Advanced Thermodynamics and Combustion
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Module - IV
Properties of Gas Mixture
Lecture - 15
Ideal Gas and Real Gas

Dear learners, greetings from IIT Guwahati, I welcome to this course Advanced Thermodynamics and Combustions; today we are going to start Module - 4 that is Properties of Gas Mixture.

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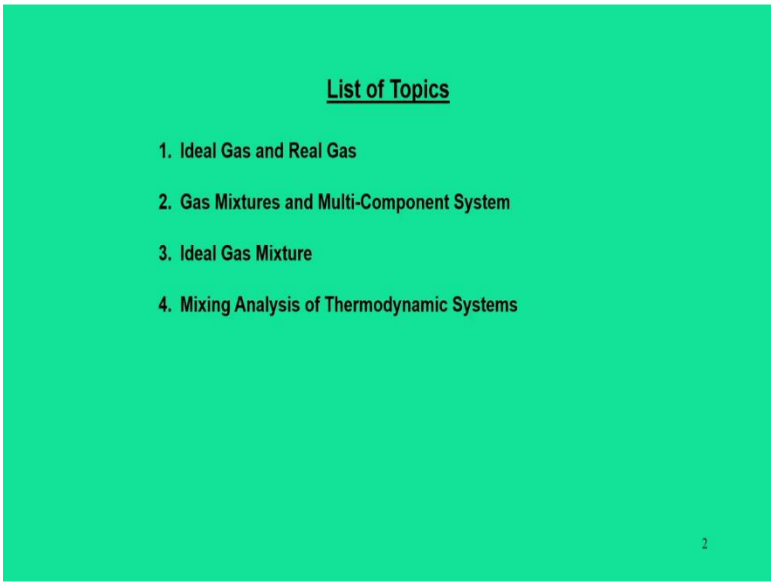

List of Topics

1. Ideal Gas and Real Gas
2. Gas Mixtures and Multi-Component System
3. Ideal Gas Mixture
4. Mixing Analysis of Thermodynamic Systems

So, in this module there will be four lectures that consist of the followings, first one is ideal gas and real gas, second one is gas mixtures and multi component systems. Then we will focus towards only for ideal gas mixture and subsequent in the last lecture we will be discussing about the mixing analysis of thermodynamic systems and in particular for a ideal gas mixture. So, in fact, till this point of time in all previous modules, we have been concentrating only on pure substance.

And now we will be concentrating more towards the mixtures and multi component systems. By this I mean this mixture can be composed of gas or liquid or solid mostly when you use the word mixture it is mainly for gases. And this mixture can also consist of different gases or different phases and the focal point of this module is to how to perform the thermodynamic analysis.

First thing and to do this thermodynamic analysis we need to find out the composition of the mixture number 1, number 2 for each constituents of the mixtures, we also need to calculate the thermodynamic properties. And all previous studies which were used for a pure substance through p-v-T relations what we have derived through Maxwell relations and other thermodynamic considerations that we are going to use it while analyzing the mixture.

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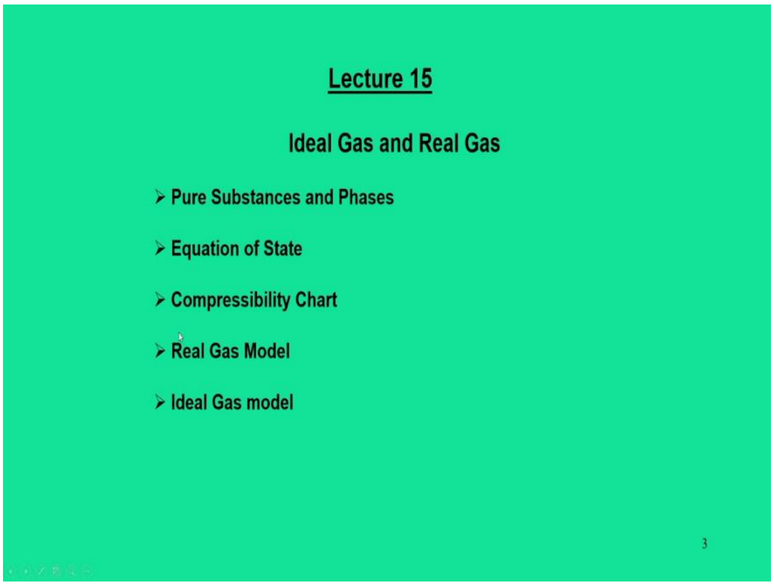

Lecture 15

Ideal Gas and Real Gas

- Pure Substances and Phases
- Equation of State
- Compressibility Chart
- Real Gas Model
- Ideal Gas model

So, with this view point let me start the first lecture and in the series it is Lecture number-15, the first lecture of the Module- 4 is Ideal Gas and Real Gas. Under this ideal gas and real gas, we will start this considerations with very basic backgrounds through some basic philosophies what we have used for pure substance phases. Then we will move on to state equations thermodynamically where we need to represent the state equation for a pure substance and gases.

Then we will introduce compressibility chart and which is mostly used for gases and we will see what is this significance, how this is correlated with the equation of state. And followed by this compressibility chart, we are going to frame some real gas models and of course, to have a thermodynamic estimate we also have to think about ideal gas model. In fact, this ideal gas model we have been using in all our basic courses.

With this ideal gas estimate we will try to see what benefit we are going to get while analyzing the state equations through a real gas model or through compressibility chart.

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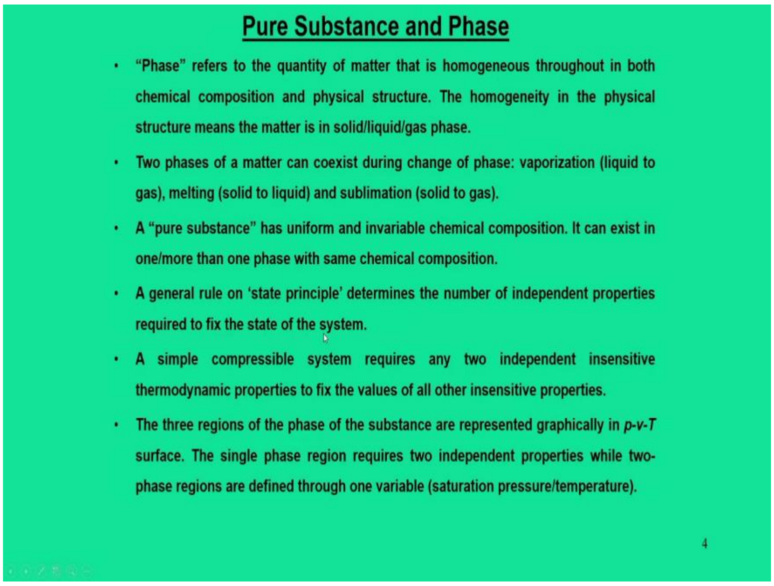

Pure Substance and Phase

- "Phase" refers to the quantity of matter that is homogeneous throughout in both chemical composition and physical structure. The homogeneity in the physical structure means the matter is in solid/liquid/gas phase.
- Two phases of a matter can coexist during change of phase: vaporization (liquid to gas), melting (solid to liquid) and sublimation (solid to gas).
- A "pure substance" has uniform and invariable chemical composition. It can exist in one/more than one phase with same chemical composition.
- A general rule on 'state principle' determines the number of independent properties required to fix the state of the system.
- A simple compressible system requires any two independent insensitive thermodynamic properties to fix the values of all other insensitive properties.
- The three regions of the phase of the substance are represented graphically in *p-v-T* surface. The single phase region requires two independent properties while two-phase regions are defined through one variable (saturation pressure/temperature).

So, let me start the first topic or first term which we call this as a pure substance and phase. Now, about this pure substance and phase, in the basic thermodynamic course most of the contents have been covered and in this lecture we will just touch upon or refresh some of our basic things before you go for the real gas modeling. So, basically the "phase" refers to the quantity of the matter which is homogeneous throughout in both chemical composition and physical structure.

The homogeneity of the physical structure means that the matter is in solid liquid or gas phase. In fact, that is the three different phase of matter, now out of this three phase two phases of matter can coexist during a change of phase. We all know; what is vaporization, where liquid changes its state to gas, melting solid goes to liquid and sublimation where solid goes to gas phase.

Now, for all this phase when you define a pure substance it has a uniform invariable chemical compositions and it can exist in one or more than one phase with same chemical composition. And we all know that the pure substance is represented through p-v-T diagram, pressure volume temperature diagram. A general rule on "state principle" determines the number of independent properties required to fix the state of the system.

Now for a simple compressible system, we require two independent insensitive thermodynamic properties to fix the values for all other insensitive properties. Or in other words there are some measured parameters and there are some derived or calculated parameters. So, the measured parameters are nothing but the independent and insensitive thermodynamic properties and that is used to calculate all other properties.

The three regions of the phase of the substance are represented graphically on a pressure volume temperature surface. The single phase region requires two independent properties while two phase regions are defined through one variable either it can be a saturated pressure or temperature.

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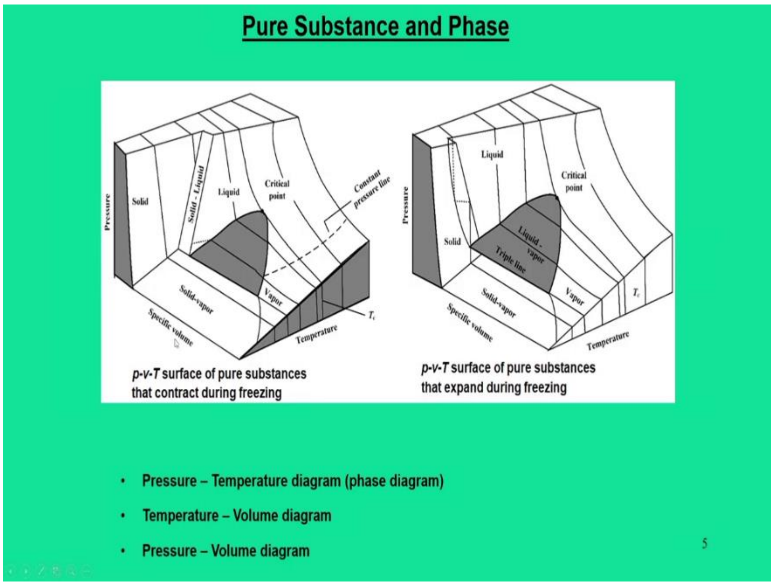

Pure Substance and Phase

p-v-T surface of pure substances that contract during freezing

p-v-T surface of pure substances that expand during freezing

- Pressure – Temperature diagram (phase diagram)
- Temperature – Volume diagram
- Pressure – Volume diagram

So, this particular diagram shows the p-v-T surface for a pure substance that contract during freezing and some substance that expands during the freezing. So, all these basic philosophies has been covered in the basic thermodynamic course, I am not going to get into this details, but what I am trying to say is that when you discuss about this p-v-T surface and this is a three dimensional structure.

Now, you have to bring down into two dimensional systems where we represent the characteristics of the substance either through pressure temperature diagram and normally we call this as a phase diagram, temperature volume diagram or pressures volume diagram.

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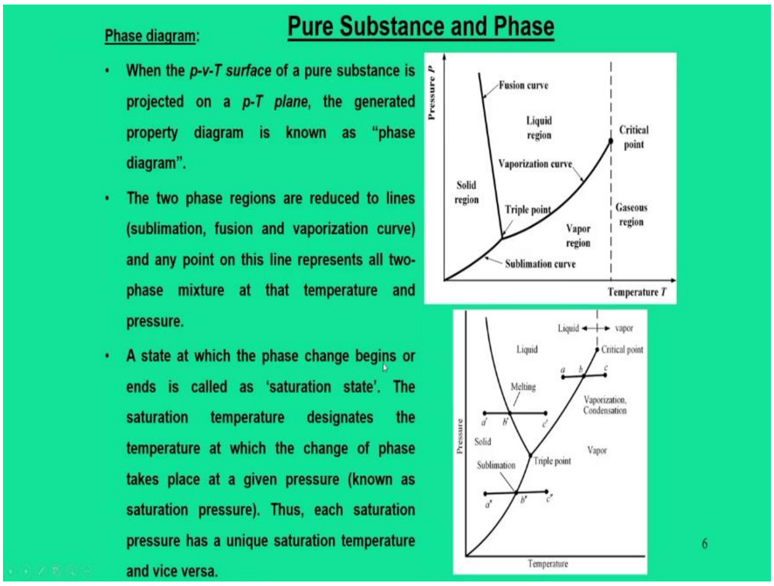

Pure Substance and Phase

Phase diagram:

- When the *p-v-T surface* of a pure substance is projected on a *p-T plane*, the generated property diagram is known as “phase diagram”.
- The two phase regions are reduced to lines (sublimation, fusion and vaporization curve) and any point on this line represents all two-phase mixture at that temperature and pressure.
- A state at which the phase change begins or ends is called as ‘saturation state’. The saturation temperature designates the temperature at which the change of phase takes place at a given pressure (known as saturation pressure). Thus, each saturation pressure has a unique saturation temperature and vice versa.

So, let us start the first diagram which is called as a phase diagram where most of the critical information are framed. Now, if you look at this pressure temperature diagram and this is nothing but the p-v-T surface is projected on a pressure temperature plane, what we observe is three different regions solid, liquid and vapour regions. The solid and vapour region is separated by a curve what we call as sublimation curve, the solid and liquid region is separated by fusion curve and the vaporization curve separates the liquid and vapour region.

And on this p-T diagrams we also define a point we call as a triple point where all the three states of the matter coexist. Now, when you talk about the critical point, at that point liquid and vapour they coexist and the same philosophy, solid goes to liquid or liquid goes to solid, melting or freezing, liquid goes to vapour or vapour comes to liquid, we call vaporization or condensation.

Now, here we use the word mostly solid goes to gas so, we call this as a sublimation. Now, on this diagram we have fixed the point what we call as triple point and the critical point. To summarize these things what we can write is that the two phase regions are reduced to lines either sublimation, fusion or vaporization curve and any point on this line represents the phase of the mixture at that temperature and pressure.

Now, state at which the phase change begins or ends is called as a ‘saturation state’. The saturation temperature normally designates the temperature at which the change of the phase takes place at a given pressure and we call this as a saturation pressure thus every saturation pressure as a unique temperature and vice versa.

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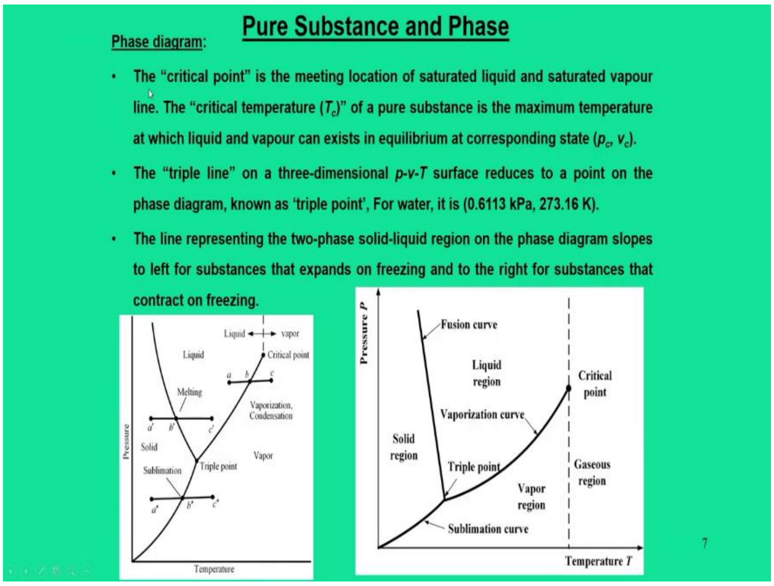

Pure Substance and Phase

Phase diagram:

- The "critical point" is the meeting location of saturated liquid and saturated vapour line. The "critical temperature (T_c)" of a pure substance is the maximum temperature at which liquid and vapour can exists in equilibrium at corresponding state (p_c, v_c).
- The "triple line" on a three-dimensional *p-v-T* surface reduces to a point on the phase diagram, known as 'triple point', For water, it is (0.6113 kPa, 273.16 K).
- The line representing the two-phase solid-liquid region on the phase diagram slopes to left for substances that expands on freezing and to the right for substances that contract on freezing.

And on this phase diagram we also define the "critical point" which is the melting location of saturated liquid and vapour. And the critical temperature T_c is defined which is the maximum temperature at which liquid and vapour can exist in equilibrium corresponding to p_c and v_c. And the "triple line" on a three-dimensional p-v-T surface reduces to a 'triple point' in a phase diagram and this triple point for the water is located at 0.6113 kPa and 273.16 Kelvin.

The line that represents the two-phase solid - liquid region on the phase diagrams slopes left for the substance that expands during the freezing and to the right for the substance that contract during the freezing this is the characteristics of the phase diagram.

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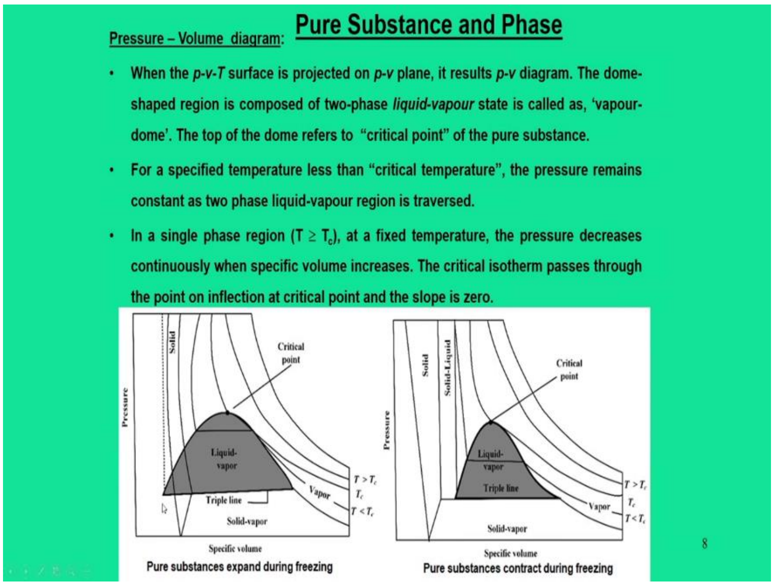

Pure Substance and Phase

Pressure – Volume diagram:

- When the *p-v-T* surface is projected on *p-v* plane, it results *p-v* diagram. The dome-shaped region is composed of two-phase *liquid-vapour* state is called as, 'vapour-dome'. The top of the dome refers to "critical point" of the pure substance.
- For a specified temperature less than "critical temperature", the pressure remains constant as two phase liquid-vapour region is traversed.
- In a single phase region ($T \geq T_c$), at a fixed temperature, the pressure decreases continuously when specific volume increases. The critical isotherm passes through the point on inflection at critical point and the slope is zero.

Pure substances expand during freezing

Pure substances contract during freezing

Then move on to pressure - volume diagram, we all know pressure volume diagram, we have pressure volume diagram for substance that expand during freezing and that contract during freezing. So, the pressure volume diagram is important because it distinguishes the liquid-vapour state or vapour - liquid state and normally it is recognized through a dome.

Now, within this dome the state of the system is liquid plus vapour mixture and outside the dome it is either liquid or vapour. In a single phase region if this temperature is greater than critical temperature, then the pressure decreases continuously when the specific volume increases. And the critical isotherm passes through the point of inflection at the critical point and slope is zero, this is the characteristics of pressure volume diagram.

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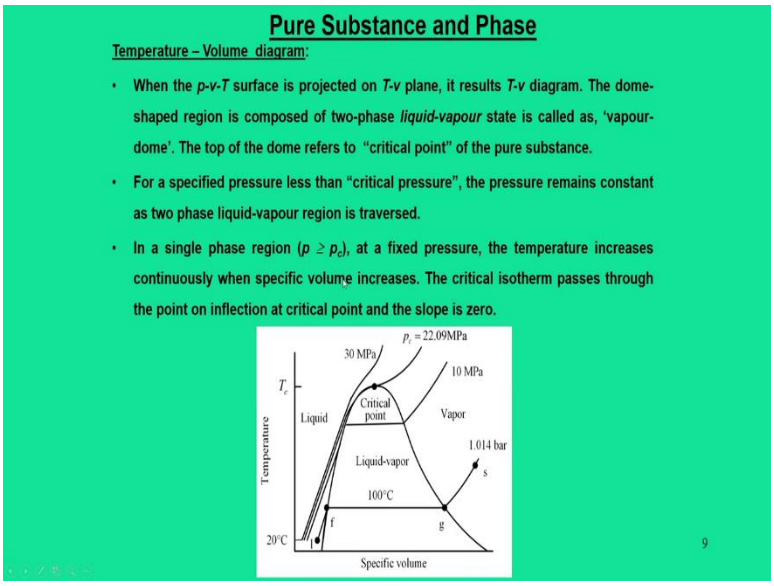

Pure Substance and Phase

Temperature – Volume diagram:

- When the *p-v-T* surface is projected on *T-v* plane, it results *T-v* diagram. The dome-shaped region is composed of two-phase *liquid-vapour* state is called as, 'vapour-dome'. The top of the dome refers to "critical point" of the pure substance.
- For a specified pressure less than "critical pressure", the pressure remains constant as two phase liquid-vapour region is traversed.
- In a single phase region ($p \geq p_c$), at a fixed pressure, the temperature increases continuously when specific volume increases. The critical isotherm passes through the point on inflection at critical point and the slope is zero.

So, in the similar line we also frame temperature volume diagram when p-v-T surface is projected on temperature volume plane. Here also we define this critical point, critical pressure, critical temperature, same logic applies here. In a single phase region when pressure is higher than the critical pressure, the temperature increases continuously when the specific volume increases. The critical isotherm also passes through the point of inflection that is at this point and the slope is zero.

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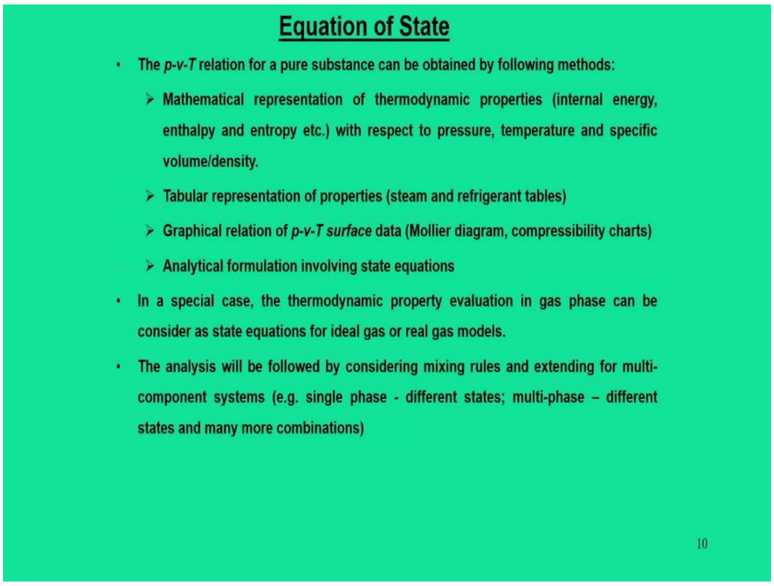

Equation of State

- The *p-v-T* relation for a pure substance can be obtained by following methods:
  - Mathematical representation of thermodynamic properties (internal energy, enthalpy and entropy etc.) with respect to pressure, temperature and specific volume/density.
  - Tabular representation of properties (steam and refrigerant tables)
  - Graphical relation of *p-v-T surface* data (Mollier diagram, compressibility charts)
  - Analytical formulation involving state equations
- In a special case, the thermodynamic property evaluation in gas phase can be consider as state equations for ideal gas or real gas models.
- The analysis will be followed by considering mixing rules and extending for multi-component systems (e.g. single phase - different states; multi-phase – different states and many more combinations)

Now, having said this we will now move on to the equation of state, now all these data which we have shown here that was the mostly for water. I mean in fact, in our study we mostly focused on the properties of the pure substance mainly concentrate for water.

But if there are many more substances and each substance must have the p-v-T data, but it is also not possible to generate the data for all the substances similar to steam table, but we have some data for refrigeration,n refrigerant tables and we also have some data for some important gases.

But the main issue is that always it is not possible to have a bulk data which are normally used to specify the state of the systems. So, the p-v-T relations for the pure substance people have considered different methods. First one is mathematical representation of thermodynamic properties; that means, you get the set of limited data and use the thermodynamic property relations that we have discussed in our earlier module.

Where properties like internal energy, enthalpy and entropy they are represented with respect to measure data that is pressure, temperature and specific volume. And tabular representation of the properties; that means, it is known that we have steam tables, we have refrigerant tables where the property relations are available in the form of data sets.

Then other way of representation of p-v-T surface is through Mollier diagrams, we all know that enthalpy entropy diagram is called as a Mollier diagrams and this is normally used when you are using rankine cycle or steam power systems. Then also we have other type of charts data, p-v surface data represented in terms of compressibility chart which we are going to discuss today.

In addition to that we have some mathematical formulations involving state equations and in fact, these equations in general are applicable to most of the substances. However, their relative accuracy may change and while doing this analytical formulation here our model comes what we call them as a real gas model. So, in a special case the thermodynamic property evaluation in gas phase and this normally considered as state equations for ideal gas or real gas models.

But these gas models are also applicable for mixing systems, multi component systems of course, we are thinking them only in the single phase and that is gas phase. And we are not going to go for any complicated multi component systems and in our focal analysis we will be talking about mixtures. We will be talking about the data when there is a combustion takes place during a chemical reactions, only these two things we are going to focus in this course.

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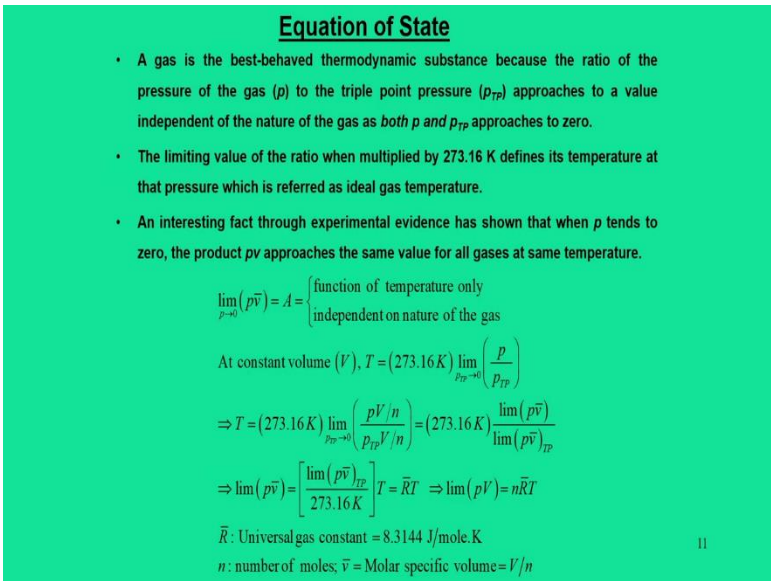

Equation of State

- A gas is the best-behaved thermodynamic substance because the ratio of the pressure of the gas (*p*) to the triple point pressure (p_{TP}) approaches to a value independent of the nature of the gas as *both p and* p_{TP} approaches to zero.
- The limiting value of the ratio when multiplied by 273.16 K defines its temperature at that pressure which is referred as ideal gas temperature.
- An interesting fact through experimental evidence has shown that when *p* tends to zero, the product *pv* approaches the same value for all gases at same temperature.

$$\lim_{p\to 0}\left(p\bar{v}\right)=A=\begin{cases}\text{function of temperature only}\\ \text{independent on nature of the gas}\end{cases}$$

$$\text{At constant volume }(V),\ T=(273.16K)\lim_{p_{TP}\to 0}\left(\frac{p}{p_{TP}}\right)$$

$$\Rightarrow T=(273.16K)\lim_{p_{TP}\to 0}\left(\frac{pV/n}{p_{TP}V/n}\right)=(273.16K)\frac{\lim\left(p\bar{v}\right)}{\lim\left(p\bar{v}\right)_{TP}}$$

$$\Rightarrow \lim\left(p\bar{v}\right)=\left[\frac{\lim\left(p\bar{v}\right)_{TP}}{273.16K}\right]T=\bar{R}T\quad\Rightarrow \lim\left(pV\right)=n\bar{R}T$$

$\bar{R}$: Universal gas constant $= 8.3144$ J/mole.K

n: number of moles; $\bar{v}$ = Molar specific volume $= V/n$

So, let us give the introduction that, what is the equation of state? How it has framed from the beginning? Now, when we talk about the equation of state we normally refer to a pure substance when it is in gaseous phase. Now, why you say is a gaseous phase? And in this gas phase we have some best behaved thermodynamic considerations.

So, a gas is considered as to be a well - behaved thermodynamic substance that is because the ratio of pressure of the gas p to the triple point pressure approaches to a value which is independent on the nature of the gas when p or triple point pressure approaches to 0; that means, when you go to zero pressure all of them behave in a similar manner. And then the limiting value of this ratio when it is multiplied by 273.16 defines the temperature at that pressure and normally we call this as a ideal gas temperatures.

This ideal gas temperature word we have been using most frequently starting from the second law of thermodynamics and of course, to some extent third law of thermodynamics when the temperature reaches to absolute 0. So, under those circumstances an interesting phenomena happens and it has been an experimental evidence that when p tends to zero the product of pv approaches to same value for all gases at that same temperatures. So, most important thing here we will be talking about molar analysis.

$$\lim_{p \to 0} \quad (p\bar{v}) = A = \begin{cases} \text{function of temperature only} \\ \text{independent on nature of the gas} \end{cases}$$

So, where $\bar{v}$ is nothing but your molar specific volume that is v/n, n stands for number of moles and when you do this molar analysis. So, instead of R which is characteristics gas constant we should be using universal gas constant $\bar{R}$ and its value is 8.3144 /mol-K. Now, to have this understanding so at constant volume $T = (273.16K) \lim_{p_{TP} \to 0} \quad \left(\frac{p}{p_{TP}}\right)$.

Now, after simplifying this we can get an important relations $\lim(p\bar{v}) = \bar{R}T$ or in other words $\lim(pV) = n\bar{R}T$. This relation is very vital for the all the subsequent analysis in for the consideration of equation of state.

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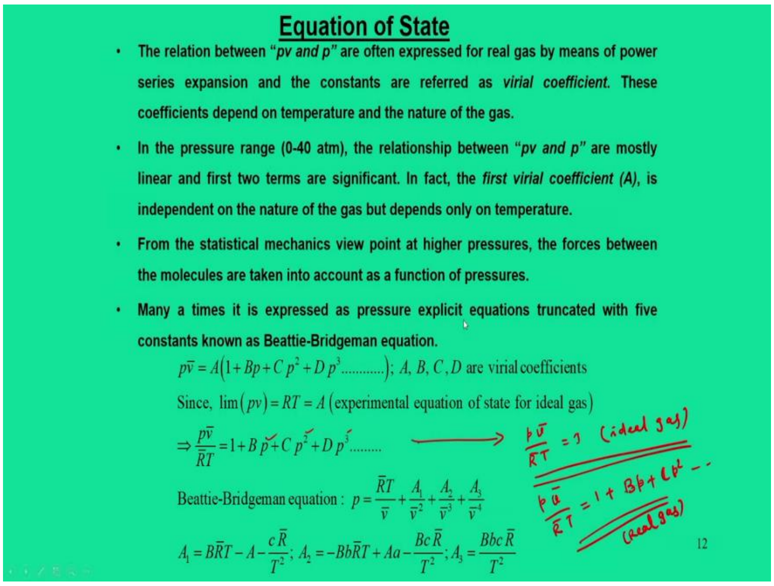

Equation of State

- The relation between "*pv and p*" are often expressed for real gas by means of power series expansion and the constants are referred as *virial coefficient.* These coefficients depend on temperature and the nature of the gas.
- In the pressure range (0-40 atm), the relationship between "*pv and p*" are mostly linear and first two terms are significant. In fact, the *first virial coefficient (A)*, is independent on the nature of the gas but depends only on temperature.
- From the statistical mechanics view point at higher pressures, the forces between the molecules are taken into account as a function of pressures.
- Many a times it is expressed as pressure explicit equations truncated with five constants known as Beattie-Bridgeman equation.

$p\bar{v} = A\left(1 + Bp + Cp^2 + Dp^3 \ldots\ldots\ldots\right)$; A, B, C, D are virial coefficients

Since, $\lim(pv) = RT = A$ (experimental equation of state for ideal gas)

$$\Rightarrow \frac{p\bar{v}}{\bar{R}T} = 1 + B\cancel{p} + C\cancel{p^2} + D\cancel{p^3} \ldots\ldots\ldots \longrightarrow \frac{p\bar{v}}{\bar{R}T} = 1 \text{ (ideal gas)}$$

$$\frac{p\bar{v}}{\bar{R}T} = 1 + Bp + Cp^2 - - \text{ (real gas)}$$

Beattie-Bridgeman equation : $p = \frac{\bar{R}T}{\bar{v}} + \frac{A_1}{\bar{v}^2} + \frac{A_2}{\bar{v}^3} + \frac{A_3}{\bar{v}^4}$

$A_1 = B\bar{R}T - A - \frac{c\bar{R}}{T^2}$; $A_2 = -Bb\bar{R}T + Aa - \frac{Bc\bar{R}}{T^2}$; $A_3 = \frac{Bbc\bar{R}}{T^2}$

Then moving further the relation between pv and p that is pressure multiplied volume and p if they are taken as independent entity, they are often expressed for real gas by means of power series expansions. Now before the equation of state is framed people used to represent this $p\bar{v} = A(1 + Bp + Cp^2 + Dp^3 \ldots\ldots\ldots\ldots)$ where A, B, C, D they are considered as virial coefficients, this is how the mathematical way of representing the equation of state.

Then after considering this experimental evidence then the revised form of the equations in the form of real coefficients is represented as $\frac{p\bar{v}}{\bar{R}T} = 1 + Bp + Cp^2 + Dp^3 \ldots\ldots\ldots$ So, what people have said that from these equations it was said when $\frac{p\bar{v}}{\bar{R}T} = 1$, it was said it to be ideal gas means ideal gas model will be followed like this and for all other situations now when it is a function of pressure then it becomes a real gas model.

So; that means, $\frac{p\bar{v}}{\bar{R}T} = 1 + Bp + Cp^2$. So, all these things when it comes it becomes a real gas model. So, this was the time when the state equations were defined through this concept of virial coefficients. Here if you look at this equation this particular parameter $\frac{p\bar{v}}{\bar{R}T}$ was considered as a function of pressure.

The other equations they consider like one Beattie - Bridgeman equations they consider instead of p, they represent this state equations in the form of T and v where both T and $\bar{v}$ becomes the parameter in the right hand side. And accordingly the virial coefficients were determined. So, it all depends whether we consider it as a pressure expression or not.

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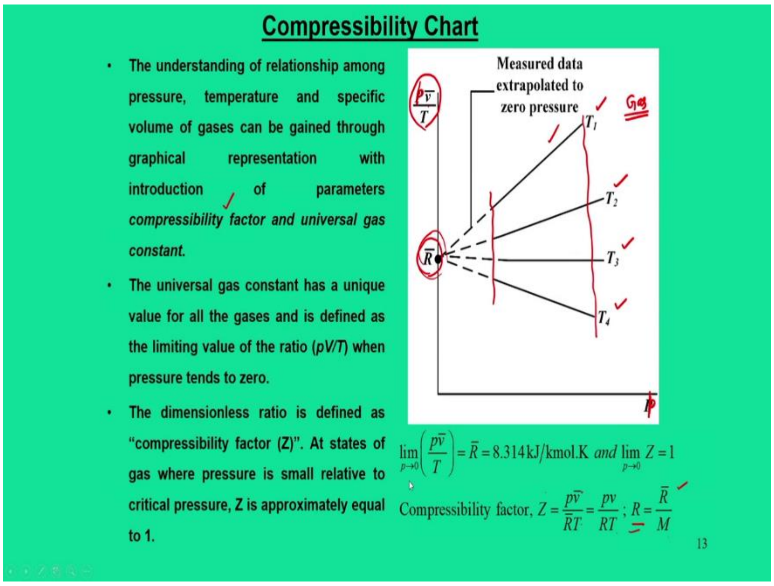

Compressibility Chart

- The understanding of relationship among pressure, temperature and specific volume of gases can be gained through graphical representation with introduction of parameters *compressibility factor and universal gas constant.*
- The universal gas constant has a unique value for all the gases and is defined as the limiting value of the ratio (pV/T) when pressure tends to zero.
- The dimensionless ratio is defined as "compressibility factor (Z)". At states of gas where pressure is small relative to critical pressure, Z is approximately equal to 1.

$\lim_{p\to 0}\left(\frac{p\bar{v}}{T}\right) = \bar{R} = 8.314\,\text{kJ/kmol.K}$ *and* $\lim_{p\to 0} Z = 1$

Compressibility factor, $Z = \frac{p\bar{v}}{\bar{R}T} = \frac{pv}{RT}$; $R = \frac{\bar{R}}{M}$

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Then moving further, when you deal with the state equations there are lot of mathematically complicacy while analyzing the data. So, what the concept that has been developed and we are going to study now is the compressibility charts. Let us represent all the data in a graphical manner. So, what this graph shows is that and of course, this compressibility chart is defined as experimental evidence for the all the gases.

To start with; what was done is that we take two parameters one is $\left(\frac{p\bar{v}}{T}\right)$ and here $\bar{v}$ is your molar specific volume and another parameter was considered as p. Now, for a given gas at temperature T_1 we can plot these values; that means, we find p, corresponding this number, $\frac{p\bar{v}}{T}$ at a given T_1, we can get the first graph.

And the second graph also was taken at temperature T_2, the third T_3 and T_4 and this is done for a particular gas. One interesting point is that now based on the data which are available to us, when they are plotted after experiment, we get a set of data may be I can say this domain of the data which are available to us is in this dome.

Now, by plotting them and you extrapolate it further, interesting fact is that it intersects the y axis that is $\frac{p\bar{v}}{T}$ axis at one point and normally what we call this $\bar{R}$; that means, you can say limiting values of $\frac{p\bar{v}}{T}$ is nothing but your $\bar{R}$. So, this is what the significance of the universal gas constant. So, people have said is that this is nothing but your universal gas constant, then it was realized whether it is true for all the gases or not so; that means, similar plots also can be generated for different gases.

So, it happens in the situation that there are lot of gases, there are lot of pure substance, many gases are there. So, in such cases instead of putting this particular graph for different gases people have used the concept of non - dimensionalizing gas. So, with this philosophy we represent this graphical concept as compressibility chart.

So, the understanding of relationship among pressure temperature and specific volume of the gas is represented through a parameter first one is the compressibility factor which we are going to introduce $Z = \frac{p\bar{v}}{\bar{R}T} = \frac{pv}{RT}; R = \frac{\bar{R}}{M}$ and R is your gas constant, $\bar{R}$ is your universal gas constant which is nothing but this particular graphical number, limiting value of $\frac{p\bar{v}}{T}$.

So, this universal gas constant has a unique value for all gases and it is defined as the limiting value of $\frac{p\bar{v}}{T}$when the pressure tends to 0. Dimensional ratio which is known as compressibility factor at states of gas where the pressure is small relative to the critical pressure the Z value is close to 1. That means, if Z is equal to 1 we can say $p\bar{v} = \bar{R}T$, but in many situation it is not true and we call them is that it is a real gas model.

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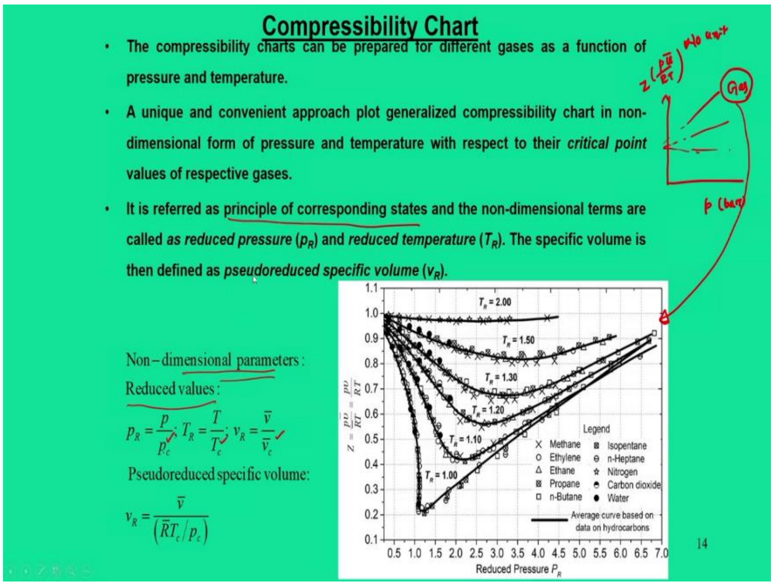

Compressibility Chart

- The compressibility charts can be prepared for different gases as a function of pressure and temperature.
- A unique and convenient approach plot generalized compressibility chart in non-dimensional form of pressure and temperature with respect to their *critical point* values of respective gases.
- It is referred as principle of corresponding states and the non-dimensional terms are called *as reduced pressure* (p_R) and *reduced temperature* (T_R). The specific volume is then defined as *pseudoreduced specific volume* (v_R).

Non – dimensional parameters :

Reduced values :

$$p_R = \frac{p}{p_c};\ T_R = \frac{T}{T_c};\ v_R = \frac{\bar{v}}{\bar{v}_c}$$

Pseudoreduced specific volume:

$$v_R = \frac{\bar{v}}{\left(\bar{R}T_c/p_c\right)}$$

So, entire idea to represent this graphical method into a non-dimensional form is the concept of principle of corresponding states. So, what I can say that if I plot Z versus pressure which was shown graphically it is true for one particular gases, but when you do this we call this as a compressibility chart for that particular gas. Now, we are going to frame a generalized compressibility chart and which is true for all the gases now to do that a non-dimensional parameters were introduced and we call this as a reduced value.

For example, we introduce the terms critical pressure p_c, critical temperature T_c and critical molar specific volume $\bar{v}_c$. Now, for each gas these numbers are unique and the actual pressure value p when it is divided by to their critical numbers it becomes a non-dimensional number which is called as a reduced pressure. So, in your in our previous analysis when this plot was done when you have pressure p and z which is nothing, but p$\frac{p\bar{v}}{\bar{R}T}$.

So, if you see this was unit less, no unit and this has some unit pressure means it is either bar or Newton per meter square and these data were taken for a given gas. So, this concept was changed with respect to this particular figure where this p is replaced with a reduced pressure p_R and this reduced pressure, for a particular gas by normalizing p with respect to its critical pressure and y axis remains what we say Z. So, likewise for different gases one can have a set of data involving and that data we can get it for different temperature ratios.

So; that means, if you look at one particular temperature let us say T_R of 1.2 then on this T_R of 1.2, we have data for methane, ethylene, ethane, propane or nitrogen, oxygen all sorts of things. So, this particular curve talks about only for T_R is equal to 1.2 and it is true for all these gases. So, this behaviour of all the gases was considered as an advantage and that is the reason we call as a well behaved, they are well behaved at reduced values.

And here another term I need to emphasize here that pseudo reduced specific volume, normally the idea is that when you see this data, the data are represented in the form of press p_R and T_R, but to calculate this corresponding v_R because they are calculated based on the critical value of the substance. But v_R was calculated based on the molar specific volume which is already there and its critical pressure and temperature. So, that is what a different name was assigned what is called as pseudo reduced specific volume.

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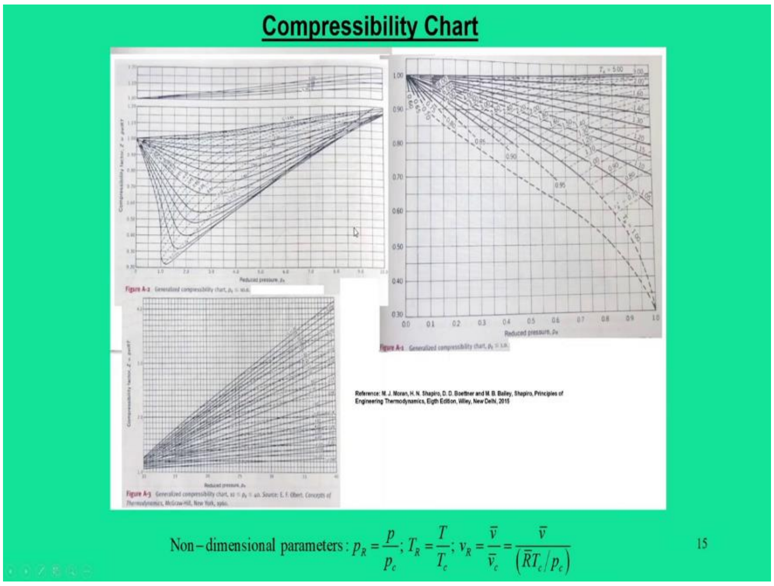

Compressibility Chart

Figure A-2 Generalized compressibility chart, $p_R \le 10.0$.

Figure A-1 Generalized compressibility chart, $p_R \le 1.0$.

Figure A-3 Generalized compressibility chart, $10 \le p_R \le 40$. Source: E. F. Obert, Concepts of Thermodynamics, McGraw-Hill, New York, 1960.

Reference: M. J. Moran, H. N. Shapiro, D. D. Boettner and M. B. Bailey, Shapiro, Principles of Engineering Thermodynamics, Eigth Edition, Wiley, New Delhi, 2015

$$\text{Non-dimensional parameters}: p_R = \frac{p}{p_c};\ T_R = \frac{T}{T_c};\ v_R = \frac{\bar{v}}{\bar{v}_c} = \frac{\bar{v}}{\left(\bar{R}T_c/p_c\right)}$$

By doing things a realistic model what we call as a compressibility chart is available in many books and I have taken the extract from this book Moran and Shapiro which talks about this compressibility chart in which the reduced pressure and Z was plotted at different T_R. And of course, in different p_R regime like this particular figure talks about $p_R < 1$, this particular figure talks about $p_R < 10$ and any things which is less than 40 between 10 and 40 it is plotted in this manner.

So, basically speaking that having knowing the value of p_R, T_R one can directly refer this compressibility chart to find Z or knowing Z and p_R we can find T_R. So, likewise and this is true for all the gases and this concept we call this as a compressibility chart.

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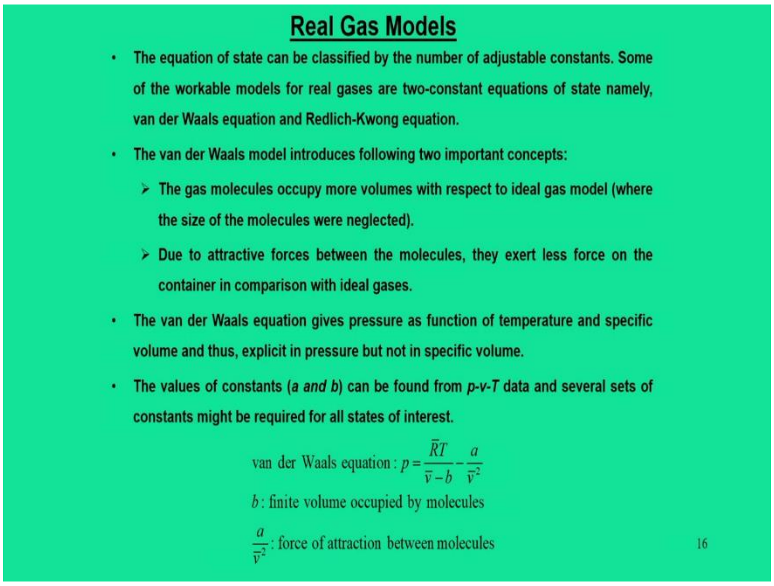

Real Gas Models

- The equation of state can be classified by the number of adjustable constants. Some of the workable models for real gases are two-constant equations of state namely, van der Waals equation and Redlich-Kwong equation.
- The van der Waals model introduces following two important concepts:
  - ➢ The gas molecules occupy more volumes with respect to ideal gas model (where the size of the molecules were neglected).
  - ➢ Due to attractive forces between the molecules, they exert less force on the container in comparison with ideal gases.
- The van der Waals equation gives pressure as function of temperature and specific volume and thus, explicit in pressure but not in specific volume.
- The values of constants (*a and b*) can be found from *p-v-T* data and several sets of constants might be required for all states of interest.

van der Waals equation : $p = \frac{\bar{R}T}{\bar{v} - b} - \frac{a}{\bar{v}^2}$

b : finite volume occupied by molecules

$\frac{a}{\bar{v}^2}$: force of attraction between molecules

Now, moving further we are now going to discuss some of the real gas model. So, till this point of time the representation was done in a graphical manner and through a compressibility chart. But here many a times people are comfortable in writing in the form of equations and we call this as a real gas model. And out of these two real gas models there are two important workable models means widely used models and they involve two constant equations like in a virial equation state there are multiple number of constants a,b,c,d like this.

But most widely used are two constant equation model, one is van der Waals gas equation, other is Redlich- Kwong equations. So, we will emphasize only these two gas equations. Now, the first one is the van der Waal gas model and in fact, we all aware of this model that when this model was introduced as a real gas model, necessary justification was made that the gas molecules occupy more volume with respect to ideal gas model where now in the ideal gas model the size of the molecules were neglected.

But in the van der Waal gas model the size of the molecules were taken into account. So, as a result the effective volume is reduced, but what happens due to attractive forces between the molecules, they exert lesser force in comparison with respect to ideal gas means the gas molecules exert less force on the container of the gas or maybe the walls of the surface in which they are contained because the force of attraction between the gas molecules.

So, a mathematical form of van der Waals equation involves by considering these two effects is $p = \frac{\bar{R}T}{\bar{v}-b} - \frac{a}{\bar{v}^2}$. So, here if you look at this equation, the parameter b takes care about the finite volume occupied by the molecules and the parameter $\frac{a}{\bar{v}^2}$ talks about the pressure value which was supposed to be for ideal gas which is higher gets reduced by an amount by $\frac{a}{\bar{v}^2}$ and here also the constants that are appearing in this equation that is a and b must be found out from the p-v-T data.

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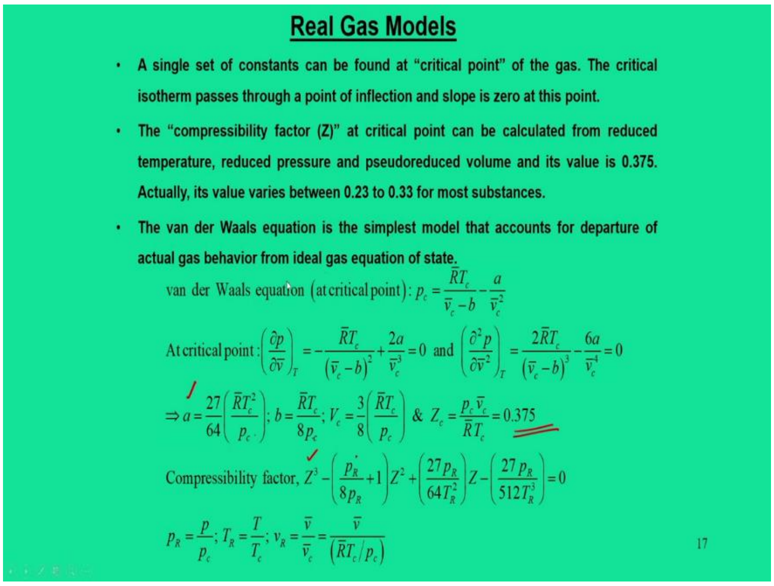

Real Gas Models

- A single set of constants can be found at "critical point" of the gas. The critical isotherm passes through a point of inflection and slope is zero at this point.
- The "compressibility factor (Z)" at critical point can be calculated from reduced temperature, reduced pressure and pseudoreduced volume and its value is 0.375. Actually, its value varies between 0.23 to 0.33 for most substances.
- The van der Waals equation is the simplest model that accounts for departure of actual gas behavior from ideal gas equation of state.

van der Waals equation (at critical point): $p_c = \frac{\bar{R}T_c}{\bar{v}_c - b} - \frac{a}{\bar{v}_c^2}$

At critical point: $\left(\frac{\partial p}{\partial \bar{v}}\right)_T = -\frac{\bar{R}T_c}{(\bar{v}_c - b)^2} + \frac{2a}{\bar{v}_c^3} = 0$ and $\left(\frac{\partial^2 p}{\partial \bar{v}^2}\right)_T = \frac{2\bar{R}T_c}{(\bar{v}_c - b)^3} - \frac{6a}{\bar{v}_c^4} = 0$

$\Rightarrow a = \frac{27}{64}\left(\frac{\bar{R}T_c^2}{p_c}\right); b = \frac{\bar{R}T_c}{8p_c}; V_c = \frac{3}{8}\left(\frac{\bar{R}T_c}{p_c}\right)$ & $Z_c = \frac{p_c \bar{v}_c}{\bar{R}T_c} = 0.375$

Compressibility factor, $Z^3 - \left(\frac{p_R}{8p_R} + 1\right)Z^2 + \left(\frac{27p_R}{64T_R^2}\right)Z - \left(\frac{27p_R}{512T_R^3}\right) = 0$

$p_R = \frac{p}{p_c}; T_R = \frac{T}{T_c}; v_R = \frac{\bar{v}}{\bar{v}_c} = \frac{\bar{v}}{(\bar{R}T_c/p_c)}$

Now, how do you find out the data for a real gas model and in particular for van der Waal equations? So, the set of single constants; that means how do you find out this value of a,b,c and then we are going to put them. So, to do that one way to look at is that we write this equation that is van der Waal equation at the critical point as $p_c = \frac{\bar{R}T_c}{\bar{v}_c - b} - \frac{a}{\bar{v}_c^2}$.

Now, at the "critical point" important phenomena that happens that is $\left(\frac{\partial p}{\partial \bar{v}}\right)_T = -\frac{\bar{R}T_c}{(\bar{v}_c - b)^2} + \frac{2a}{\bar{v}_c^3} = 0 \; and \; \left(\frac{\partial^2 p}{\partial \bar{v}^2}\right)_T = \frac{2\bar{R}T_c}{(\bar{v}_c - b)^3} - \frac{6a}{\bar{v}_c^4} = 0$.

So, at critical point the differentiation of these two equations will give you the constant values $a = \frac{27}{64}\left(\frac{\bar{R}T_c^2}{p_c}\right); b = \frac{\bar{R}T_c}{8p_c}; V_c = \frac{3}{8}\left(\frac{\bar{R}T_c}{p_c}\right) \& Z_c = \frac{p_c\bar{v}_c}{\bar{R}T_c} = 0.375$.

So, this is the consequence that we get from this van der Waal's gas equations to get this constant term. Now, putting these equations one can also find out the compressibility factor equations which is in the cubical form $Z^3 - \left(\frac{p_R}{8p_R} + 1\right)Z^2 + \left(\frac{27p_R}{64T_R^2}\right)Z - \left(\frac{27p_R}{512T_R^3}\right) = 0$. So, this is how the van der Waal's equations is modelled which considered as a real gas model and in fact, when you compare it with your actual model or behaviour it sees that van der Waal equation is the simplest model that accounts the departure of an ideal gas behaviour for an actual gas.

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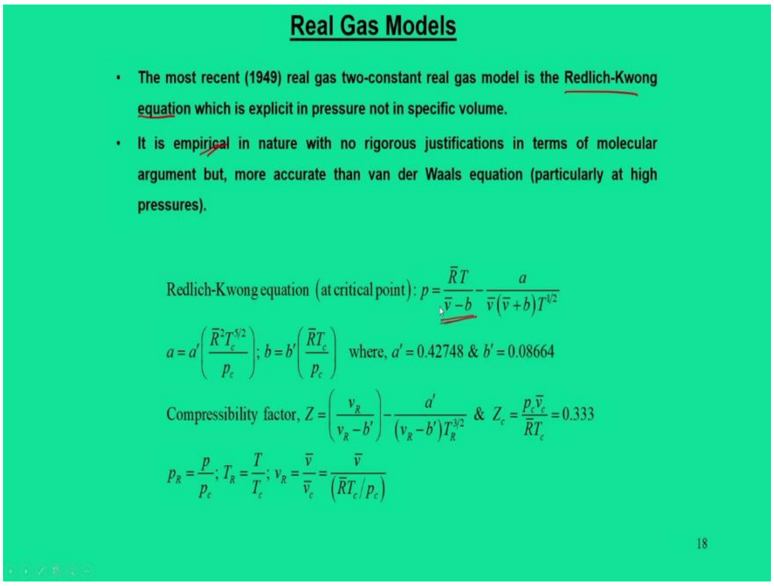

Real Gas Models

- The most recent (1949) real gas two-constant real gas model is the Redlich-Kwong equation which is explicit in pressure not in specific volume.
- It is empirical in nature with no rigorous justifications in terms of molecular argument but, more accurate than van der Waals equation (particularly at high pressures).

Redlich-Kwong equation (at critical point): $p = \frac{\bar{R}T}{\bar{v} - b} - \frac{a}{\bar{v}(\bar{v}+b)T^{1/2}}$

$a = a'\left(\frac{\bar{R}^2T_c^{5/2}}{p_c}\right); b = b'\left(\frac{\bar{R}T_c}{p_c}\right)$ where, $a' = 0.42748$ & $b' = 0.08664$

Compressibility factor, $Z = \left(\frac{v_R}{v_R - b'}\right) - \frac{a'}{(v_R - b')T_R^{3/2}}$ & $Z_c = \frac{p_c\bar{v}_c}{\bar{R}T_c} = 0.333$

$p_R = \frac{p}{p_c}; T_R = \frac{T}{T_c}; v_R = \frac{\bar{v}}{\bar{v}_c} = \frac{\bar{v}}{(\bar{R}T_c/p_c)}$

And the other model which is the most recent model and that is in the 1949. So, it is a real gas two-constant equations and it is known as Redlich - Kwong equation and this equation is explicit in pressure not in the specific volume. And in fact, the van der Waal while framing, necessary justification was done in terms of volume, in terms of force, but what has been done is that Redlich - Kwong equation, it is a empirical in nature.

And the equations were done such that there is no necessary justification could have been made why these numbers were taken into account. But; however, it has been proven that it is a better or accurate than the van der Waal equations particularly at high pressures; that means, at high pressures the inaccuracy of van der Waal equations becomes significant.

So, during that point of time Redlich- Kwong equation was used and this particular equation is $p = \frac{\bar{R}T}{\bar{v}-b} - \frac{a}{\bar{v}(\bar{v}+b)T^{\frac{1}{2}}}$.

And with these things other compressibility factor equations were derived. So, we are not going to get into these details. Here I have just written these values of course, these are not of interest for us rather we are only concentrating only these equations.

$$Z = \left(\frac{v_R}{v_R - b'}\right) - \frac{a'}{(v_R - b')T_R^{\frac{3}{2}}} \;\&\; Z_c = \frac{p_c \bar{v}_c}{\bar{R}T_c} = 0.333$$

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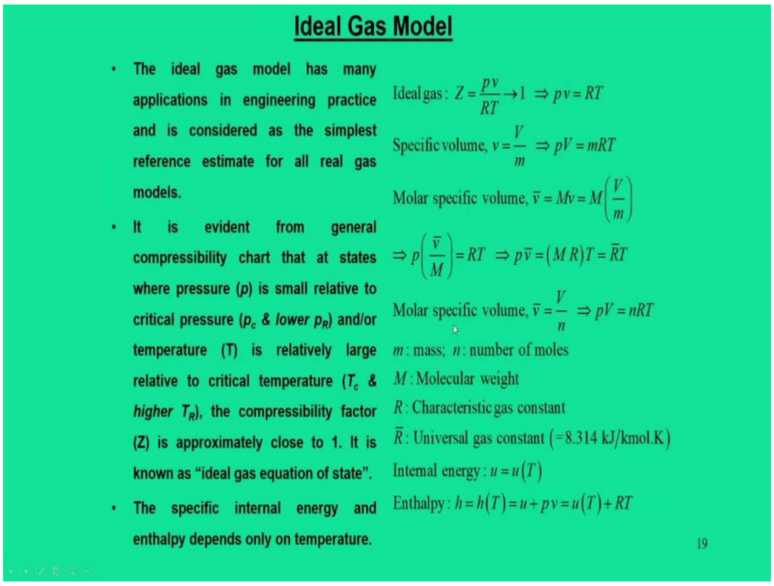

Ideal Gas Model

- The ideal gas model has many applications in engineering practice and is considered as the simplest reference estimate for all real gas models.
- It is evident from general compressibility chart that at states where pressure (p) is small relative to critical pressure (p_c & *lower* p_R) and/or temperature (T) is relatively large relative to critical temperature (T_c & *higher* T_R), the compressibility factor (Z) is approximately close to 1. It is known as "ideal gas equation of state".
- The specific internal energy and enthalpy depends only on temperature.

Ideal gas: $Z = \frac{pv}{RT} \to 1 \Rightarrow pv = RT$

Specific volume, $v = \frac{V}{m} \Rightarrow pV = mRT$

Molar specific volume, $\bar{v} = Mv = M\left(\frac{V}{m}\right)$

$\Rightarrow p\left(\frac{\bar{v}}{M}\right) = RT \Rightarrow p\bar{v} = (MR)T = \bar{R}T$

Molar specific volume, $\bar{v} = \frac{V}{n} \Rightarrow pV = nRT$

m: mass; n: number of moles

M: Molecular weight

R: Characteristic gas constant

$\bar{R}$: Universal gas constant (=8.314 kJ/kmol.K)

Internal energy: $u = u(T)$

Enthalpy: $h = h(T) = u + pv = u(T) + RT$

Now, apart from giving all these explanations for compressibility chart, real gas model, p-v-T surface the one best thing that remains is that we have to use this ideal gas model. And this ideal gas model is the benchmark or reference level, now why I should go for real gas model. If an ideal gas model can predict accurately or without going into mathematical complications it is better that we should go for the ideal gas model and till this point of time we have been following this ideal gas model.

And just to summarize in fact, we all are used to this ideal gas model, just to summarize when you use this ideal gas model we first thing we say $Z = \frac{pv}{RT} \to 1$ and the here while using this equations we consider molar specific volume $v = \frac{V}{m}$ where we say $p\left(\frac{\bar{v}}{M}\right) = RT$.

Other way of looking at is that instead of specific volume we use the molar specific volume where we are introducing the molecular weight of the substance.

Then based on this molar specific volume we can write $p\bar{v} = (MR)T = \bar{R}T$ and of course, molar specific volume is defined by $\bar{v} = \frac{V}{n} \Rightarrow pV = nRT$. So, one equation is $pV = mRT$, other equation is $pV = nRT$. And apart from this we also say that for an ideal gas, the internal energy is a function of temperature only in fact, we have already proved this through our thermodynamic relations enthalpy is also function of temperature.

Because enthalpy consists of $u + pv$ already u is a function of temperature, but pv is also function of RT for an ideal gas. So, because of this reason enthalpy is also function of temperature only. And one other point that I need to emphasize that general compressibility chart that at states pressure p relative to critical pressure or lower pressure and temperature T allows us that the compressibility factor becomes close to 1 and we call this as a ideal gas equation of state.

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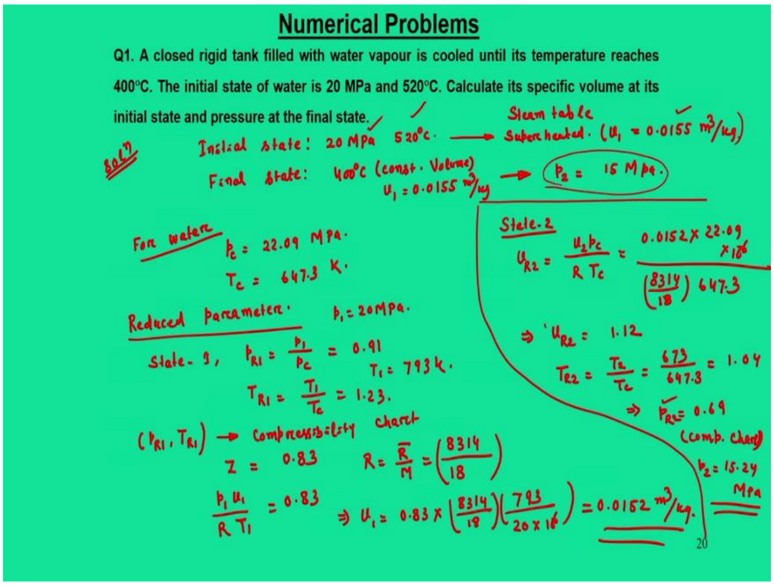

Numerical Problems

Q1. A closed rigid tank filled with water vapour is cooled until its temperature reaches 400°C. The initial state of water is 20 MPa and 520°C. Calculate its specific volume at its initial state and pressure at the final state.

Soln

Initial state: 20 MPa 520°C $\longrightarrow$ Steam table Superheated. ($v_1 = 0.0155\ m^3/kg$)

Final state: 400°C (const. Volume) $v_1 = 0.0155\ m^3/kg$ $\rightarrow$ $\boxed{p_2 = 15\ MPa.}$

For water $p_c = 22.09$ MPa. $T_c = 647.3$ K.

Reduced parameter. $p_1 = 20$ MPa.

State-1, $p_{R1} = \frac{p_1}{p_c} = 0.91$ $T_1 = 793$ K.

$T_{R1} = \frac{T_1}{T_c} = 1.23$.

$(p_{R1}, T_{R1}) \rightarrow$ Compressibility chart

$Z = 0.83$ $R = \frac{\bar{R}}{M} = \left(\frac{8314}{18}\right)$

$\frac{p_1 v_1}{R T_1} = 0.83$ $\Rightarrow v_1 = 0.83 \times \left(\frac{8314}{18}\right)\left(\frac{793}{20 \times 10^6}\right) = 0.0152\ m^3/kg.$

State-2

$v_{R2} = \frac{v_2 p_c}{R T_c} = \frac{0.0152 \times 22.09 \times 10^6}{\left(\frac{8314}{18}\right) 647.3}$

$\Rightarrow v_{R2} = 1.12$

$T_{R2} = \frac{T_2}{T_c} = \frac{673}{647.3} = 1.04$

$\Rightarrow p_{R2} = 0.69$ (comp. chart)

$p_2 = 15.24$ MPa

So, with this I come to the end of this particular lecture, now we will try to solve 1 or 2 important problems based on our understanding about this lecture. The first problem talks about the rigid tank contains water vapour and this water vapour is cooled until the temperature reaches to 400 C, the initial state of water is given as 20 MPa and 520 C. So, we need to find out the specific volume at its initial state and the pressure at the final state.

So, as you see in this figure it is very easy that one can use this steam table data to find the thermodynamic states. So, here we are trying to emphasize that how this particular problem, we are going to solve by using the concept of compressibility chart or by knowing the critical point or critical temperature and pressure of water vapour.

So, to start with what data has been given us we have this initial state, final state is 400 C and since it is a closed rigid tank there is no change in the volume. So, it is a constant volume process. So, from the steam table, for this initial state we can refer superheated region and that super region we can find its specific volume $v_1 = 0.0155\, m^3/kg.$

Now, at same constant volume that is at temperature 400 C, it will also give the final pressure $p_2 = 15\, MPa.$ So, this data is based on the steam table data, but our job is not with respect to using steam table rather you have to use the concept of critical parameters. So, by critical parameters means, for water if you require any thermodynamic data book we can find $p_c = 22.09\, MPa, T_c = 647.3\, K.$

Now, we have to find the reduced parameter $p_{R1} = \frac{p_1}{p_c} = 0.91; T_{R1} = \frac{T_1}{T_c} = 1.23.$ So, we have state coordinates.

So, this we have to apply it for generalized compressibility chart and this will give you the value $Z = 0.83.$ And $Z = \frac{p_1 v_1}{RT_1}; R = \frac{\bar{R}}{M} = \frac{8314}{18}$

$$v_1 = 0.83 \times \left(\frac{8314}{18}\right)\left(\frac{793}{20 \times 10^6}\right) = 0.0152\, m^3/kg$$

Whereas our steam table data was $0.015\, m^3/kg.$ Now, for state 2 we can follow the similar process, but here the process was a constant volume process. So, you do not have data for pressure. So, you have to rely on the reduced volume parameter

$$v_R = \frac{v_2 p_c}{RT_c} = \frac{0.0152 \times 22.09 \times 10^6}{\frac{8314}{18} \times 647.3} = 1.12;\ \ T_{R2} = \frac{T_2}{T_c} = 1.04 \Rightarrow p_{R2}$$
$$= 0.69\ (From\ chart) \Rightarrow p_2 = 15.24\, MPa$$

So, state 2 is 15.24 mega pascal, but the steam table data was given as 15 mega pascal. So, of course, there is a relative accuracy while considering these two models.

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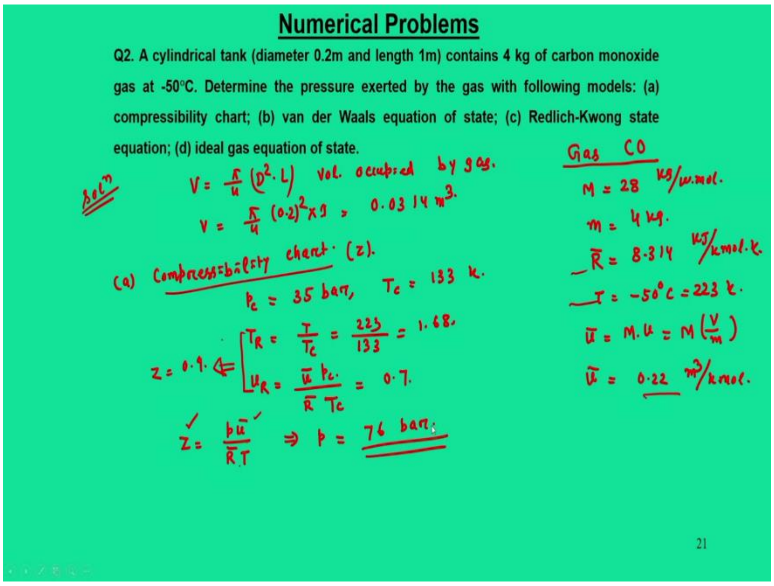

Numerical Problems

Q2. A cylindrical tank (diameter 0.2m and length 1m) contains 4 kg of carbon monoxide gas at -50°C. Determine the pressure exerted by the gas with following models: (a) compressibility chart; (b) van der Waals equation of state; (c) Redlich-Kwong state equation; (d) ideal gas equation of state.

Sol^n

$V = \frac{\pi}{4}(D^2 \cdot L)$ vol. occupied by gas.

$V = \frac{\pi}{4}(0.2)^2 \times 1 = 0.0314\ m^3.$

(a) Compressibility chart. (z).

$p_c = 35$ bar, $T_c = 133$ K.

$$z = 0.9 \Leftarrow \left[\begin{array}{l} T_R = \frac{T}{T_c} = \frac{223}{133} = 1.68. \\ v_R = \frac{\bar{v}\, p_c}{\bar{R}\, T_c} = 0.7. \end{array}\right.$$

$Z = \frac{p\bar{v}}{\bar{R}T} \Rightarrow p = \underline{\underline{76 \text{ bar}}}$

Gas CO

$M = 28$ kg/k.mol.

$m = 4$ kg.

$\bar{R} = 8.314$ kJ/kmol.K.

$T = -50°C = 223$ K.

$\bar{v} = M.v = M\left(\frac{V}{m}\right)$

$\bar{v} = \underline{0.22}\ m^3/kmol.$

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And the next problem that we are going to solve about the consistency of equation of states what we have data is that. We have a cylindrical tank whose dimension is given 0.2 m diameter and 1 m length. It consists of 4 kg of carbon monoxide at -50 C. Now, we need to find out the pressure exerted by the gas models, we also know that there are many methods are available we can use it in the compressibility chart, we can use van der Waal equations, we can use ideal gas equation, we can use Redlich - Kwong state equations.

Now, let us see that in each of these methods what is the accuracy level or what is the value that we are going to get? So, the data that given is $V = \frac{\pi}{4}D^2L = 0.0314\, m^3$. Now, we have this gas which is given as CO carbon monoxide. So, for which we have this molecular weight 28 kg/kmol and this mass is given as 4 kg and we also know R$\bar{R} = 8.314\ k/kmol - K.$

So, first thing data we have to use compressibility chart. So, to do that we need to find Z and to do that we require p_c and that value from the data table for CO is noted as 35 bar, T_c is 133 K.

$$T_R = \frac{T}{T_c} = \frac{223}{133} = 1.68;\ v_R = \frac{\bar{v}\ \ p_c}{\bar{R}T_c}\ where\ \bar{v}\ \ = M\left(\frac{V}{m}\right) = 0.22\frac{m^3}{kmol};\ \Rightarrow v_R = 0.7$$

So, we have this information, using this compressibility chart will give you Z is equal to 0.9.

$$Z = \frac{p\bar{v}}{\bar{R}T} \Rightarrow p = 76\ bar$$

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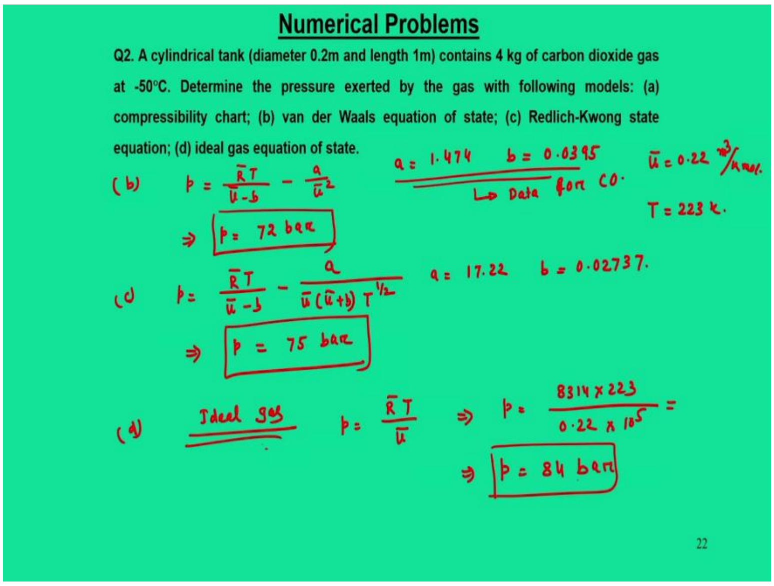

Numerical Problems

Q2. A cylindrical tank (diameter 0.2m and length 1m) contains 4 kg of carbon dioxide gas at -50°C. Determine the pressure exerted by the gas with following models: (a) compressibility chart; (b) van der Waals equation of state; (c) Redlich-Kwong state equation; (d) ideal gas equation of state.

(b) $p = \frac{\bar{R}T}{\bar{v}-b} - \frac{a}{\bar{v}^2}$ $a = 1.474$ $b = 0.0395$ → Data for CO. $\bar{v} = 0.22\ m^3/kmol.$ $T = 223\ K.$

$\Rightarrow \boxed{p = 72\ bar}$

(c) $p = \frac{\bar{R}T}{\bar{v}-b} - \frac{a}{\bar{v}(\bar{v}+b)T^{1/2}}$ $a = 17.22$ $b = 0.02737.$

$\Rightarrow \boxed{p = 75\ bar}$

(d) Ideal gas $p = \frac{\bar{R}T}{\bar{v}} \Rightarrow p = \frac{8314 \times 223}{0.22 \times 10^5} =$

$\Rightarrow \boxed{p = 84\ bar}$

Then we will go to van der Waals equations.

$$p = \frac{\bar{R}T}{\bar{v} - b} - \frac{a}{\bar{v}^2}$$

Now, here $a = 1.474$, $b = 0.0395$. So, these two we have to find from the data from the thermodynamic book for CO and $\bar{v}\ = 0.22\frac{m^3}{kmol}$. So, by inserting this value we can calculate p is 72 bar.

Third one is Redlich- Kwong equations.

$$p = \frac{\bar{R}T}{\bar{v} - b} - \frac{a}{\bar{v}(\bar{v} + b)T^{\frac{1}{2}}}; a = 17.22; b = 0.02737; \Rightarrow p = 75\ bar$$

And last one which is what we call as a simplest one ideal gas and if nothing is given then we must use this gas equations $p = \frac{\bar{R}T}{\bar{v}} = 84\ bar$.

So, as it is clear that ideal gas model always gives the higher pressures and closer to ideal gas model is your Redlich - Kwong model and real gas model through van der Waal equation gives us 72 bar and of course, compressibility chart data give 76 bar which is closer to van der Waals equation. This is how we can say the relative accuracy of predictions while using the real gas concepts. So, with this I conclude this lecture for today.

Thank you for your attention.