Engineering Thermodynamics
Professor Jayant K Singh
Department of Chemical Engineering
Indian Institute of Technology Kanpur
Lecture 13
Equations of state and compressibility chart

Okay. So, welcome back! This is the last part of the module of properties. So, we were discussing about the property table. Okay.

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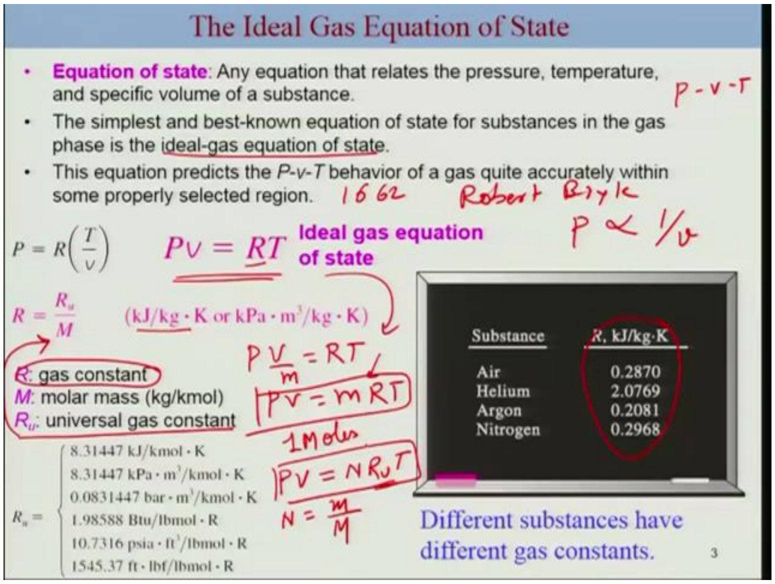

The Ideal Gas Equation of State

- **Equation of state**: Any equation that relates the pressure, temperature, and specific volume of a substance.
- The simplest and best-known equation of state for substances in the gas phase is the ideal-gas equation of state.
- This equation predicts the *P-v-T* behavior of a gas quite accurately within some properly selected region.

P - v - T

1662 Robert Biyk

$P \propto 1/v$

$P = R\left(\frac{T}{v}\right)$

$Pv = RT$ Ideal gas equation of state

$R = \frac{R_u}{M}$ (kJ/kg · K or kPa · m³/kg · K)

R: gas constant
M: molar mass (kg/kmol)
*R*ᵤ: universal gas constant

$$R_u = \begin{cases} 8.31447 \text{ kJ/kmol} \cdot \text{K} \\ 8.31447 \text{ kPa} \cdot \text{m}^3\text{/kmol} \cdot \text{K} \\ 0.0831447 \text{ bar} \cdot \text{m}^3\text{/kmol} \cdot \text{K} \\ 1.98588 \text{ Btu/lbmol} \cdot \text{R} \\ 10.7316 \text{ psia} \cdot \text{ft}^3\text{/lbmol} \cdot \text{R} \\ 1545.37 \text{ ft} \cdot \text{lbf/lbmol} \cdot \text{R} \end{cases}$$

$P\frac{V}{m} = RT$

$\boxed{PV = mRT}$

1 Moles

$\boxed{PV = NR_uT}$

$N = \frac{m}{M}$

Substance	R, kJ/kg·K
Air	0.2870
Helium	2.0769
Argon	0.2081
Nitrogen	0.2968

Different substances have different gas constants.

Now we are going to discuss equation of state, basically equation of state is nothing but which we let us P v T in some analytical form which allows one to a make a use of the equations to solve problems. So, the simplest and the best known equation of state is basically the ideal gas equation of state. And it was around 1662 when Robert Biyk found out that the pressure proportional to 1 by specific value okay.

And that led to the development of P v is equal to RT okay. So, what is R here, R apparently is a constant proportionally constant and this turns out to be the gas constant okay. This R is in the units of kilojoules per kelvin and this R values is dependent on the substance. Now you can divide the R as you can write this expression in the different form, you can write this expression as this and you can write it P v m R T.

So, this is a the traditional ideal gas equation of state, you can also write in terms of moles, okay. So, we know that moles, 1 mole contains the Avogadro number of molecules or one mole is equivalent to a molecular weight of a substance okay in grams. So, if we convert this in a moles than essentially you are going to get this kind of expression, okay where N is the mass okay divided by molecular weight. And therefore your gas constants get modified and this written as R u.

So, this is the, is the universal gas constant here okay. And the universal gas constant is related to gas constant in this form. So, we can write this expression or this expression depending on whether you have information on mass or the moles.

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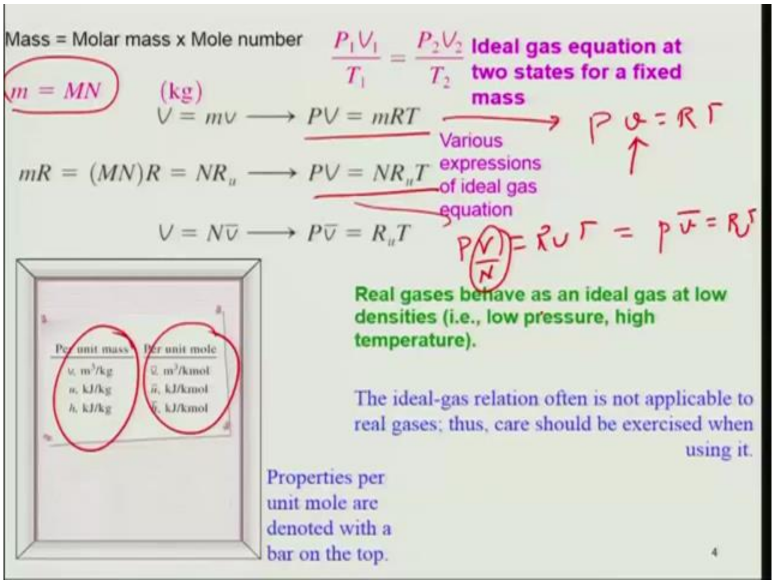

Mass = Molar mass x Mole number

$$m = MN \quad \text{(kg)}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Ideal gas equation at two states for a fixed mass

$$V = mv \longrightarrow PV = mRT \longrightarrow Pv = RT$$

$$mR = (MN)R = NR_u \longrightarrow PV = NR_u T$$

Various expressions of ideal gas equation

$$V = N\bar{v} \longrightarrow P\bar{v} = R_u T$$

$$P\left(\frac{V}{N}\right) = R_u T = P\bar{v} = R_u T$$

Per unit mass	Per unit mole
v, m³/kg	$\bar{v}$, m³/kmol
u, kJ/kg	$\bar{u}$, kJ/kmol
h, kJ/kg	$\bar{h}$, kJ/kmol

Real gases behave as an ideal gas at low densities (i.e., low pressure, high temperature).

The ideal-gas relation often is not applicable to real gases; thus, care should be exercised when using it.

Properties per unit mole are denoted with a bar on the top.

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So, as I have mentioned already that you mass and moles are (con) connected by this, so you can write this in terms of moles or in terms of mass. You can also write in a mole in the simpler form where you divide N both side such that this is P v by N equal to R u T and this particular expression becomes molar property or molar volume, earlier we have written this as RT where this was specific volume.

Now this would be P v equal to R u T. So, this is another form of writing an ideal gas expression. So, as I said this is a per unit mass basis this is a per unit mole basis. Now the real gas behaves as an ideal gas only at extremely low density, which essentially means low pressure okay.

And you can approximated to there is a region where this ideal gas behavior is same, but it is not valid for all the conditions that is what we need to develop new location of stat, so that something which we are going to a study later okay.

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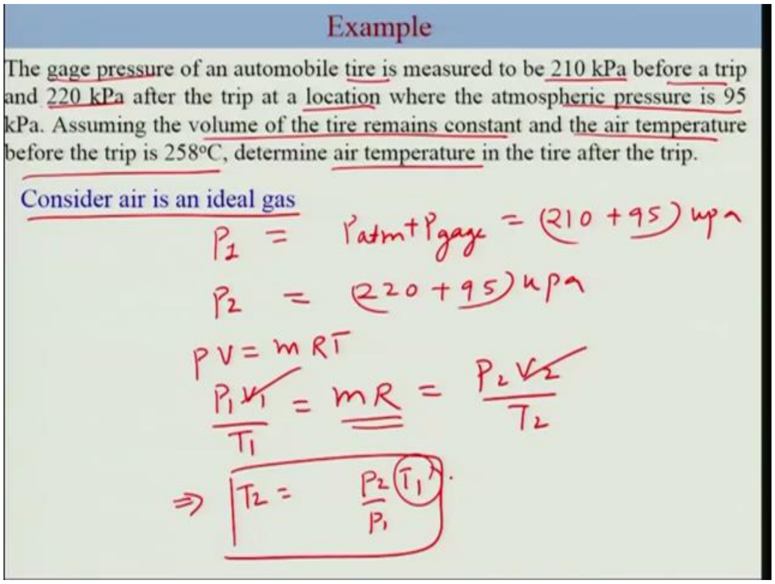

Example

The gage pressure of an automobile tire is measured to be 210 kPa before a trip and 220 kPa after the trip at a location where the atmospheric pressure is 95 kPa. Assuming the volume of the tire remains constant and the air temperature before the trip is 258°C, determine air temperature in the tire after the trip.

Consider air is an ideal gas

$$P_1 = P_{atm} + P_{gage} = (210 + 95)\,\text{kpa}$$

$$P_2 = (220 + 95)\,\text{kpa}$$

$$PV = mRT$$

$$\frac{P_1 \cancel{V_1}}{T_1} = \underline{\underline{mR}} = \frac{P_2 \cancel{V_2}}{T_2}$$

$$\Rightarrow \boxed{T_2 = \frac{P_2}{P_1} T_1}$$

So, let us take an example how we make use of this ideal gas equations. So, the example is that you have measured the gage pressure of an automobile tire before a trip it was 210kilopascal. After you undergone the trip the pressure become 220kilopascal at a location where there atmospheric pressure is 95kilopascal. So, we have to find out the temperature in the tire after the trip before, so what we assuming is that volume of the tire is constant and the what is given is the air temperature before the trip was 258degree Celsius.

So, what we are going to do the first thing is we are going to consider air as an ideal gas and then you find out the pressure let say before the trip is P 1 okay. This would be P atmosphere plus P gage okay. Which was before it was 210 plus 95 kilopascal then we have P 2 in a similar way P 2 is going to be 220 plus 95 kilopascal.

So, you are aware of the pressure you based on this information. Now if you are using ideal gas, so we know ideal gas is P v whether you take based on mass, whether you take based on moles because of the fact the volume remain constant, the mass is going to be constant.

Now because mass is also constant (())(5:22) close system and as well as the number moles is going to be constant okay. So, whether we take let say m RT in this form or then we can write before the trip information, okay. So, this is going to be T 1 MR okay. This should be same as T2 because this is a constant.

Now V 1 and V 2 is constant which essentially means I should be able to find T 2 as P 2 by P 1 T1 and this is along we are going to solve this problem by replacing P 1 and P 2 by this value and T 1 we know 258 degree Celsius.

So, this is the way to solve simple problem such as by making use of gas approximate into ideal gas equation of state okay.

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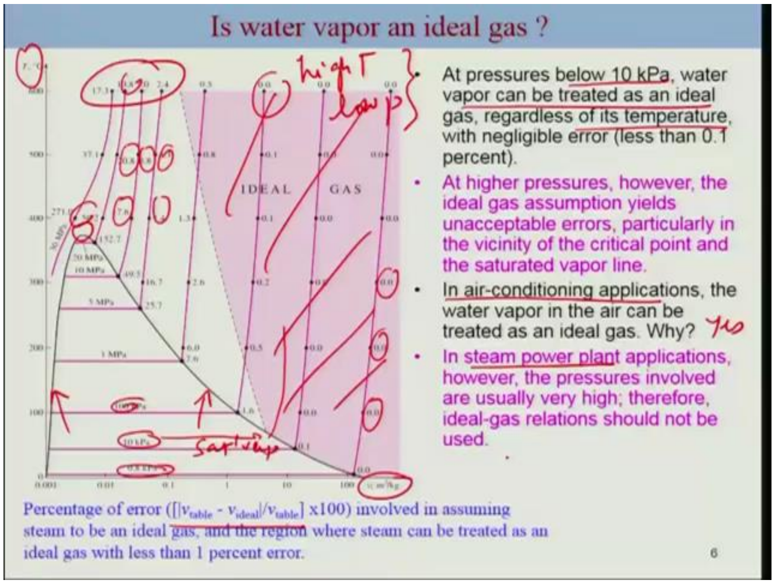

Is water vapor an ideal gas ?

- At pressures below 10 kPa, water vapor can be treated as an ideal gas, regardless of its temperature, with negligible error (less than 0.1 percent).
- At higher pressures, however, the ideal gas assumption yields unacceptable errors, particularly in the vicinity of the critical point and the saturated vapor line.
- In air-conditioning applications, the water vapor in the air can be treated as an ideal gas. Why? yes
- In steam power plant applications, however, the pressures involved are usually very high; therefore, ideal-gas relations should not be used.

Percentage of error ($[|v_{table} - v_{ideal}|/v_{table}]$ x100) involved in assuming steam to be an ideal gas, and the region where steam can be treated as an ideal gas with less than 1 percent error.

So, what about other vapors, other gases such as a water vapor is it in ideal gas. So, let us take a look of this table this is a T v plot and this is your specific region of a vapor plus liquid again this is your saturated liquid and this is your saturated vapor line okay and this is your critical point.

Now what you see is this value here, these values are nothing but the percentage of error from steam table, from the table which we are used earlier. The error with respect to we used for example ideal gas. So, ideal gas values on the corresponding ideal gas let say specific value and how much it deviates from this steam table values. In terms of percentage of error this is a representation.

The zero indicate that this you perfectly representable, ideal gas approximation this case okay which is of course this region we have to find okay and this is also at low pressure. So, this look at this, this is at very low pressure, these are low pressure regions okay. And as you go a higher pressure the values starts deviating.

So, this ideal gas approximation does not work, near the critical point 56.2% is extremely large and that is where we understand that at a pressure 10 kilopascal water, vapor can treated as an ideal gas you can see 10kilopascal here okay. This region is pretty much can be represented by ideal gas.

And regardless of this temperature, so that means even if you increase the temperature, this is extremely high temperature okay. High temperature low pressure, so high temperature low pressure ideal gas approximation (())(7:59). On the other hand if you increase the pressure the deviation is quite large and hence it is now going to work, near the critical point of course is not going to work. So, in case of a air conditioning application can be make use of ideal gas approximation and the and the answer is yes, why because the pressure of air conditioning applications are very low.

However you cannot make use of ideal gas approximation for the case of steam power plant because it usually operated high pressure.

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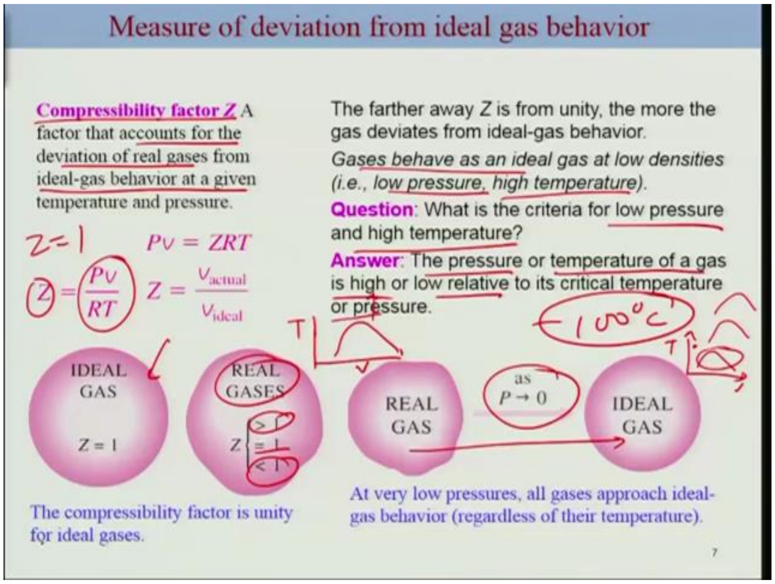

Measure of deviation from ideal gas behavior

Compressibility factor Z A factor that accounts for the deviation of real gases from ideal-gas behavior at a given temperature and pressure.

$Z=1$

$Pv = ZRT$

$Z = \frac{Pv}{RT}$ $\quad Z = \frac{v_{actual}}{v_{ideal}}$

The farther away *Z* is from unity, the more the gas deviates from ideal-gas behavior.

Gases behave as an ideal gas at low densities (i.e., low pressure, high temperature).

Question: What is the criteria for low pressure and high temperature?

Answer: The pressure or temperature of a gas is high or low relative to its critical temperature or pressure.

100°C

The compressibility factor is unity for ideal gases.

At very low pressures, all gases approach ideal-gas behavior (regardless of their temperature).

Now it is nice to make use an ideal gas equation of state but it has limited application because it suitable only for certain range as we have already seen high temperature low pressure region, but we desire to have equation of state which was in a wide range of applications.

Now so ideal gas is a easy inconvenient to use but it deviates from the real gas properties for certain condition. And this is why we need to also look at a certain parameters which identify this kind of deviation and this parameter of factor which we call is compressibility factor okay. And this is the factor that accounts for other deviation of real gas from ideal gas behavior at a given temperature and pressure.

So, we can write in this form that Z is nothing but P v by R T okay. So, for the case of ideal gas Z is 1, okay. And any deviation from Z equal 1 is a representation of deviation from the real gas properties or from the ideal gas behavior. So, real gas can have a greater than 1, can have equal to 1 values or less than 1. So, if you deviates from Z equal 1, the real gas actually deviates from the ideal gas behavior.

So, this is quite useful in many application which we make use of it. Now we know that gases behave as an ideal gas at low density that is low pressure and high temperature we have already illustrated this or based on the graph which we have used, which essentially means as, as pressure is low the real gas behaves like ideal gas.

But what is the criterion for low pressure and high temperature. So, you take an example let say minus 100degree Celsius is this temperature low or high okay and that is where it depends on the substance.

For water it is certainly low, but for nitrogen and other gases is very very high why because for nitrogen, for example the critical temperature is around minus 140 degree Celsius. So, this temperature is much higher, thus the pressure or temperature for gas is high or low (())(10:35) to the critical temperature or pressure.

So, if you look at any plot okay. You have to look at any plot like this. So, temperature is higher only when is a wave the critical point. So, you can have a many different substance which can have different kind of plots, so I can draw it here.

So, you may have like this for one substance you may have another substance like this another substance all in the same thermodynamic variable and this temperature here may be high for this substance but it is may be low for other substance. So, the criteria for low and high temperature is related to the critical temperature or pressure.

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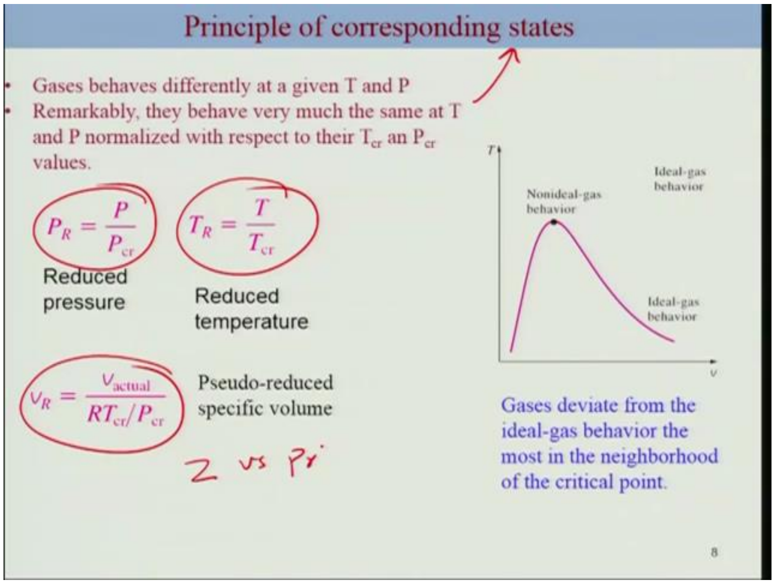

Principle of corresponding states

- Gases behaves differently at a given T and P
- Remarkably, they behave very much the same at T and P normalized with respect to their T_{cr} an P_{cr} values.

$$P_R = \frac{P}{P_{cr}}$$

Reduced pressure

$$T_R = \frac{T}{T_{cr}}$$

Reduced temperature

$$v_R = \frac{v_{actual}}{RT_{cr}/P_{cr}}$$

Pseudo-reduced specific volume

Z vs Pr

Gases deviate from the ideal-gas behavior the most in the neighborhood of the critical point.

And is something quite interesting because if you take various different gases and take the properties and reduced it with their critical property it turns out the lot many gases which as similar nature such as methane, propane, ethane it is starts behaving similarly in the reduced plots.

So, they have remarkably same property, if you reduced the temperature and pressure with their critical properties. So, in some sense which means that you have taken out the characteristics nature if the molecules but dividing the property with their critical properties. So, this is what we say of the principle of corresponding state and this is the basis of that, where we make use of this reduced pressure, reduced temperature which is nothing but the pressure divided by their critical pressure of the substance and same with the reduced temperature.

And you can also calculate V R okay. So, now it based on this you would be surprise to see that Z verses P r for many different gases they have almost similar plots and that is what it allows us to calculate or come up with this kind of plot such as what we call it here is compressibility chart.

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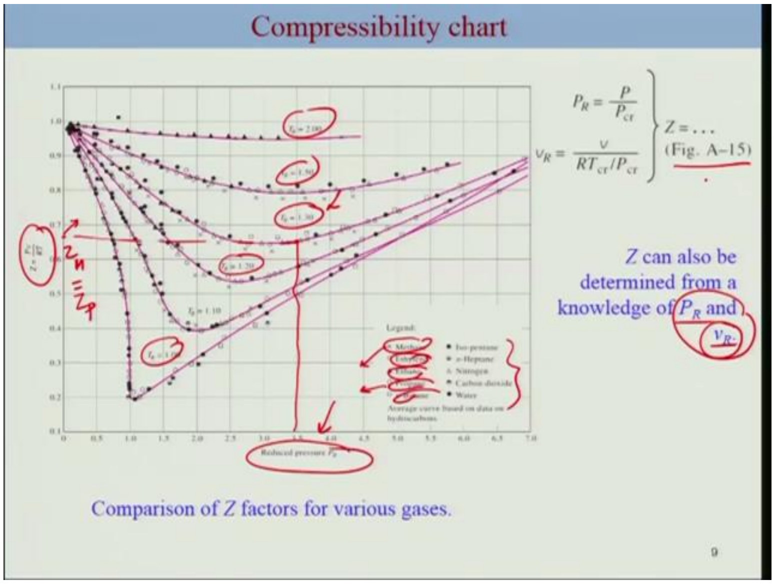

Compressibility chart

$$P_R = \frac{P}{P_{cr}}$$

$$v_R = \frac{v}{RT_{cr}/P_{cr}}$$

$Z = \ldots$ (Fig. A–15)

Z can also be determined from a knowledge of P_R and v_R.

Comparison of Z factors for various gases.

So, the compressibility chart it contains Z by the function of reduced P r or many different gases okay this all gases but I say you can say this symbols represent the they all far in a frame curve and this line here is T r.

So, essentially this line has a specific reduced temperature values. So, what does it means, so if you take a let say methane and propane. So, methane and let say propane okay. And you take a value of reduced pressure, at certain point you and for a specific T r values, you can find out the Z value okay. So, Z for methane should will be same as that for propane, as long as there P r and T r for the both the system is same. So, based on this you can do a calculation and obtained the Z values and find out where deviation from the ideality.

Z also can be determine from in the knowledge of P r and V r that is what we said, the VR can be used to calculate.

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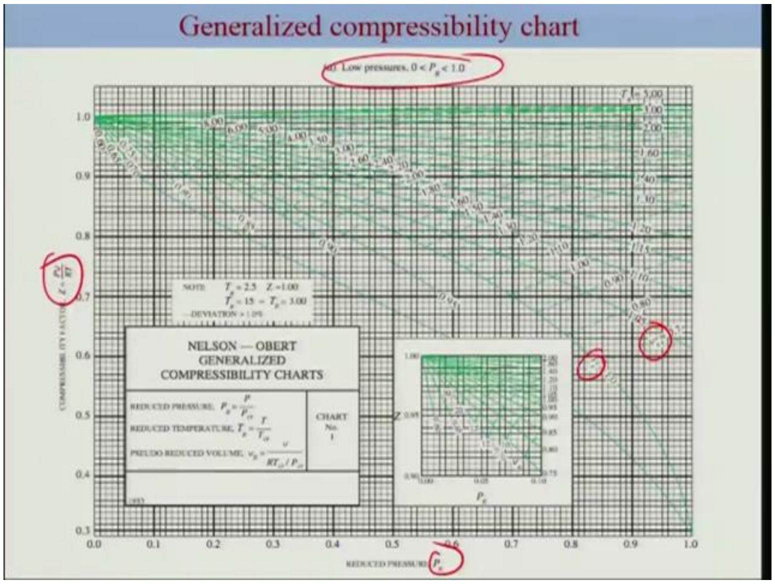

Generalized compressibility chart

So, the figure A 15 in that happened this, the text books contains more complicated more rigorous kind of plot which actually is the more of a based on the, what I showed in the previous slide and made use of some rigorous fitting and this is the plot or the chart which we commonly use. So, this is for the low pressure region, so here you have a P r you have gain a Z and then you have your T r and as well as there is also included V r the reduced volume. We can make use of this particular chart to solve certain problems.

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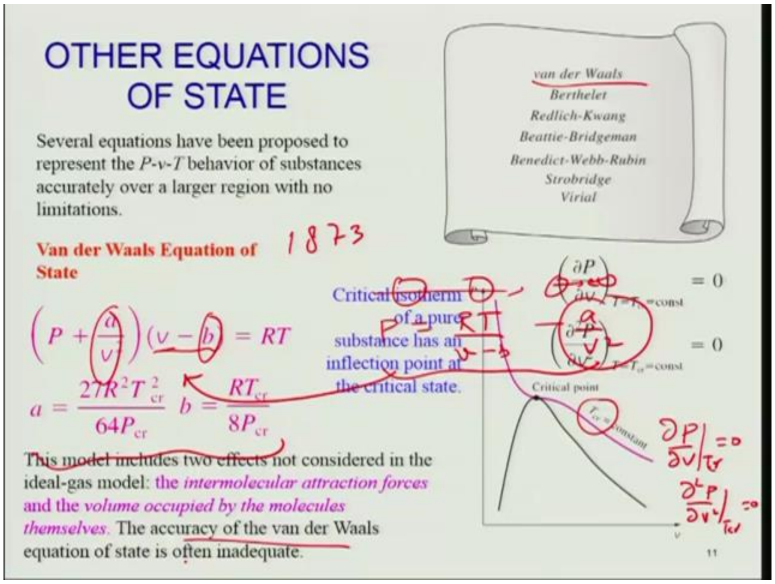

OTHER EQUATIONS OF STATE

Several equations have been proposed to represent the P-v-T behavior of substances accurately over a larger region with no limitations.

van der Waals
Berthelet
Redlich-Kwang
Beattie-Bridgeman
Benedict-Webb-Rubin
Strobridge
Virial

Van der Waals Equation of State 1873

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

$$a = \frac{27R^2T_{cr}^2}{64P_{cr}} \quad b = \frac{RT_{cr}}{8P_{cr}}$$

Critical isotherm of a pure substance has an inflection point at the critical state.

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

$$\left(\frac{\partial P}{\partial v}\right)_{T=T_{cr}=\text{const}} = 0$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_{cr}=\text{const}} = 0$$

$$\left.\frac{\partial P}{\partial v}\right|_{T_{cr}} = 0 \qquad \left.\frac{\partial^2 P}{\partial v^2}\right|_{T_{cr}} = 0$$

This model includes two effects not considered in the ideal-gas model: the *intermolecular attraction forces* and the *volume occupied by the molecules themselves*. The accuracy of the van der Waals equation of state is often inadequate.

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Now as I said the desired to developed equation of state has been prominently and still is ongoing effort for industrial applications. Because what we desires is to come up with equations which we can solve, when a computers make instead of using tables all the type, but we can realize that these are very difficult job because of the nature of the P V T surfaces and a complicated nature of the molecules.

That is why many specific equations of state has been developed. It started way back by van der Waals which wanted to change their ideal gas equation of stare by including the nature of the intermolecular forces and as well as the size of the molecule. So, it was in 1873 by van der Waals which came up with this modification of ideal gas equation okay. And what he did was introduced this terms which represent a specific nature of their molecule.

Molecules do have volume and hence there is the volume of the system reduces because certain volume is occupied by the molecule. So, that is why the effective volume is less and what about this term. Now in case of a ideal gas it does not have any interaction, ideal gas molecule can just pass through each other. So, they can just pass through each other without colliding, on the other hand due to the interaction between the molecules they will collide.

So, essentially you can think from the number of collision on a wall of the container due to the interaction (())(15:32) collision will reduced. So, you can think of this equation of (())(15:37) is that, you can write this ideal gas equation of state in this form and when you include the volume of the molecules you have to reduce the volume here and further the pressure gets reduced due to the interaction of the molecules by this term, okay. And this particular expression can be written in this way.

So, this is a contribution or rather the reduction in the pressure due to the intermolecular interaction. So, that was the van der Waals equation of state. Now you can find out this particular variables a and b by a taking help from the the nature of the curve going through the critical part. So, at critical point for given temperature or for critical temperature it undergoes inflect the curve undergoes inflection hence the first derivative of pressure with respect to volume at T critical should be zero and as well as the second derivative should be zero, okay.

And thus based on this you can calculate a and b in terms of T r and P r okay. So, this is how it will come. So, this model is used for long time but is not very (())(16:50) from many different regions of the phase okay.

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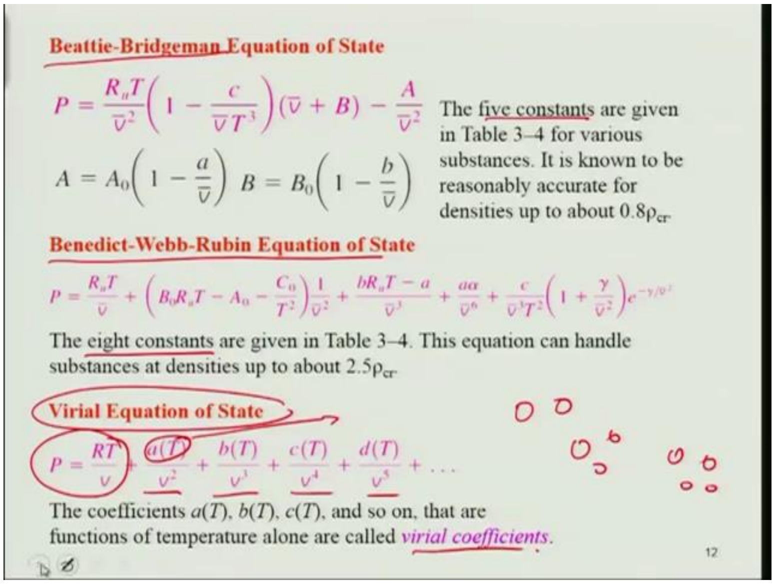

Beattie-Bridgeman Equation of State

$$P = \frac{R_u T}{\bar{v}^2}\left(1 - \frac{c}{\bar{v} T^3}\right)(\bar{v} + B) - \frac{A}{\bar{v}^2}$$

$$A = A_0\left(1 - \frac{a}{\bar{v}}\right) \quad B = B_0\left(1 - \frac{b}{\bar{v}}\right)$$

The five constants are given in Table 3–4 for various substances. It is known to be reasonably accurate for densities up to about $0.8\rho_{cr}$.

Benedict-Webb-Rubin Equation of State

$$P = \frac{R_u T}{\bar{v}} + \left(B_0 R_u T - A_0 - \frac{C_0}{T^2}\right)\frac{1}{\bar{v}^2} + \frac{b R_u T - a}{\bar{v}^3} + \frac{a\alpha}{\bar{v}^6} + \frac{c}{\bar{v}^3 T^2}\left(1 + \frac{\gamma}{\bar{v}^2}\right)e^{-\gamma/\bar{v}^2}$$

The eight constants are given in Table 3–4. This equation can handle substances at densities up to about $2.5\rho_{cr}$.

Virial Equation of State

$$P = \frac{RT}{v} + \frac{a(T)}{v^2} + \frac{b(T)}{v^3} + \frac{c(T)}{v^4} + \frac{d(T)}{v^5} + \ldots$$

The coefficients $a(T)$, $b(T)$, $c(T)$, and so on, that are functions of temperature alone are called *virial coefficients*.

And thus they has been many different developers by introducing more variable in there equation. So, for example this is Beattie Bridgeman equation of state it has 5 constants and then you have Benedict Webb Rubin equation which has 8 constants.

And naturally this is fitted to the experimental values and then we have obtained this variables okay. Not all of them have a very sound theoretical reasons for having this terms okay. This is mainly derived from the van der Waals and later on added where this different terms.

Now the 1 which has a very sound theoretical diagram is Virial equation of sate. So, Virial equation of state has this ideal gas term and then the other term is added which is a contribution to the interaction between 2 particles, interaction due to 3particles or due to 4 particle cluster and so forth.

Because of you can consider the gas phase to made of this different different component and this the real coefficient is a just a function of temperature.

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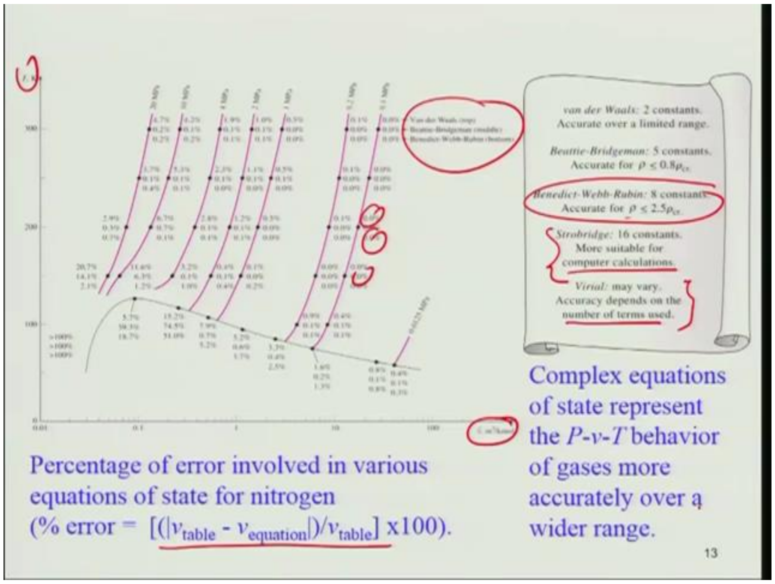

van der Waals: 2 constants.
Accurate over a limited range.

Beattie-Bridgeman: 5 constants.
Accurate for $\rho \leq 0.8\rho_{cr}$

Benedict-Webb-Rubin: 8 constants.
Accurate for $\rho \leq 2.5\rho_{cr}$

Strobridge: 16 constants.
More suitable for
computer calculations.

Virial: may vary.
Accuracy depends on the
number of terms used.

Complex equations of state represent the *P*-*v*-*T* behavior of gases more accurately over a wider range.

Percentage of error involved in various equations of state for nitrogen
(% error = $[(|v_{\text{table}} - v_{\text{equation}}|)/v_{\text{table}}] \times 100$).

So, let see how it phase when you put it in a real scenario for the real gas, this is a nitrogen and this is a again temperature versus molar volume, in this case plot and we have plotted for various different equation of state and the values which is represented here is an error, just like we had earlier for water and clearly some of them do does very good job.

So, the summary is here it turns out that the Benedict Webb Rubin pretty good okay for accurate for density okay quite higher up, up till 2.5 times at their critical density. This Strobridge is quite useful for the computer calculations. Virial based equation of state, though it is quite useful but it has limited utility because Virial coefficient are that known for many systems, only few Virial coefficients are known up till 4 to 5, but if you want to increase that accuracy of Virial equation of state we have to include more number of term.

So, thus we see from this small example that complex equation of state is required to capture the P v T properties or diagram of simple system, simple gases okay.

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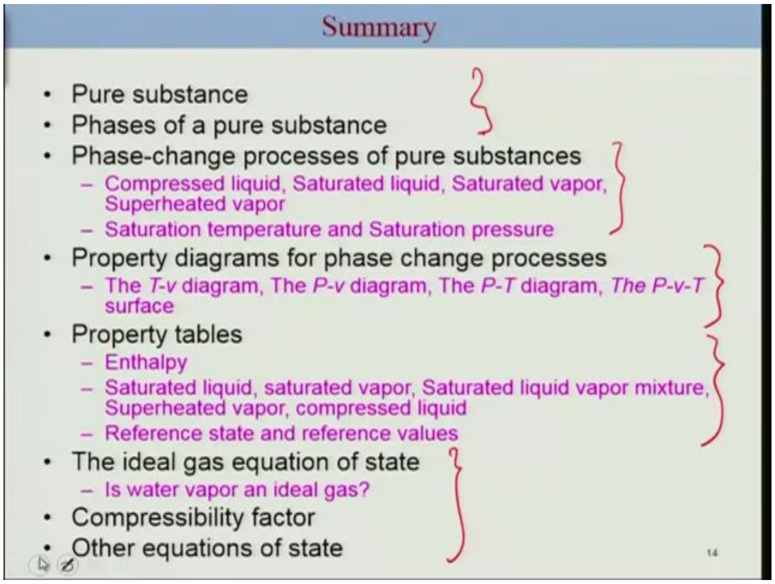

Summary

- Pure substance
- Phases of a pure substance
- Phase-change processes of pure substances
  - Compressed liquid, Saturated liquid, Saturated vapor, Superheated vapor
  - Saturation temperature and Saturation pressure
- Property diagrams for phase change processes
  - The *T-v* diagram, The *P-v* diagram, The *P-T* diagram, *The P-v-T* surface
- Property tables
  - Enthalpy
  - Saturated liquid, saturated vapor, Saturated liquid vapor mixture, Superheated vapor, compressed liquid
  - Reference state and reference values
- The ideal gas equation of state
  - Is water vapor an ideal gas?
- Compressibility factor
- Other equations of state

Okay with that let us go to summery of this particular module. So, we started with a definition of pure substance, phases of pure substance. We went through the phase change process, we describe the compressed liquid, saturated liquid, superheated and the systems. Then we went to the property diagram and the phase change and how to describe the phase change on property diagram.

We also illustrated the use of property tables by doing some examples and finely we ended today with equation of state staring with ideal gas equation of state led into other complicated equation of state okay. So, with that this is the end of this particular chapter and next we are going to look at the energy analysis of a close system.