G^R}{RT}\right) = \int_{P_{ref}}^{P_2} \frac{V^R}{RT}\,dP$$

And then we said that, we had assumed constant temperature but we got it in terms of values G R by R T is in terms of V R still V R by R T d P this is good but we wanted an easier way of estimating that.

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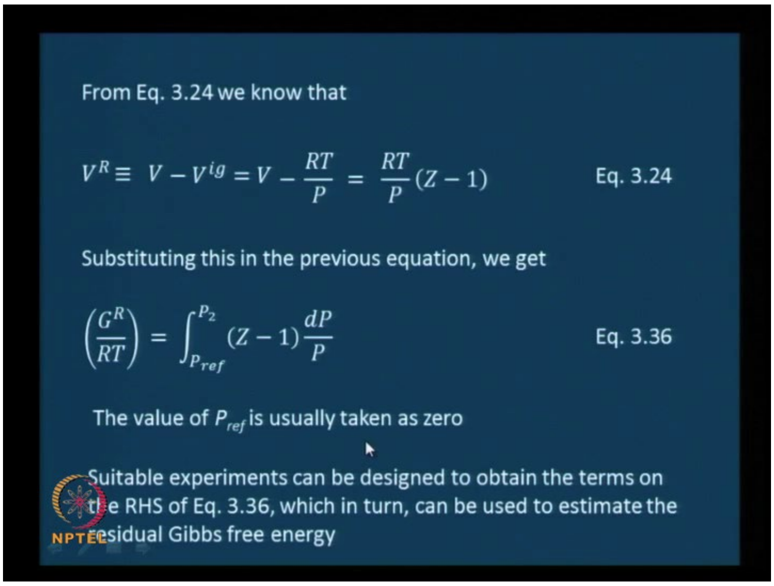

From Eq. 3.24 we know that

$$V^R \equiv V - V^{ig} = V - \frac{RT}{P} = \frac{RT}{P}(Z-1) \qquad \text{Eq. 3.24}$$

Substituting this in the previous equation, we get

$$\left(\frac{G^R}{RT}\right) = \int_{P_{ref}}^{P_2} (Z-1)\frac{dP}{P} \qquad \text{Eq. 3.36}$$

The value of P_{ref} is usually taken as zero

Suitable experiments can be designed to obtain the terms on the RHS of Eq. 3.36, which in turn, can be used to estimate the residual Gibbs free energy

Therefore, we wrote it in terms of Z.

$$\left(\frac{G^R}{RT}\right) = \int_{P_{ref}}^{P_2} (Z-1)\frac{dP}{P}$$

And we said that the value of P_{ref} is usually taken as zero.

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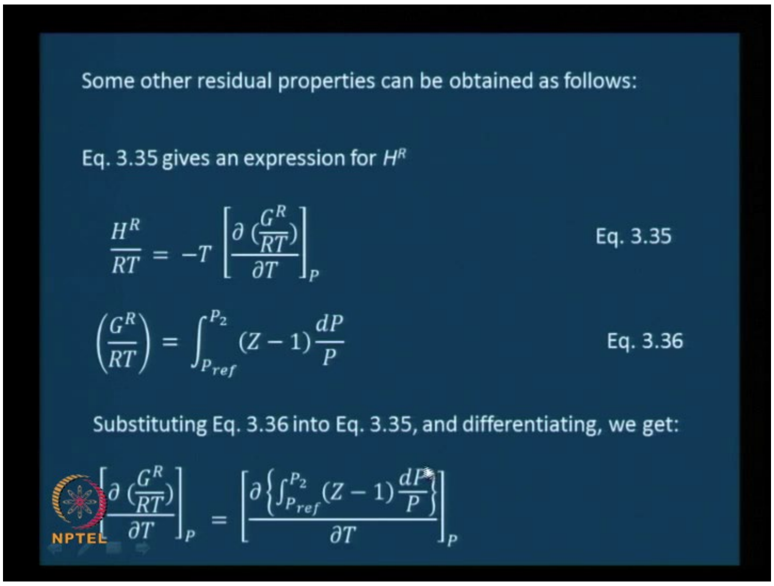

Some other residual properties can be obtained as follows:

Eq. 3.35 gives an expression for H^R

$$\frac{H^R}{RT} = -T\left[\frac{\partial\left(\frac{G^R}{RT}\right)}{\partial T}\right]_P \qquad \text{Eq. 3.35}$$

$$\left(\frac{G^R}{RT}\right) = \int_{P_{ref}}^{P_2}(Z-1)\frac{dP}{P} \qquad \text{Eq. 3.36}$$

Substituting Eq. 3.36 into Eq. 3.35, and differentiating, we get:

$$\left[\frac{\partial\left(\frac{G^R}{RT}\right)}{\partial T}\right]_P = \left[\frac{\partial\left\{\int_{P_{ref}}^{P_2}(Z-1)\frac{dP}{P}\right\}}{\partial T}\right]_P$$

Then, we had expressions for the other thermodynamic residual properties in terms of measurable properties, this you have already seen. While deriving this we went through a situation, where we needed to differentiate an integral for doing that, we use the generalized Leibniz rule, which gave us a means to differentiate or partially differentiate a definite integral.

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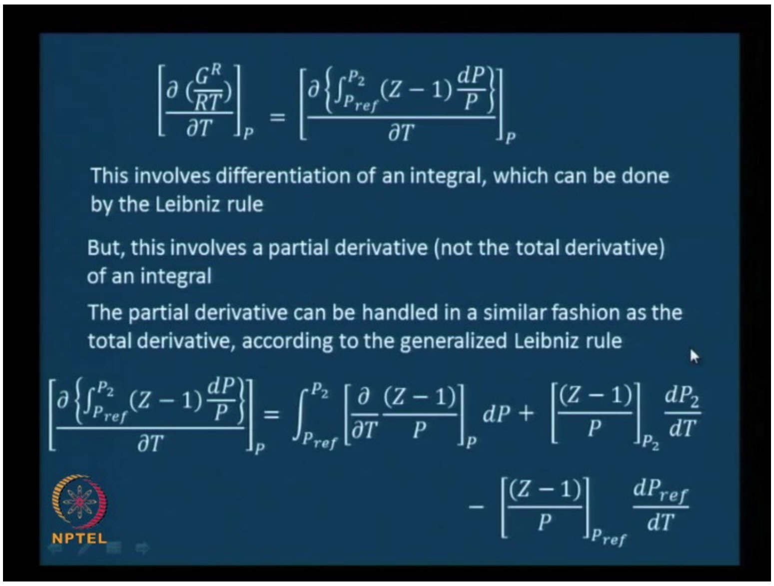

$$\left[\frac{\partial\left(\frac{G^R}{RT}\right)}{\partial T}\right]_P = \left[\frac{\partial\left\{\int_{P_{ref}}^{P_2}(Z-1)\frac{dP}{P}\right\}}{\partial T}\right]_P$$

This involves differentiation of an integral, which can be done by the Leibniz rule

But, this involves a partial derivative (not the total derivative) of an integral

The partial derivative can be handled in a similar fashion as the total derivative, according to the generalized Leibniz rule

$$\left[\frac{\partial\left\{\int_{P_{ref}}^{P_2}(Z-1)\frac{dP}{P}\right\}}{\partial T}\right]_P = \int_{P_{ref}}^{P_2}\left[\frac{\partial}{\partial T}\frac{(Z-1)}{P}\right]_P dP + \left[\frac{(Z-1)}{P}\right]_{P_2}\frac{dP_2}{dT} - \left[\frac{(Z-1)}{P}\right]_{P_{ref}}\frac{dP_{ref}}{dT}$$

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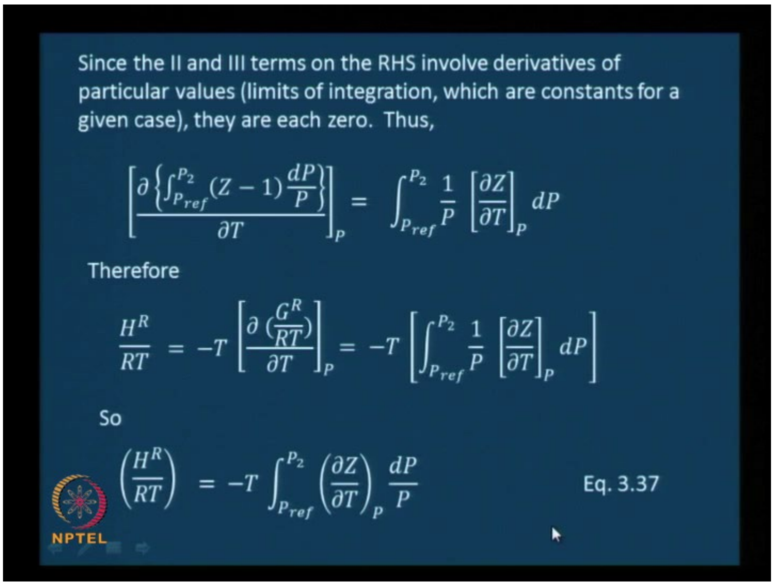

Since the II and III terms on the RHS involve derivatives of particular values (limits of integration, which are constants for a given case), they are each zero. Thus,

$$\left[\frac{\partial\left\{\int_{P_{ref}}^{P_2}(Z-1)\frac{dP}{P}\right\}}{\partial T}\right]_P = \int_{P_{ref}}^{P_2}\frac{1}{P}\left[\frac{\partial Z}{\partial T}\right]_P dP$$

Therefore

$$\frac{H^R}{RT} = -T\left[\frac{\partial\left(\frac{G^R}{RT}\right)}{\partial T}\right]_P = -T\left[\int_{P_{ref}}^{P_2}\frac{1}{P}\left[\frac{\partial Z}{\partial T}\right]_P dP\right]$$

So

$$\left(\frac{H^R}{RT}\right) = -T\int_{P_{ref}}^{P_2}\left(\frac{\partial Z}{\partial T}\right)_P\frac{dP}{P} \qquad \text{Eq. 3.37}$$

Here. So, after doing all that, we ended up with

$$\left(\frac{H^R}{RT}\right) = -T\int_{P_{ref}}^{P_2}\left(\frac{\partial Z}{\partial T}\right)_P\frac{dP}{P}$$

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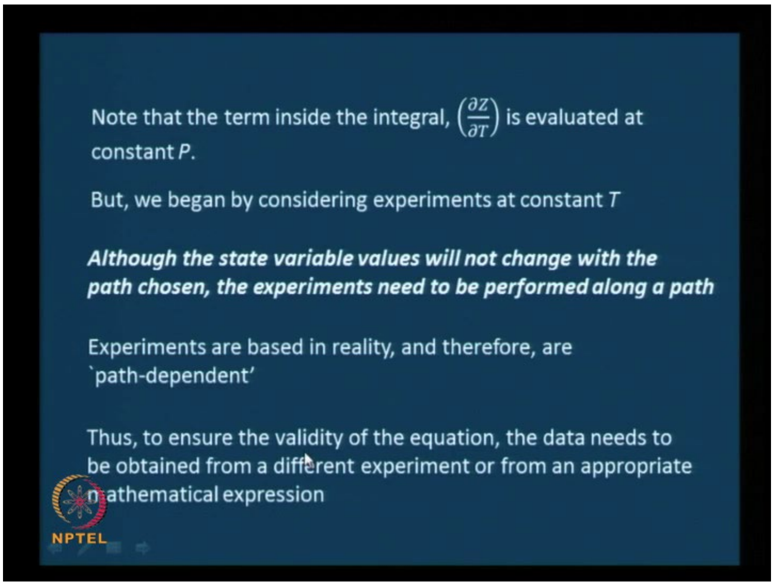

Note that the term inside the integral, $\left(\frac{\partial Z}{\partial T}\right)$ is evaluated at constant P.

But, we began by considering experiments at constant T

Although the state variable values will not change with the path chosen, the experiments need to be performed along a path

Experiments are based in reality, and therefore, are `path-dependent'

Thus, to ensure the validity of the equation, the data needs to be obtained from a different experiment or from an appropriate mathematical expression

Then, we also noted that although the state variable values will not change with the path chosen. The experiments that are designed, to evaluate these are path dependent, they need to be performed along path. Therefore, we need appropriate conditions, experimental conditions or appropriate mathematical expressions.

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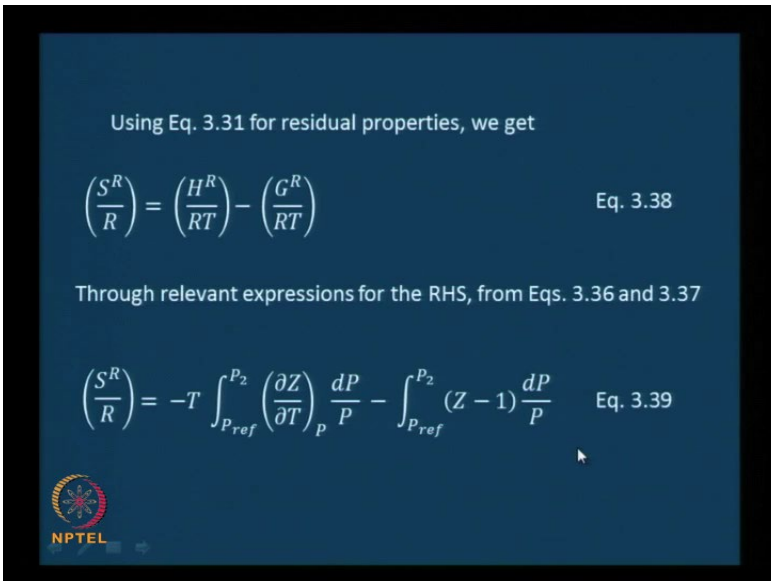

Using Eq. 3.31 for residual properties, we get

$$\left(\frac{S^R}{R}\right) = \left(\frac{H^R}{RT}\right) - \left(\frac{G^R}{RT}\right) \qquad \text{Eq. 3.38}$$

Through relevant expressions for the RHS, from Eqs. 3.36 and 3.37

$$\left(\frac{S^R}{R}\right) = -T\int_{P_{ref}}^{P_2}\left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_{P_{ref}}^{P_2}(Z-1)\frac{dP}{P} \qquad \text{Eq. 3.39}$$

Then these are the other residual properties in terms of GR by RT and other things that we know. And in terms of the easily measurable values

$$\left(\frac{S^R}{R}\right) = -T\int_{P_{ref}}^{P_2}\left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_{P_{ref}}^{P_2}(Z-1)\frac{dP}{P}$$

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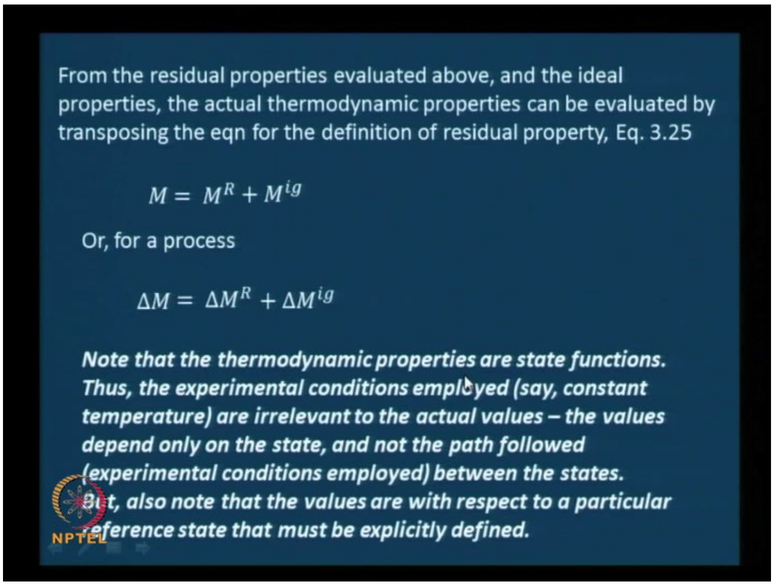

From the residual properties evaluated above, and the ideal properties, the actual thermodynamic properties can be evaluated by transposing the eqn for the definition of residual property, Eq. 3.25

$$M = M^R + M^{ig}$$

Or, for a process

$$\Delta M = \Delta M^R + \Delta M^{ig}$$

Note that the thermodynamic properties are state functions. Thus, the experimental conditions employed (say, constant temperature) are irrelevant to the actual values – the values depend only on the state, and not the path followed (experimental conditions employed) between the states. But, also note that the values are with respect to a particular reference state that must be explicitly defined.

We said that, this is quite obvious, once we have the residual value the actual value is nothing, but the residual value plus the ideal gas value. Therefore, if you have the ideal gas value, then you could find the actual value or for a process, when you are going between points or states 1 and 2. M_2 minus M_1 or

$$\Delta M = \Delta M^R + \Delta M^{ig}$$

We also noted that the thermodynamics properties of state functions. Thus the experimental conditions employed say constant temperature are irrelevant to the actual values. The values depend only on the state and not on the path followed or the experimental conditions employed between the states. But also note that the values are with respect to a particular reference state and must be explicitly defined.

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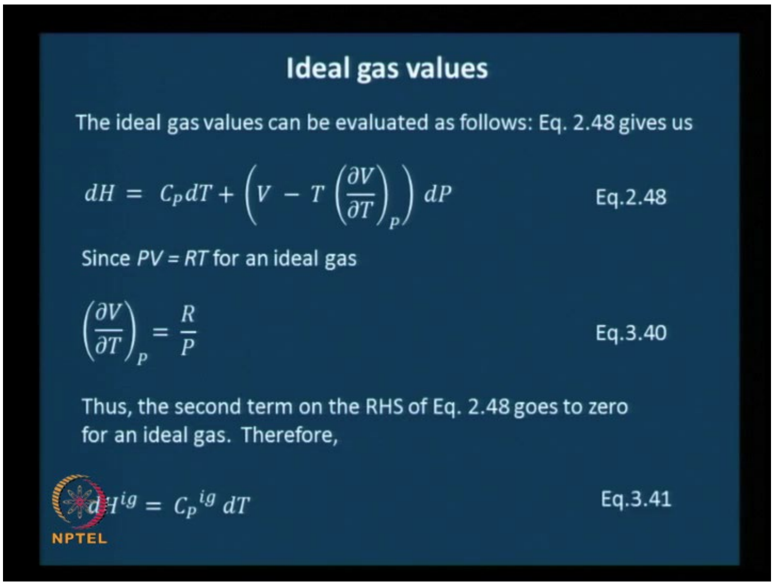

Ideal gas values

The ideal gas values can be evaluated as follows: Eq. 2.48 gives us

$$dH = C_P dT + \left(V - T\left(\frac{\partial V}{\partial T}\right)_P\right) dP \qquad \text{Eq.2.48}$$

Since $PV = RT$ for an ideal gas

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \qquad \text{Eq.3.40}$$

Thus, the second term on the RHS of Eq. 2.48 goes to zero for an ideal gas. Therefore,

$$dH^{ig} = C_P{}^{ig}\, dT \qquad \text{Eq.3.41}$$

Then we came up with ways to get the ideal gas values, because we said the residual value plus the ideal gas values is actual value, we spent good amount of time getting the residual value first. And then we looked at how to get the ideal gas values without spending too much time here, we have derived all these.

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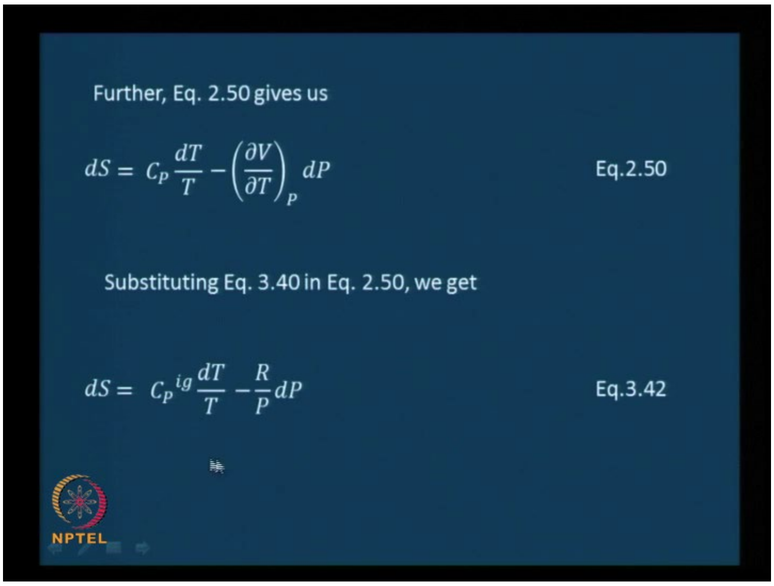

Further, Eq. 2.50 gives us

$$dS = C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP \qquad \text{Eq.2.50}$$

Substituting Eq. 3.40 in Eq. 2.50, we get

$$dS = C_P{}^{ig} \frac{dT}{T} - \frac{R}{P} dP \qquad \text{Eq.3.42}$$

This was the expression

$$dS = C_P{}^{ig} \frac{dT}{T} - \frac{R}{P} dP$$

Therefore, by integrating that you could get the ideal gas value for S. For process values between point 1 and 2 the differences in values.

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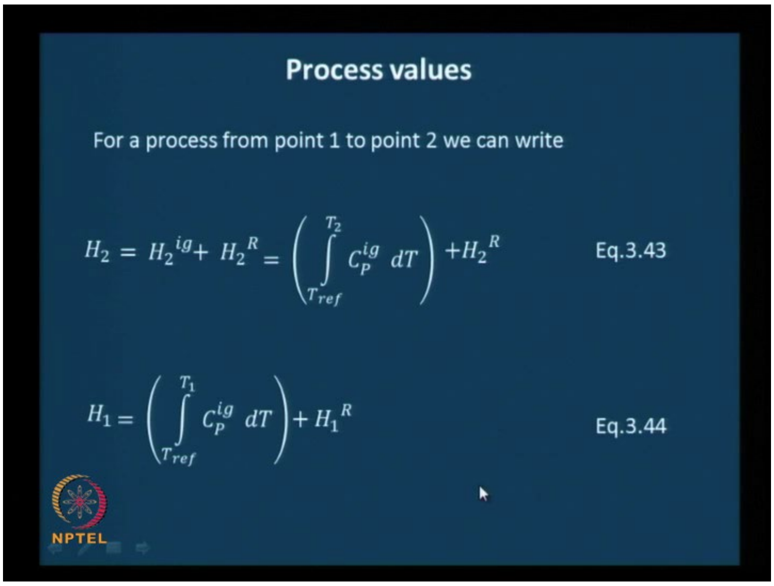

Process values

For a process from point 1 to point 2 we can write

$$H_2 = H_2{}^{ig} + H_2{}^{R} = \left(\int_{T_{ref}}^{T_2} C_P^{ig}\, dT\right) + H_2{}^{R} \qquad \text{Eq.3.43}$$

$$H_1 = \left(\int_{T_{ref}}^{T_1} C_P^{ig}\, dT\right) + H_1{}^{R} \qquad \text{Eq.3.44}$$

We first wrote them and then wrote them in terms of the easily measurable P V T. And a few other C_P and So on.

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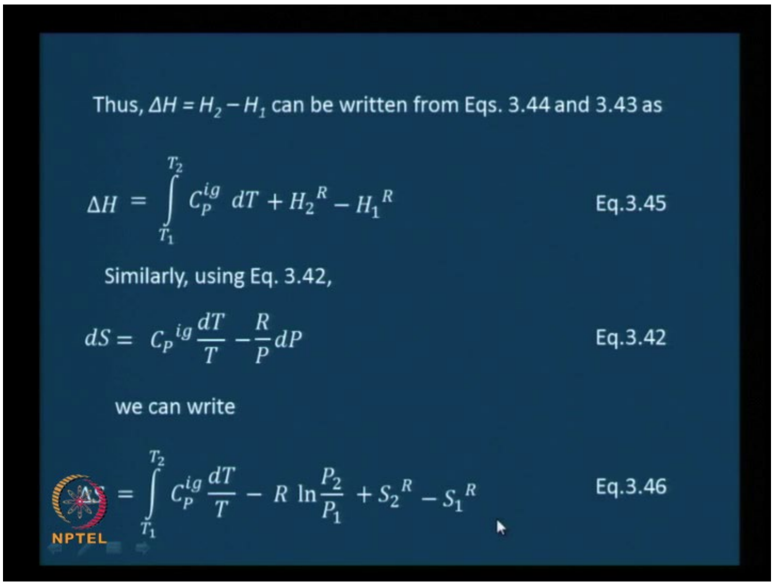

Thus, $\Delta H = H_2 - H_1$ can be written from Eqs. 3.44 and 3.43 as

$$\Delta H = \int_{T_1}^{T_2} C_P^{ig}\, dT + H_2{}^{R} - H_1{}^{R} \qquad \text{Eq.3.45}$$

Similarly, using Eq. 3.42,

$$dS = C_P{}^{ig}\frac{dT}{T} - \frac{R}{P}dP \qquad \text{Eq.3.42}$$

we can write

$$\Delta S = \int_{T_1}^{T_2} C_P^{ig}\frac{dT}{T} - R\ln\frac{P_2}{P_1} + S_2{}^{R} - S_1{}^{R} \qquad \text{Eq.3.46}$$

Delta H was

$$\Delta H = \int_{T_1}^{T_2} C_P^{ig}\, dT + H_2{}^{R} - H_1{}^{R}$$

And delta S was

$$\Delta S = \int_{T_1}^{T_2} C_P^{ig} \frac{dT}{T} - R \ln\frac{P_2}{P_1} + S_2{}^R - S_1{}^R$$

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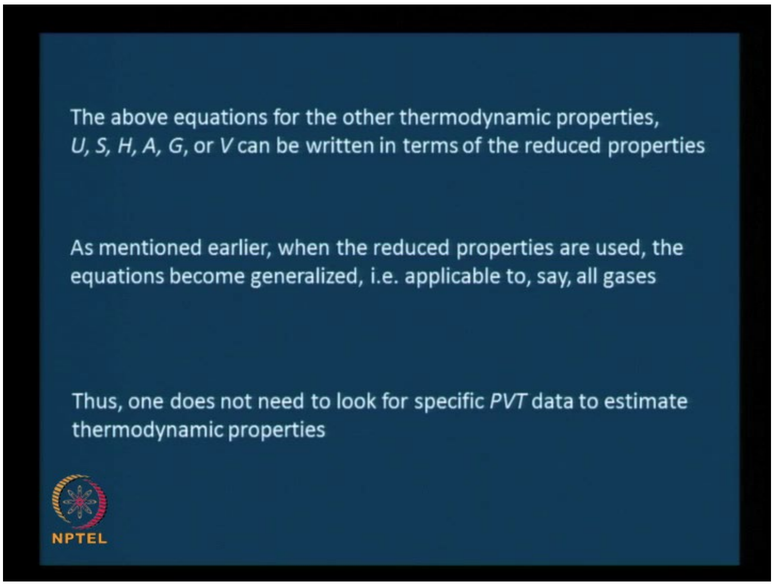

The above equations for the other thermodynamic properties, *U, S, H, A, G*, or *V* can be written in terms of the reduced properties

As mentioned earlier, when the reduced properties are used, the equations become generalized, i.e. applicable to, say, all gases

Thus, one does not need to look for specific *PVT* data to estimate thermodynamic properties

We said that the above equations for the other thermodynamic properties can also be written in terms of the reduced properties, we had looked at not only two or three. And the reduced properties, when the reduced properties are used the equations become generalized, they become applicable to say all gases. Therefore, we need not look at specific P V T data to estimate thermodynamic properties. That was the advantage that we saw.

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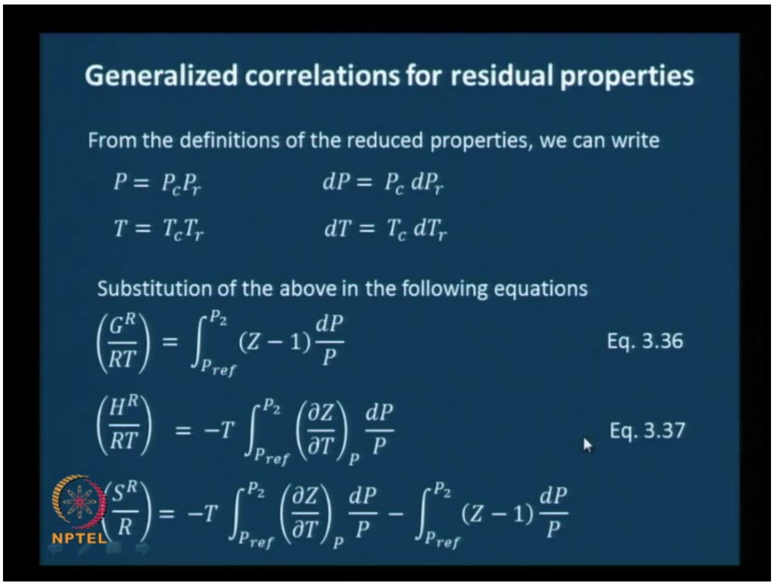

Generalized correlations for residual properties

From the definitions of the reduced properties, we can write

$P = P_c P_r \qquad dP = P_c\, dP_r$

$T = T_c T_r \qquad dT = T_c\, dT_r$

Substitution of the above in the following equations

$$\left(\frac{G^R}{RT}\right) = \int_{P_{ref}}^{P_2} (Z-1)\frac{dP}{P} \qquad \text{Eq. 3.36}$$

$$\left(\frac{H^R}{RT}\right) = -T\int_{P_{ref}}^{P_2} \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \qquad \text{Eq. 3.37}$$

$$\left(\frac{S^R}{R}\right) = -T\int_{P_{ref}}^{P_2} \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_{P_{ref}}^{P_2} (Z-1)\frac{dP}{P}$$

There are generalized correlations for residual properties also and the advantage is that, we just mentioned. We went ahead and derived those generalized correlations let me just present these generalized correlations these are the correlations in terms of the actual properties.

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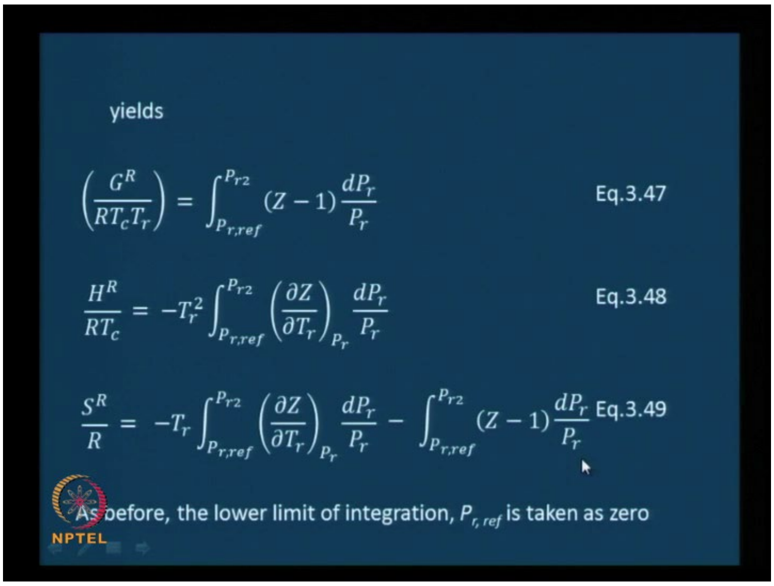

yields

$$\left(\frac{G^R}{RT_cT_r}\right) = \int_{P_{r,ref}}^{P_{r2}} (Z-1)\frac{dP_r}{P_r} \qquad \text{Eq.3.47}$$

$$\frac{H^R}{RT_c} = -T_r^2\int_{P_{r,ref}}^{P_{r2}} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} \qquad \text{Eq.3.48}$$

$$\frac{S^R}{R} = -T_r\int_{P_{r,ref}}^{P_{r2}} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} - \int_{P_{r,ref}}^{P_{r2}} (Z-1)\frac{dP_r}{P_r} \qquad \text{Eq.3.49}$$

As before, the lower limit of integration, $P_{r,\,ref}$ is taken as zero

And we had substituted to get equations 3.47, 3.48 and 3.49 in terms of reduced properties.

$$\left(\frac{G^R}{RT}\right) = \int_{P_{ref}}^{P_2} (Z-1)\frac{dP}{P}$$

$$\left(\frac{H^R}{RT}\right) = -T \int_{P_{ref}}^{P_2} \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P}$$

$$\left(\frac{S^R}{R}\right) = -T \int_{P_{ref}}^{P_2} \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_{P_{ref}}^{P_2} (Z-1)\frac{dP}{P}$$

And the same way that we took, P_{ref} is zero we also take $P_{r\ ref}$ as zero for as a lower limit of integration.

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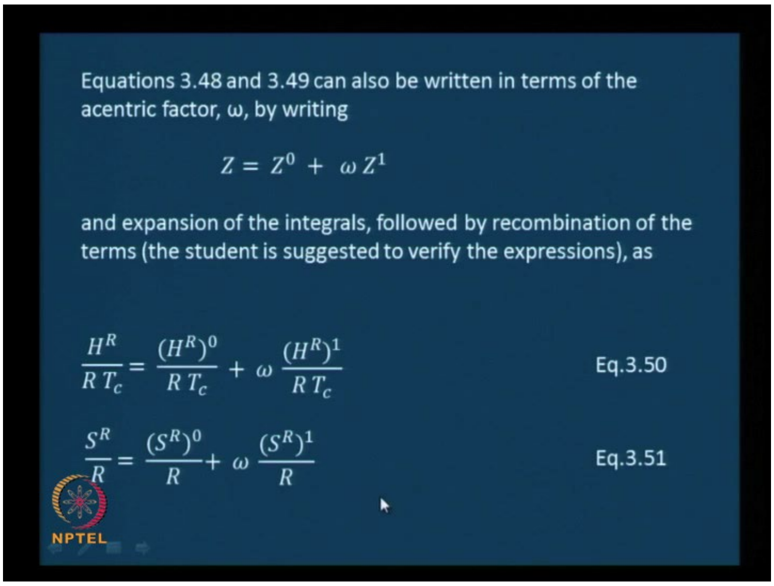

Equations 3.48 and 3.49 can also be written in terms of the acentric factor, ω, by writing

$$Z = Z^0 + \omega Z^1$$

and expansion of the integrals, followed by recombination of the terms (the student is suggested to verify the expressions), as

$$\frac{H^R}{R\,T_c} = \frac{(H^R)^0}{R\,T_c} + \omega \frac{(H^R)^1}{R\,T_c} \quad \text{Eq.3.50}$$

$$\frac{S^R}{R} = \frac{(S^R)^0}{R} + \omega \frac{(S^R)^1}{R} \quad \text{Eq.3.51}$$

We said that, we could write these equations in the generalized form. Also in terms of Z^0 and Z^1 because then we can use the tables that are available to us and the explicit form as

$$\frac{H^R}{R\,T_c} = \frac{(H^R)^0}{R\,T_c} + \omega \frac{(H^R)^1}{R\,T_c}$$

$$\frac{S^R}{R} = \frac{(S^R)^0}{R} + \omega \frac{(S^R)^1}{R}$$

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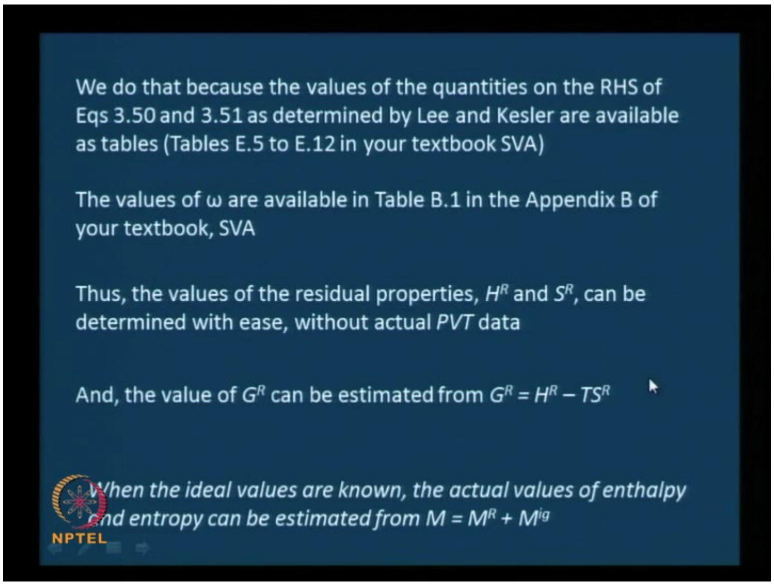

We do that because the values of the quantities on the RHS of Eqs 3.50 and 3.51 as determined by Lee and Kesler are available as tables (Tables E.5 to E.12 in your textbook SVA)

The values of ω are available in Table B.1 in the Appendix B of your textbook, SVA

Thus, the values of the residual properties, H^R and S^R, can be determined with ease, without actual *PVT* data

And, the value of G^R can be estimated from $G^R = H^R - TS^R$

When the ideal values are known, the actual values of enthalpy and entropy can be estimated from $M = M^R + M^{ig}$

And the values are available the groups the 0 group and the 1 group, the values are available in tables E 5 to E 12 in appendix e of your text book.

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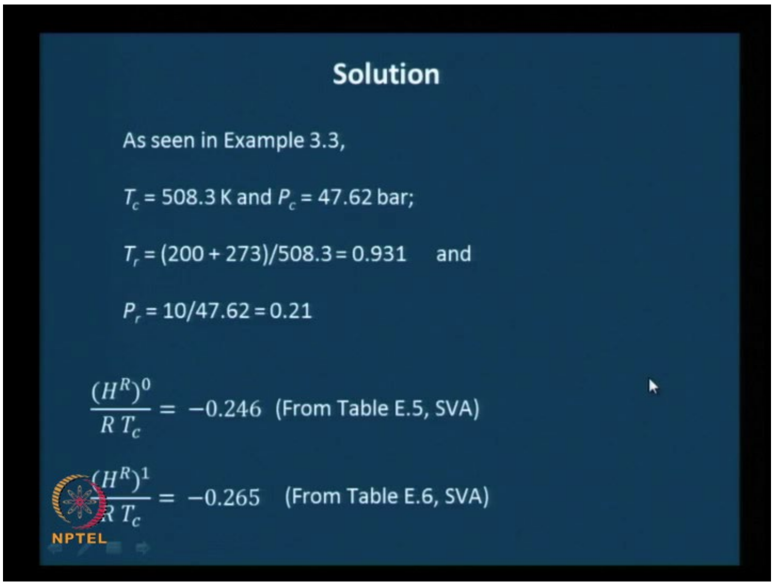

Solution

As seen in Example 3.3,

$T_c = 508.3$ K and $P_c = 47.62$ bar;

$T_r = (200 + 273)/508.3 = 0.931$ and

$P_r = 10/47.62 = 0.21$

$$\frac{(H^R)^0}{R\,T_c} = -0.246 \quad \text{(From Table E.5, SVA)}$$

$$\frac{(H^R)^1}{R\,T_c} = -0.265 \quad \text{(From Table E.6, SVA)}$$

Then we worked out an example to look at, how to use the correlation, the generalized correlation in terms of the reduced properties, to get at useful values. Please take a look at that whenever you have a time, the last thing that we saw was the estimation of the fugacity coefficient for a pure substance.

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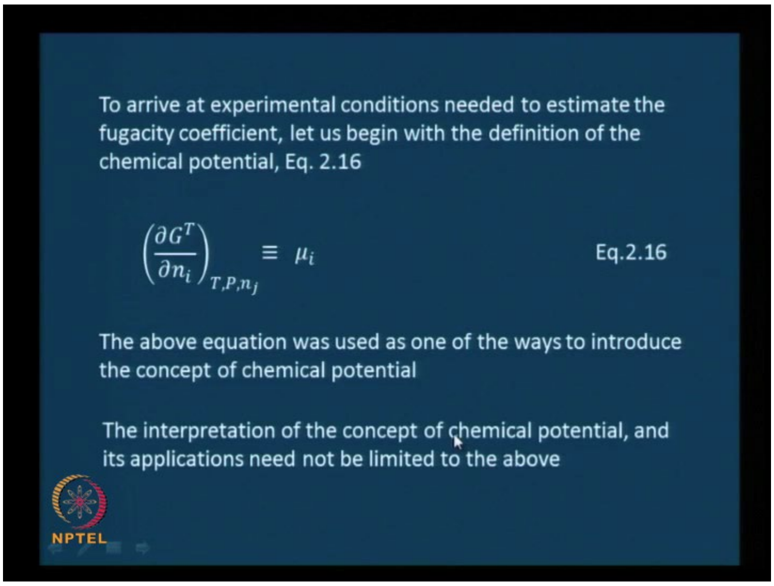

To arrive at experimental conditions needed to estimate the fugacity coefficient, let us begin with the definition of the chemical potential, Eq. 2.16

$$\left(\frac{\partial G^T}{\partial n_i}\right)_{T,P,n_j} \equiv \mu_i \qquad \text{Eq.2.16}$$

The above equation was used as one of the ways to introduce the concept of chemical potential

The interpretation of the concept of chemical potential, and its applications need not be limited to the above

And to do that, we started out with the definition of the chemical potential for a species, we went into the interpretations of the chemical potential please take a look at it is very interesting I would not do it again now. And we went into writing the definition for a pure substance and writing down equations for a closed system in terms of the chemical potential for a pure substance.

Then we went ahead with the derivation to get to this particular expression, which is the fundamental expression of phi 1.

$$\ln(\emptyset^1) = \int_0^{P_1} \left(\frac{V}{R\,T} - \frac{1}{P}\right) dP$$

This is the fugacity coefficient, and in terms of the compressibility factor this can be written as

$$\ln(\emptyset^1) = \int_0^{P_1} \left(\frac{Z-1}{P}\right) dP$$

since we know so many ways to get at the Z value. We could use all those methods here to get also at the phi 1 value and then we worked out this example. This example was a slightly more complicated one in terms of needing slightly higher level skills of integration, which we saw. Not very difficult. But it needs a higher level skill from what was required to solve the previous set of problems. And we went through solving the problem to get at the fugacity co-efficient of isopropanol.

So, that was all that we did in module 3. When we start the next class, we will start with module 4 and look at solutions. So far, it was pure substance. Next, we mix pure substances together we get solutions and we look in properties of solutions. See you then.