Basic Principles and Calculations in Chemical Engineering

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Module – 4: Basic Principles of Compressible System

Lecture – 4.2

State Equation of Non-Ideal Gas and Calculation

Welcome to massive open online course on Basic Principles and Calculations in Chemical Engineering. In module 4, we were discussing something about state question of ideal gas and based on that some calculations, some material balance we have covered. So, under this module 4, basic principles of compressible system, in this lecture, we will try to describe more about that you know state equation, but in this case especially for non-ideal gas state equation and also based on their equations, we will try to do some problems on further calculations.

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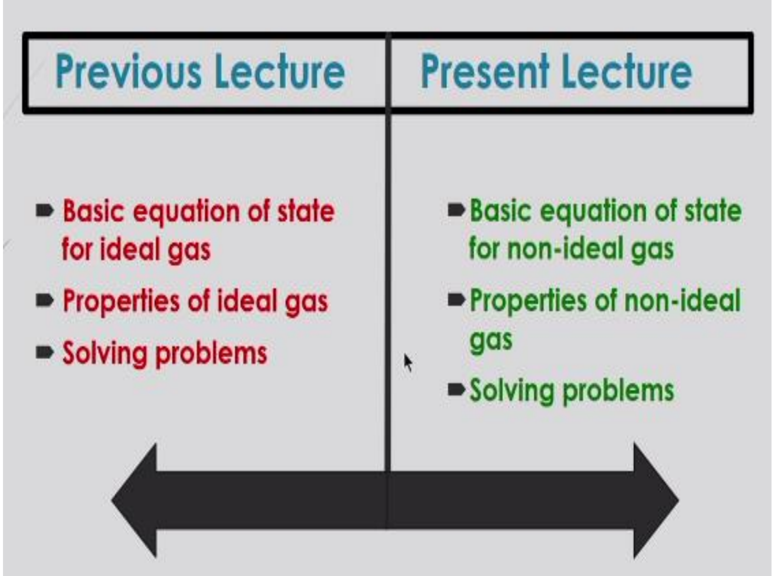

Previous Lecture	Present Lecture
- Basic equation of state for ideal gas - Properties of ideal gas - Solving problems	- Basic equation of state for non-ideal gas - Properties of non-ideal gas - Solving problems

Now, we will describe about that what are the different basic equations of state or non-ideal gas and also how that properties of that non-ideal gas will be changing and how we can solve the problems, we will describe here in this lecture.

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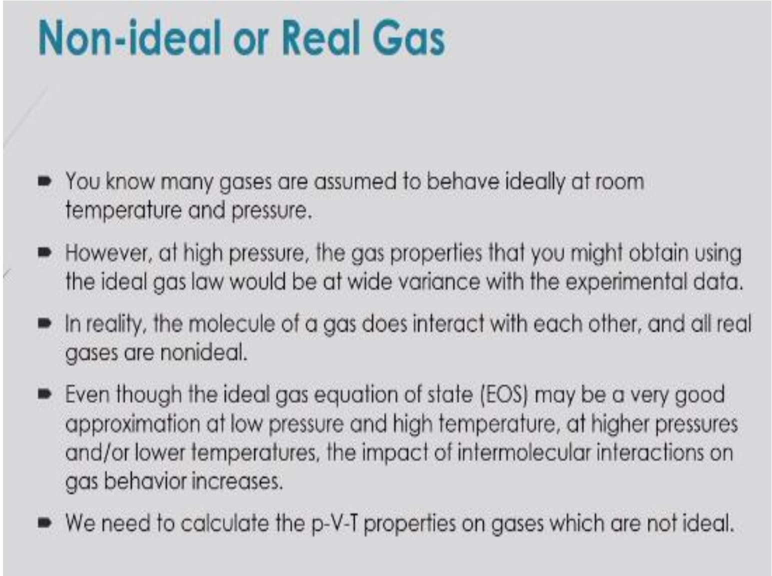

Non-ideal or Real Gas

- You know many gases are assumed to behave ideally at room temperature and pressure.
- However, at high pressure, the gas properties that you might obtain using the ideal gas law would be at wide variance with the experimental data.
- In reality, the molecule of a gas does interact with each other, and all real gases are nonideal.
- Even though the ideal gas equation of state (EOS) may be a very good approximation at low pressure and high temperature, at higher pressures and/or lower temperatures, the impact of intermolecular interactions on gas behavior increases.
- We need to calculate the p-V-T properties on gases which are not ideal.

Now, as you know that of course real gas that will be regarded as non-ideal gas and that many gases are assumed to behave actually ideally at room temperature and pressure that we know. However, at high pressure, the gas properties that you might obtain using the ideal gas law that would be at wide variance with experimental data. So, that means at high pressure and temperature, we can say that we are not actually having that properties of ideal gas here. So, this gas will be behaving at particular conditions differently from that ideal gas.

Here in this case, suppose the behavior will be changing in wide variance as for experimental data because here in this case, the molecule of this real gases or you can say that non-ideal gases does not actually in that state or it will interact with each other and all real gases will be in that case non-ideal. So, in this case in reality, the molecule of a gas does interact with each other and all real gases will be considered as non-ideal, even though the ideal gas equation of state maybe a very good approximation at low pressure and high temperature.

At higher pressure and lower temperatures, the impact of that intermolecular interactions on gas behavior increases there. What does it mean? Here, we will see that we have actually used one ideal gas equation to represent this ideal gas behavior, but in that same direction, if we consider ideal gas equation of state for this calculation of behavior of real gas you will see, there will be some approximated value you can get at low pressure and high pressure for the real gases.

But at higher pressures, we will not get the same value that will be used, you know that differences for these real gases at higher pressure and also you can say that low pressures, low temperatures. So, in that case, the impact of that intermolecular interactions on the gas behavior that will be changed because of this higher pressure and lower temperature and because of what we can say that this ideal gas equation cannot be approximately give the same value at higher pressure or lower pressure

So, in that case, we need to calculate that pressure, volume and temperature properties on gases, which are not actually ideal that also to be considered in the same fashion of that ideal gas equation. So, before going to that, we have to understand that what is the difference of that ideal and the non-ideal gases.

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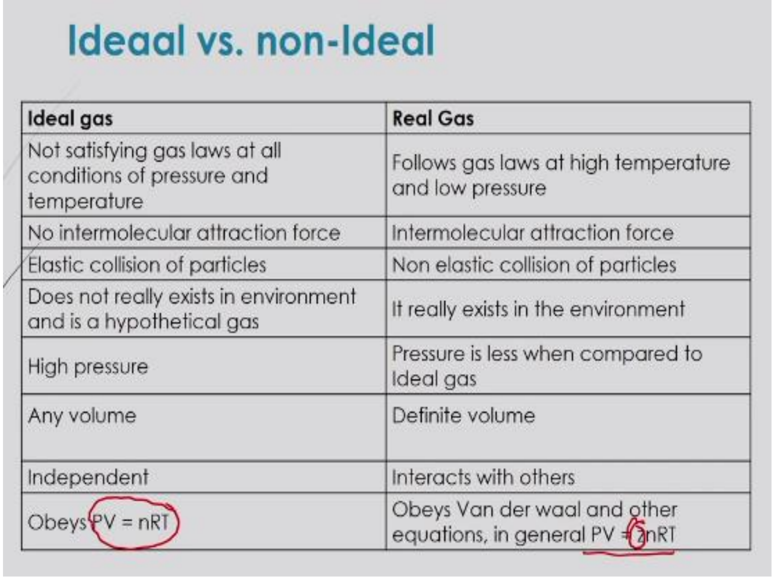

Ideaal vs. non-Ideal

Ideal gas	Real Gas
Not satisfying gas laws at all conditions of pressure and temperature	Follows gas laws at high temperature and low pressure
No intermolecular attraction force	Intermolecular attraction force
Elastic collision of particles	Non elastic collision of particles
Does not really exists in environment and is a hypothetical gas	It really exists in the environment
High pressure	Pressure is less when compared to Ideal gas
Any volume	Definite volume
Independent	Interacts with others
Obeys PV = nRT	Obeys Van der waal and other equations, in general PV = ZnRT

You will see that ideal gases that it will not satisfy the laws of that ideal gas at all conditions of pressure and temperature, whereas that real gas will follow the gas laws at high temperature and low pressure. There will be certain equations where you can use this that real gas behavior by which you can interpret that real gas behavior, and in ideal gases, you will see that no intermolecular attraction force will be there, whereas in real gases that intermolecular attraction force will be there.

In ideal gases, there is elastic collision of the particles whenever it will be moving in a particular temperature and pressure, whereas in real gases, you will not get any elastic collision of the particles during its movement. In ideal gases, you will see that it will not actually really exist in environment and is a hypothetical gas, whereas this real gas does really exist in the environment, whereas as this ideal gas we will see that occupy any volume, whereas real gas will occupy certain or definite volume.

Ideal gas it will be independent, whereas real gas interacts with other. This ideal gas obeys PV is equal to nRT you know ideal gas equation, whereas this real gas will follow some other equations like Van der waal equations and other equations of state and in general you can express that non-ideal equation in the fashion of that ideal equation as PV is equal to znRT, here z is called compressibility factor, whereas in the ideal gas equation you are not having that z factor here, only PV is equal to nRT, but in this real gas we are introducing one compressibility factor to express the general expression of the equation of state.

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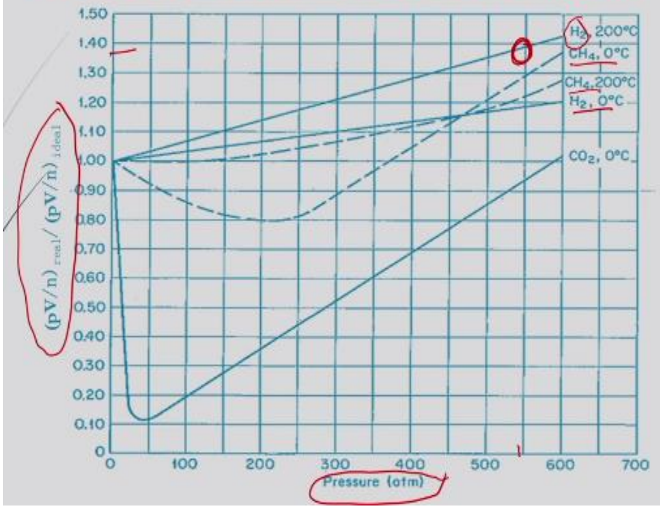
Deviation of real gases from ideal gas at high pressure



Source: D. M. Himmelblau, J. B. Riggs, Basic Principles and Calculations in Chemical Engineering, 7/8th Ed., Prentice Hall of India, 2012.

Here see in this slide one graphical representation as given by Himmelblau in his text book that how that real gases are deviated from the ideal gas at high pressure. You he will see that here this pV by n that means p into you know specific volume, pressure into specific volume of real gas and pressure into specific volume for ideal gas in the y axis whereas in x axis it will be pressure. So, at different pressure how that real gases properties of that product of pressure and specific volume is changing.

So, see that at higher pressure, you will see that these real gases this factor will be higher than that ideal gases here. So, interesting that in this suppose there is a point here, you will see that this point will be almost 1.37 like this. So, at this condition, you will see that at higher pressure more than 500 atmospheric pressure, you will see that this real gases behavior of this pV will be one point almost three seven times of that ideal gases. At a particular temperature is around 200 degree Celsius for hydrogen gases.

So, similarly for other gases also you will see that this ideality or you can say that how it will be deviated at this high pressure and also real gases behavior how it will be magnified at this high pressure for different gases. So, from this graph you can easily calculate what should be that factor here real properties compared to that ideal properties.

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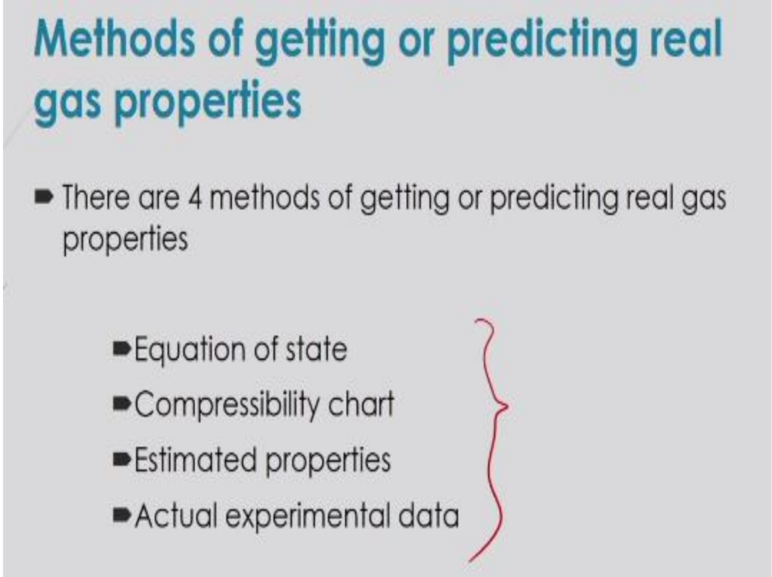

Methods of getting or predicting real gas properties

- There are 4 methods of getting or predicting real gas properties
    - Equation of state
    - Compressibility chart
    - Estimated properties
    - Actual experimental data

Now, in general you will see that there are 4 methods of getting or predicting real gas properties are there. You can predict that you know real gas properties either by equation of state or by compressibility chart or by estimated properties or by actual experimental data. So, either of these 4 methods you can follow to predict or guess or you can say that estimate that non ideal behavior of the gases or real gases behavior by this.

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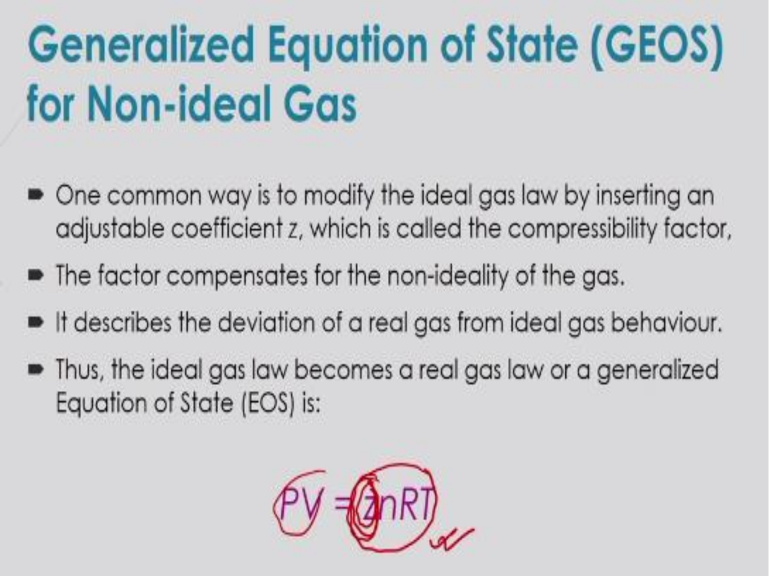

Generalized Equation of State (GEOS) for Non-ideal Gas

- One common way is to modify the ideal gas law by inserting an adjustable coefficient z, which is called the compressibility factor,
- The factor compensates for the non-ideality of the gas.
- It describes the deviation of a real gas from ideal gas behaviour.
- Thus, the ideal gas law becomes a real gas law or a generalized Equation of State (EOS) is:

$$PV = znRT$$

So, let us consider that generalized equation of state by which you can express that non ideality behavior or you can say that real gas equation for expressing its pressure and also volume at a particular temperature. So, one common way is to modify that ideal gas law by inserting some adjustable coefficient that is called z here. So, this z it is called that compressibility factor. Now, from that ideal gas equation that is PV is equal to only nRT, here on the right hand side you will see that we are just multiplying one factor that is z.

It is called adjustable factor which will be actually giving the same fashion of ideal gas equation, and in this case, this z it is called compressibility factor and this compressibility factor you will get from this real gas behavior and based on which you can say what should be the pressure and volume they are based on this compressibility factor and it will give you that corresponding value of PV data for this real gas. So, we are actually expressing the same fashion of that ideal gas equation, here PV is equal to nRT where we are just multiplying one factor z here.

So, that will be is equal to PV is equal znRT. Now, this factor actually compensates for the non-ideality of the gas and it describes of the deviation of a real gas from ideal gas behavior. And also you can say that this ideal gas law whatever you know expressed by this compressibility factor will you know give the generalized form of that equation of state.

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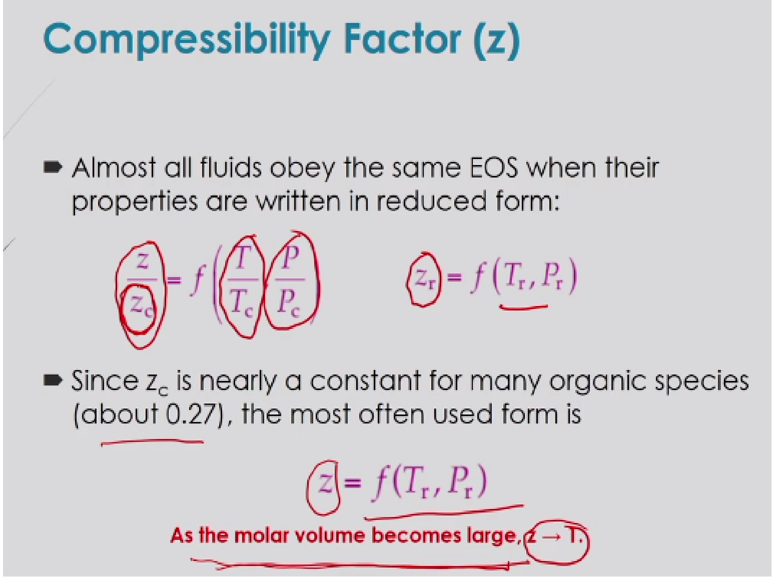

Compressibility Factor (z)

- Almost all fluids obey the same EOS when their properties are written in reduced form:

$$\frac{z}{z_c} = f\left(\frac{T}{T_c}, \frac{P}{P_c}\right) \qquad z_r = f(T_r, P_r)$$

- Since z_c is nearly a constant for many organic species (about 0.27), the most often used form is

$$z = f(T_r, P_r)$$

As the molar volume becomes large, $z \to T$.

Now, based on this generalized form of this equation of state, you will see that there are several real gas equations that is developed by different investigator, different scientists, and there they have suggested different equations for predicting non-ideal behavior of the non-ideal gas or real gas. So, in that case this compressibility factor, whatever it is considered in this real gas behavior that should be actually expressed by that temperature and pressure at its critical condition.

Now, in that case, this almost all fluids you can say that will obey the same equation of state when their properties are written in reduced form. What is that reduced form, that means here, if we consider that know compressibility factor, this will be actually represented by z by zc, what is that, z is compressibility factor at a certain temperature and pressure, whereas zc is nothing bad that that compressibility factor is at critical condition.

We will describe what is that critical condition, that means higher that you will see that the gas will not be able to be liquefied at higher pressure or that particular temperature. So, that point of that temperature and pressure will be regarded as critical point of that temperature and pressure. So, if you express this compressibility factor based on that critical condition, it will be denoted by zc. So, z by zc it will be regarded as a reduced form of that compressibility factor.

So, this reduced form of this compressibility factor will be a function of reduced form of temperature and reduced form of pressure like this. So, we can say that reduced form of compressibility factor is a function of Tr and Pr, Tr is reduced temperature and Pr is reduced pressure, and this Tr is defined as T by Tc, that means T at certain that is temperature and Tc is the behavior at critical temperature. Since here this zc is nearly a constant for many organic species, it is actually about 0.27, just remember this and the most often used form is then we can write here z, z will be able to function of Tr and Pr.

So, this is why we can say that this reduced form of this compressibility factor will be a function of reduced temperature and reduced pressure and as a molar volume of in that case that the gases, real gases will become converting into or tends to 1 for the compressibility factor if it is going to 1 there. That means, as the molar volume becomes large, we can say that z will be tends to 1. So, compressibility factor is near about 1, means it will give you that large molar volume of that gas.

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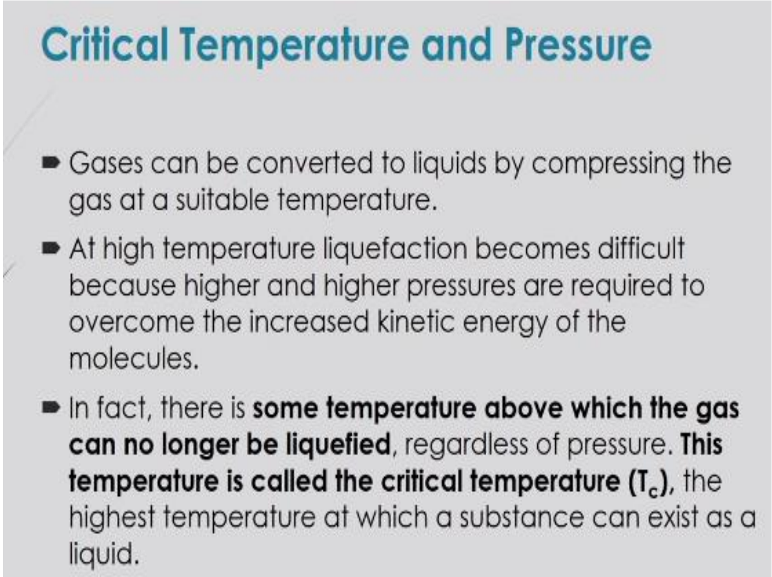

Critical Temperature and Pressure

- Gases can be converted to liquids by compressing the gas at a suitable temperature.
- At high temperature liquefaction becomes difficult because higher and higher pressures are required to overcome the increased kinetic energy of the molecules.
- In fact, there is **some temperature above which the gas can no longer be liquefied**, regardless of pressure. **This temperature is called the critical temperature (T_c)**, the highest temperature at which a substance can exist as a liquid.

So, here we told that that critical temperature and pressure what is that. So, gases can be converted to liquids by compressing the gases at a suitable temperature. At high temperature, liquefaction becomes difficult because higher and higher pressures are required to work on the increased kinetic energy of the molecules. In fact, there is some temperature above which the gas can no longer be liquefied regardless of pressure. This temperature is called the critical temperature. We can say that the highest temperature at which the substance can exist as a liquid, it will be regarded as that critical temperature.

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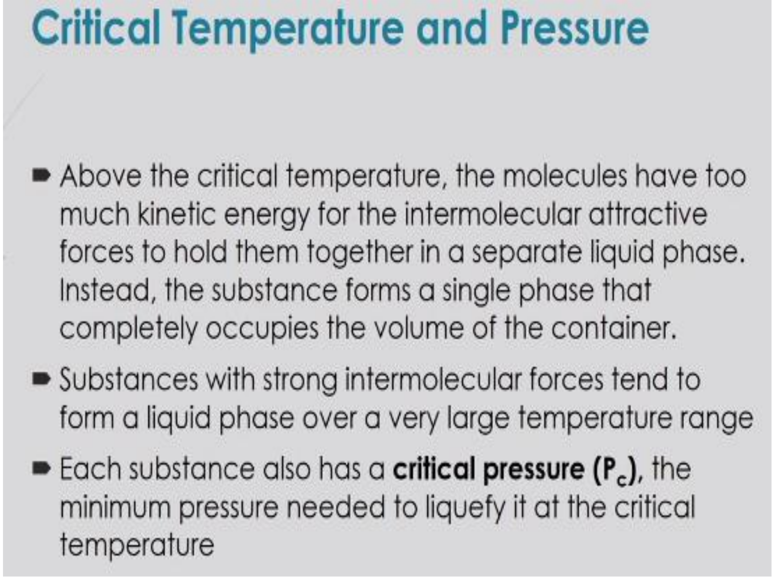

Critical Temperature and Pressure

- Above the critical temperature, the molecules have too much kinetic energy for the intermolecular attractive forces to hold them together in a separate liquid phase. Instead, the substance forms a single phase that completely occupies the volume of the container.
- Substances with strong intermolecular forces tend to form a liquid phase over a very large temperature range
- Each substance also has a **critical pressure (P_c)**, the minimum pressure needed to liquefy it at the critical temperature

Above the critical temperature, the molecules have too much kinetic energy for the intermolecular attractive forces to hold them together in a separate liquid phase. Instead, the substance forms a single phase that completely occupies the volume of the container. The substances with strong intermolecular forces that tend to form a liquid phase over a high large temperature range, in that case the substance will also have a critical pressure and it will be the minimum pressure that is required to liquefy it at the critical temperature.

So, we can say that above this critical temperature, molecules have too much kinetic energy for the intermolecular attractive forces to hold them together in a separate liquid phase and also substances with strong intermolecular forces will tend to form a liquid phase over a very large temperature range.

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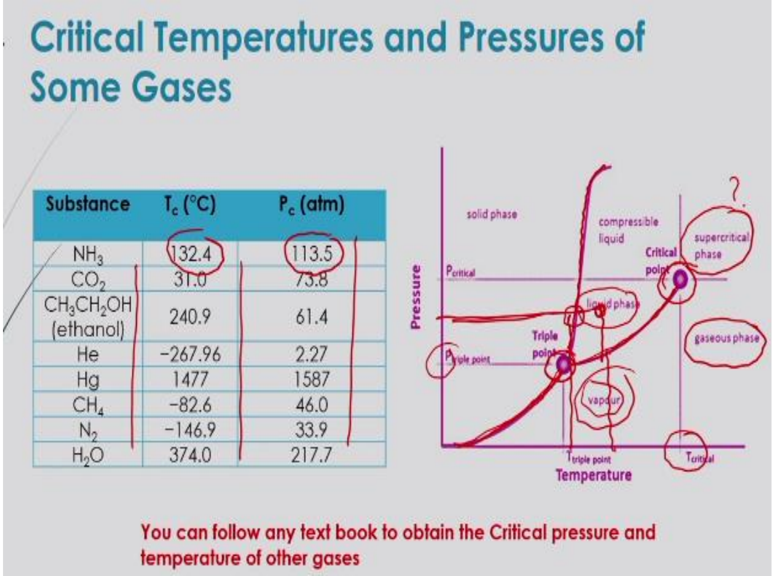

Critical Temperatures and Pressures of Some Gases

Substance	T_c (°C)	P_c (atm)
NH_3	132.4	113.5
CO_2	31.0	73.8
CH_3CH_2OH (ethanol)	240.9	61.4
He	−267.96	2.27
Hg	1477	1587
CH_4	−82.6	46.0
N_2	−146.9	33.9
H_2O	374.0	217.7

You can follow any text book to obtain the Critical pressure and temperature of other gases

Now, here in this figure it is given that critical temperature and pressure of some gases are given in this stable. For ammonia, this critical temperature will be 132.4, whereas critical pressure will be is equal to 113.5. Similarly, for other gases this critical temperature and critical pressures are given here and here in this figure you see that if we represent this non-ideal behavior of this gas, you will see that beyond this critical point at this temperature, this gaseous mixture will not actually be able to converting into that liquid form.

So, at this critical temperature, even what is the corresponding critical pressure at this condition you will see, beyond this critical pressure and temperature, you will see that there will be no formation of liquid gases there and beyond this you will see that there will be properties of the gases will drastically changes. So, these ranges of that operating condition of temperature and pressure will be regarded as the supercritical condition and the phase whatever will give you that behavior it will be called as supercritical phase behavior.

You will see that this at a certain temperature, even at a low temperature, even low pressure, you will see that at a certain condition, you will see that some like water, it will give you that vapor, liquid and solid 3 phases at a particular point. That would be called as triple point and these are called that equilibrium condition of each different phases. So, in this case, you will see substances by this profile, it will be representing as some equilibrium between here solid and vapor, whereas this equilibrium profile will give you that equilibrium between that liquid and vapor.

In this case, here this line will give you that equilibrium point of that solid and liquid there. So, in this way, you can say that at different pressure and temperature, that substances can be changed into its different form just by changing its temperature and pressure. So, at high pressure, that means beyond this critical condition, these gases will not be liquefied, whereas before this critical point, you can say that some substances you say that gases will be regarded as vapor.

Even at a particular temperature from this, you will see that and if you change the pressure, high pressure you will see that the gas maybe you know converting into a liquid phase. Again for a fixed temperature and if you change that pressure even at this condition, you will see that this liquid also it will be changing at a particular pressure if you change the temperature from that initial point here. So, here in this way, you can say that you can change the temperature and pressure and accordingly you can get the different points in this region of the different phases. That means here, that phase will be converted at a particular temperature and pressure.

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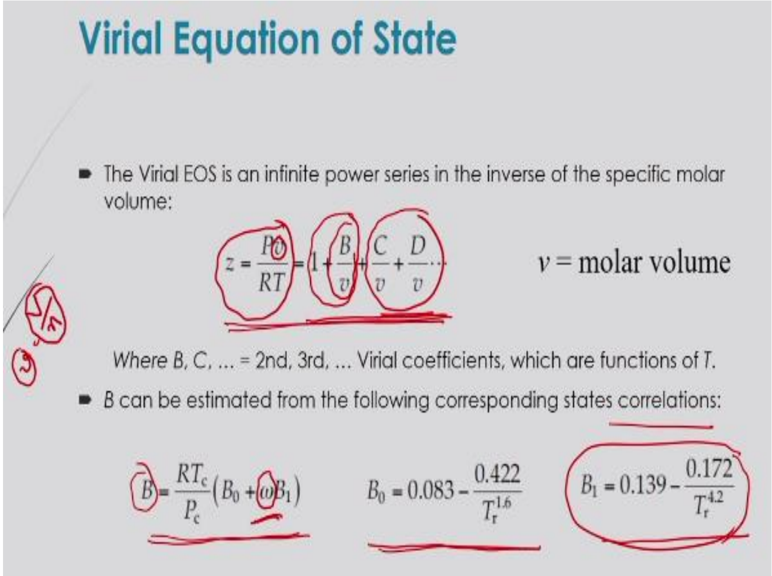

Virial Equation of State

- The Virial EOS is an infinite power series in the inverse of the specific molar volume:

$$z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v} + \frac{D}{v} \cdots \qquad v = \text{molar volume}$$

Where B, C, ... = 2nd, 3rd, ... Virial coefficients, which are functions of T.

- B can be estimated from the following corresponding states correlations:

$$B = \frac{RT_c}{P_c}(B_0 + \omega B_1) \qquad B_0 = 0.083 - \frac{0.422}{T_r^{1.6}} \qquad B_1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

Now to represent that non-ideal gas behavior, according to that concept of ideal gas equation, so we are considering here that non-ideal gas general form of equation of that it will be you know Pv is equal to zRT, here small v is nothing but that the molar volume, here this small v is nothing but capital V by n, capital V is you know that volume of that gas and n is number of moles. So, small v that is a specific volume in mole basis that is called molar volume. So, this V by n is represented here small v.

So, we can write that from the equation of Pv is equal to you know znRT, we can write here z will be is equal to here Pv by RT. So, this Pv by RT or z that is compressibility factor, you can represent it as a function of specific molar volume. So, it can be represented by this 1+ B by v + C by v + D by v, where B, C, D are all coefficients, those coefficients are called Virial coefficients and Virial coefficients are actually depending on the temperature of that particular system.

You will see that this is C and D values are relatively going to smaller compared to that this second Virial coefficients. So, accordingly, we can say that if we neglect these two terms of right hand side, so remaining portion is 1 + B by v. So, from this 1 + B y v, you can directly calculate what should be the compressibility factor z. Now, in this case, this B can be estimated from the following correlations given here. So, these coefficients basically depends on critical temperature and critical pressure.

So, this B value can be expressed as B is equal to here RTc divided by Pc into B0 + omega into B1, whereas this B0 is a constant that also depending on that reduced temperature. This is the equation to represent is B0 here and B1 also is one constant, that B1 also is expressed by this correlation given here in the slides, whereas you know that omega is called acentric factor, this acentric factor will be described later on also. This some another factor, that also is depending on critical temperature and pressure there.

So, if you know that the acentric factor and also that critical temperature and pressure, you will be able to find out what will be B value there, and once you know that B value, then what should be the compressibility factor you can calculate from this equation.

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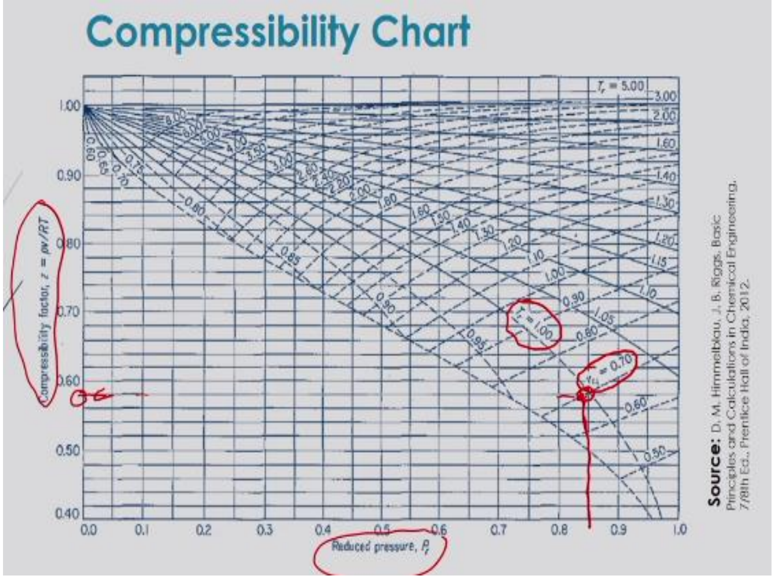

Compressibility Chart

Source: D. M. Himmelblau, J. B. Riggs, Basic Principles and Calculations in Chemical Engineering, 7/8th Ed., Prentice Hall of India, 2012.

Now, here one compensability chart is given. This is basically the compressibility factor is as a function of reduced pressure, it is given here. So, this compressibility factor versus reduced pressure, it is made, it is also taken from Himmelblau that is from your textbook. So, you can go through that. Here see that how that compressibility factor, it will be changing with reduced molar volume of that particular gases and also how it will be changing with reduced temperature and also how it will be changing with your reduced pressure there.

So, at a particular reduced temperature, that means T by Tc and also reduced molar volume there if you know that, then you can easily calculate at a particular reduced pressure, what should be the compressibility factor. Let us have these some gases here, suppose this reduced molar volume is here at this point and also that reduced temperature is 1, then at this particular reduced pressure, what should be the compressibility factor here it will you can get it from this point. So, this way you can read what should be the compressibility factor from this chart.

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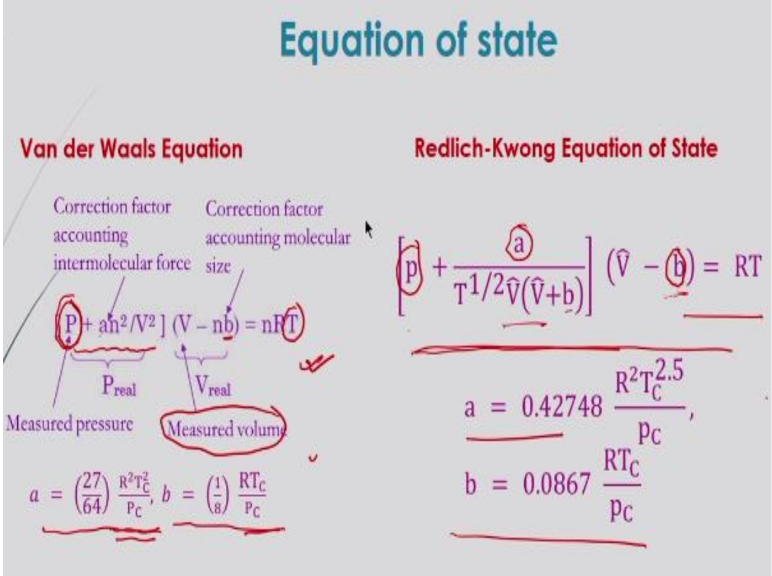

Equation of state

Van der Waals Equation

Correction factor accounting intermolecular force

Correction factor accounting molecular size

$$\underbrace{[P + an^2/V^2]}_{P_{real}}\ \underbrace{(V - nb)}_{V_{real}} = nRT$$

Measured pressure

Measured volume

$$a = \left(\frac{27}{64}\right)\frac{R^2T_C^2}{P_C},\ b = \left(\frac{1}{8}\right)\frac{RT_C}{P_C}$$

Redlich-Kwong Equation of State

$$\left[p + \frac{a}{T^{1/2}\hat{V}(\hat{V}+b)}\right](\hat{V} - b) = RT$$

$$a = 0.42748\,\frac{R^2T_C^{2.5}}{p_C},$$

$$b = 0.0867\,\frac{RT_C}{p_C}$$

Now, we told that there are several equations of state that is suggested by different investigators, different scientists, different academicians. Also you can say that how that real gas behavior can be expressed based on their intermolecular force, even their molecular size. So, in this case Van der Waals equation of state is one of the important equation of state for the real gases by which you can calculate its pressure and also volume for that real gases at its particular temperature and pressure.

So, in this case, see here, Van der Waal equation is given in the slide. Here it is p P + a into n square divided by V square into V minus nb that will be is equal to nRT. Here also P into V, here this part is regarded as P real that is P + an square by V square. Here a is some coefficient, it is actually depending on the critical temperature and pressure and its value is given here by this correlation and here V real that is denoted by V minus nb, here b is also coefficient, this b is calculated by this equation, here also it is depending on the critical temperature and pressure.

You will see that 2 coefficients are here a and b, this a actually is correction factor that is accounting intermolecular force of that real gases, whereas b is another factor that accounts the molecular size of that particular gases. So, based on which that Van der Waal suggested this equation of state to represent the non-ideal behavior of the gases. So, here in this case, if you know the measured pressure and also measured volume, you can easily calculate what should be the remaining factor of that a and b there just by equating that experimental data with this equation.

So, one way you can express that what should be a value and b value, that a and b value you can express by this critical temperature and pressure. Also if you know that measured volume at a certain temperature for that real gases and also if you know that a and b value of that coefficient at this particular critical reduced temperature or reduced pressure or you can say that critical temperature and pressure, then you can easily calculate what should be the pressure of that real gases.

Whereas we have calculated the behavior of ideal gases only by PV is equal to nRT, here in this case, that will not give you the exact result for that real gases, that is why for real gases, you have to use this Van der Waal equations because that real gases behavior will be different from that ideal gases, because of that some intermolecular force and also size of that real gases will matter. So, that is why based on that intermolecular behavior, the Van der Waals given this equation of Van der Waal equations to represent that non-ideal behavior of the gases.

Similarly, another investigator that is called Redlich-Kwong equation of state by which you can express that real gases' behavior for the pressure and volume. So, here also, this equation even this is also you will see that at this equation here, you will see the molar volume of that real gases and also some coefficient here b is given here. So, based on these, you can calculate what should be the pressure if you know that molar volume is there.

So, this again that this Redlich-Kwong equation depending on these 2 parameter this a and b, those are actually depending on that intermolecular force and intramolecular or molecular size there, and this coefficients are again depending on that critical temperature and pressure, and by this correlation, you can directly calculate or estimate the value of a and b. Once you know that a and b by this correlations and if you know that molar volume at a particular temperature, then you can easily calculate what will be the pressure of this real gases by this Redlich-Kwong equation.

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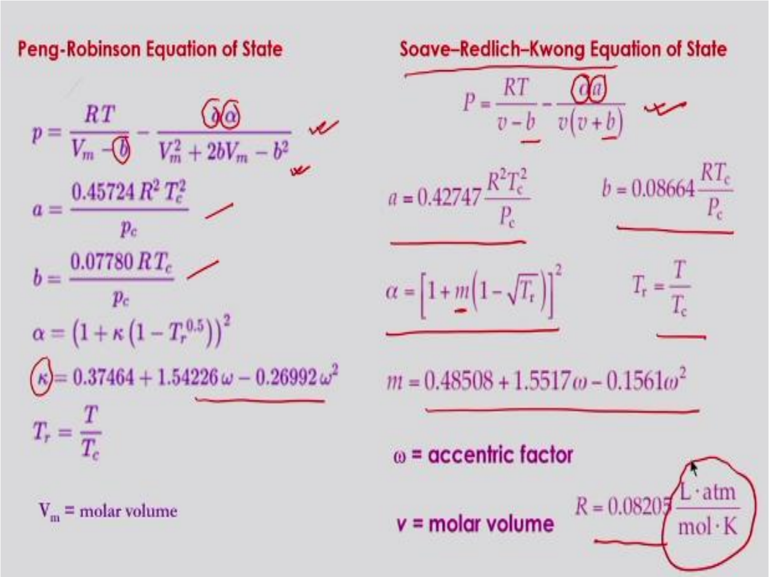

Peng-Robinson Equation of State

$$p = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m^2 + 2bV_m - b^2}$$

$$a = \frac{0.45724\, R^2 T_c^2}{p_c}$$

$$b = \frac{0.07780\, R T_c}{p_c}$$

$$\alpha = \left(1 + \kappa\left(1 - T_r^{0.5}\right)\right)^2$$

$$\kappa = 0.37464 + 1.54226\,\omega - 0.26992\,\omega^2$$

$$T_r = \frac{T}{T_c}$$

V_m = molar volume

Soave–Redlich–Kwong Equation of State

$$P = \frac{RT}{v - b} - \frac{\alpha a}{v(v + b)}$$

$$a = 0.42747\frac{R^2 T_c^2}{P_c} \qquad b = 0.08664\frac{RT_c}{P_c}$$

$$\alpha = \left[1 + m\left(1 - \sqrt{T_r}\right)\right]^2 \qquad T_r = \frac{T}{T_c}$$

$$m = 0.48508 + 1.5517\omega - 0.1561\omega^2$$

ω = accentric factor

v = molar volume

$$R = 0.08205\,\frac{\mathrm{L\cdot atm}}{\mathrm{mol\cdot K}}$$

Similarly, other equations are also familiar to calculate or predict that real gases’ pressure or volume. So, those are Peng-Robinson equation of state here given. Here again, some factors are here some a and alpha, even you know that b, even you can say that this alpha value that is acentric factor, also this alpha value depending on that some acentric factor. In that case, you will see that some other factors it is denoted that is called K that is also depending on the acentric factor and also we can see that this coefficient a and b are depending on that critical temperature and pressure and Vm is here molar volume.

So, based on this equation also, you can calculate what should be the pressure. Similarly, you can use that SRK equation it is called, Soave-Redlich-Kwong equation. Here also this equation expressed in terms of some coefficient b and also here alpha and a. Here a is defined by this correlation, b is defined by this correlation, alpha is again depending on that acentric factor and reduced temperature and this reduced temperature defined as here T and Tc and this alpha is equal to here 1 + m into 1 minus root over Tr whole square.

This m is basically that has a function of acentric factor and r is ideal gas constant or universal gas constant that is you know 0.08205 at this unit of liter atmosphere per mole Kelvin. So, from these equations, you can easily calculate what should be the pressure and volume at a particular temperature there.

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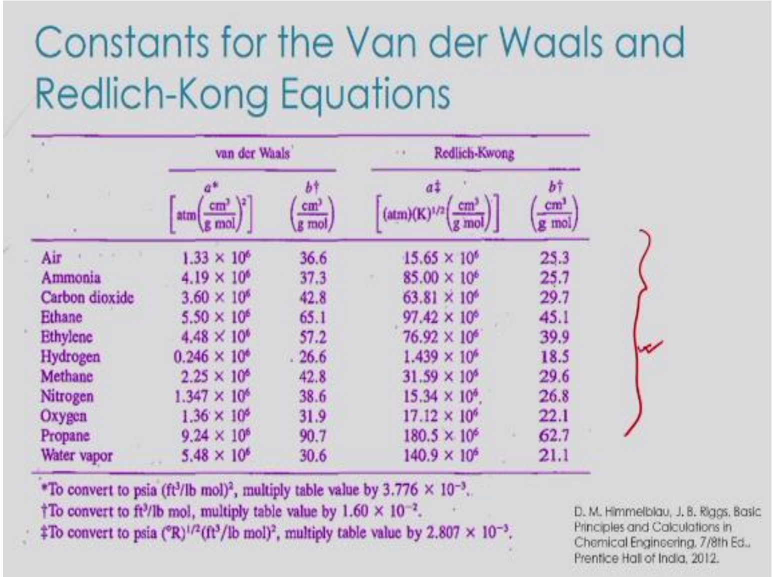

Constants for the Van der Waals and Redlich-Kong Equations

	van der Waals		Redlich-Kwong	
	a^* $\left[\text{atm}\left(\frac{\text{cm}^3}{\text{g mol}}\right)^2\right]$	$b^\dagger$ $\left(\frac{\text{cm}^3}{\text{g mol}}\right)$	$a^\ddagger$ $\left[(\text{atm})(\text{K})^{1/2}\left(\frac{\text{cm}^3}{\text{g mol}}\right)\right]$	$b^\dagger$ $\left(\frac{\text{cm}^3}{\text{g mol}}\right)$
Air	1.33×10^6	36.6	15.65×10^6	25.3
Ammonia	4.19×10^6	37.3	85.00×10^6	25.7
Carbon dioxide	3.60×10^6	42.8	63.81×10^6	29.7
Ethane	5.50×10^6	65.1	97.42×10^6	45.1
Ethylene	4.48×10^6	57.2	76.92×10^6	39.9
Hydrogen	0.246×10^6	26.6	1.439×10^6	18.5
Methane	2.25×10^6	42.8	31.59×10^6	29.6
Nitrogen	1.347×10^6	38.6	15.34×10^6	26.8
Oxygen	1.36×10^6	31.9	17.12×10^6	22.1
Propane	9.24×10^6	90.7	180.5×10^6	62.7
Water vapor	5.48×10^6	30.6	140.9×10^6	21.1

*To convert to psia $(\text{ft}^3/\text{lb mol})^2$, multiply table value by 3.776×10^{-5}.

†To convert to $\text{ft}^3/\text{lb mol}$, multiply table value by 1.60×10^{-2}.

‡To convert to psia $(°\text{R})^{1/2}(\text{ft}^3/\text{lb mol})^2$, multiply table value by 2.807×10^{-3}.

D. M. Himmelblau, J. B. Riggs, Basic Principles and Calculations in Chemical Engineering, 7/8th Ed., Prentice Hall of India, 2012.

Now, constants for the Van der Waals and Redlich-Kwong equations are given here in this table for different gases. That means a value, b value what should be that. So from this table, you can take this a and b value directly without calculating that a and b constants from the correlations. So, you can directly use the table for your a and b and after getting a and b, if you directly put that a and b in your respective Van der Waal equation or Redlich-Kwong equation, then you can easily calculate what should be the pressure or volume.

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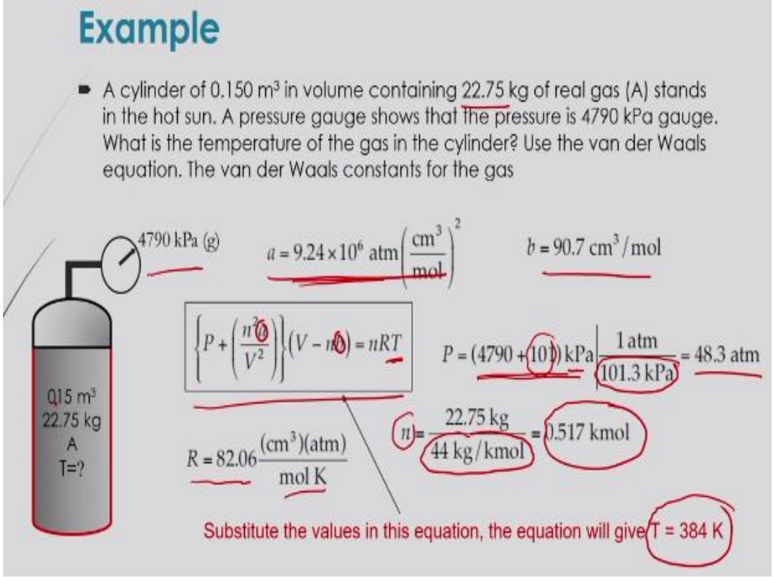

Example

- A cylinder of 0.150 m³ in volume containing 22.75 kg of real gas (A) stands in the hot sun. A pressure gauge shows that the pressure is 4790 kPa gauge. What is the temperature of the gas in the cylinder? Use the van der Waals equation. The van der Waals constants for the gas

$a = 9.24 \times 10^6 \text{ atm}\left(\frac{\text{cm}^3}{\text{mol}}\right)^2$ $\quad b = 90.7 \text{ cm}^3/\text{mol}$

$$\boxed{\left\{P + \left(\frac{n^2 a}{V^2}\right)\right\}(V - nb) = nRT}$$

$$P = (4790 + 101)\text{ kPa}\left|\frac{1\text{ atm}}{101.3\text{ kPa}}\right. = 48.3\text{ atm}$$

$$R = 82.06\frac{(\text{cm}^3)(\text{atm})}{\text{mol K}} \qquad n = \frac{22.75\text{ kg}}{44\text{ kg/kmol}} = 0.517\text{ kmol}$$

Substitute the values in this equation, the equation will give T = 384 K

Now, let us do an example based on this Van der Waal equation or you know other equation of state. Now, as an example you can say that if suppose a cylinder of 0.15 meter cube in volume containing 22.75 kg of real gas A stands in the hot sun. Now, a pressure gauge shows that the pressure is 4790 kilopascal that is in gauge. What is the temperature of the gas in the cylinder that you have to find out? Now, in this case, you can use the Van der Waal equations because here this gas is real gas.

So, you cannot use that ideal gas equation to find out that here temperature. So, in this case if we use that Van der Waal equation, for that what we should required to calculate? in this case, this is your Van der Waal equations, for this you need to calculate a value, you need to calculate b value. So, a value can be calculated based on that correlation, so you can get directly this equation or either you can take it from the tables, so this a value will be like this and b value will be is equal to similarly 90.7 or you can calculate it from the correlations that is given in the earlier slides.

Once you know this a and b value, then again you have to calculate what should be the n value there because and n is also to be calculated, what will be the number of moles of that gases? Because in this case, it is given that cylinder contains 22.75 kg of real gas. In this case if real gas, here molecular weight is 44 let it be here. So, in this case, the number of moles will be is equal to here 0.517 kilomole. Pressure is given there, I think what is the pressure given, it is you know that 4790 kilopascal.

So, here it will be absolute pressure will be is equal to, this is gauge pressure, so absolute pressure will be is equal to 4790 + 101, this is your atmospheric pressure. So you have to add it up to get the absolute pressure. This is in kilopascal, you know that 101.3 kilopascal is equivalent to 1 atmosphere, so you can convert it to absolute pressure into atmosphere. This is 48.3 atmosphere. Then R value is as far that atmosphere it is you know that 82.06 centimeter cube into atmosphere per mole K.

You can say that after the substitution of these n value, a value, b value, and also volume, volume is given to you, it is given 0.150 meter cube, so, you have to convert it to centimeter cube and then finally, you can calculate that what should be the temperature from this equation. So, this is coming this will be equal to 384 Kelvin after substitution of all these parameters there. So, finally, we can say that the gas in the cylinder will have this temperature of 384 K.

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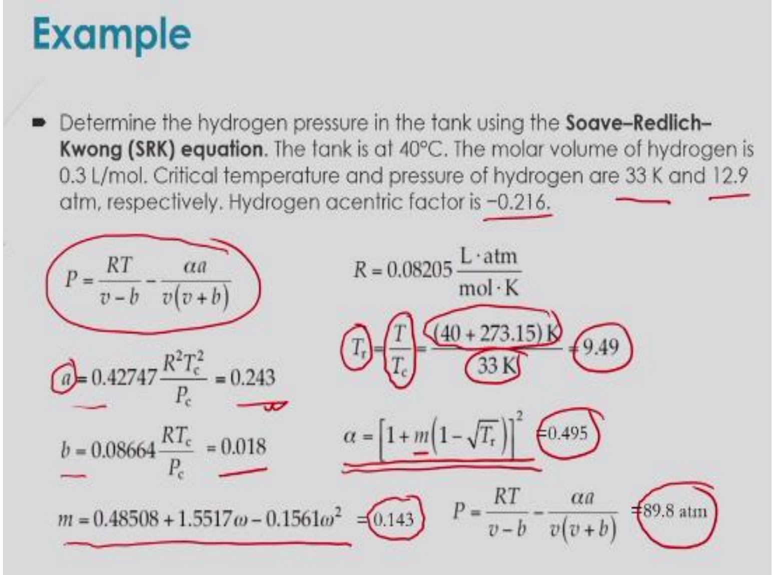

Example

- Determine the hydrogen pressure in the tank using the **Soave–Redlich–Kwong (SRK) equation**. The tank is at 40°C. The molar volume of hydrogen is 0.3 L/mol. Critical temperature and pressure of hydrogen are 33 K and 12.9 atm, respectively. Hydrogen acentric factor is −0.216.

$$P = \frac{RT}{v-b} - \frac{\alpha a}{v(v+b)}$$

$$R = 0.08205 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}$$

$$T_r = \frac{T}{T_c} = \frac{(40+273.15)\ \text{K}}{33\ \text{K}} = 9.49$$

$$a = 0.42747 \frac{R^2 T_c^2}{P_c} = 0.243$$

$$b = 0.08664 \frac{RT_c}{P_c} = 0.018$$

$$\alpha = \left[1 + m\left(1 - \sqrt{T_r}\right)\right]^2 = 0.495$$

$$m = 0.48508 + 1.5517\omega - 0.1561\omega^2 = 0.143$$

$$P = \frac{RT}{v-b} - \frac{\alpha a}{v(v+b)} = 89.8\ \text{atm}$$

Another example. In this case, you have to determine the hydrogen pressure in a tank by using SRK equation, that is Soave-Redlich-Kwong equation. The tank is at 40 degrees Celsius it is there. The molar volume of the hydrogen is 0.3 liter per mole. Now, critical temperature and pressure of the hydrogen are given as 33 K and 12.9 atmosphere respectively. Now, hydrogen acentric factor is given as minus 0.216. So, what should be the hydrogen pressure in the tank?

So, you can use this equation, SRK equation. Based on that, you are having this P is equal to RT by v minus b minus alpha a by v into v + b. So, in this case, you need to calculate first what should be the a value there by this correlation, in this case since this correlation or this value of a is depending on critical temperature and pressure, this critical temperature and pressure of hydrogen is given to you. So, finally, you can calculate what should be the a value.

Similarly, what should be the b value, again if you substitute the Tc and Pc, there you will get this value 0.018 and then you have to calculate what should be the m value there because to calculate that alpha value it is required that m value. So, m value is function of acentric factor, this acentric factor is given to you. So, if you substitute that eccentric factor omega here in this equation, you can calculate what should be the m value her, so m is coming as 0.143.

Then finally, you can get what should be the alpha value here, before calculating this alpha value, you have to calculate what is the reduced temperature, because this reduced temperature is defined as T by Tc, T is given to you and then Tc is also given to you. So, finally, you are getting 9.49 as Tr and then what should be the alpha value. After substituting of this m value and Tr value, you can get this alpha 0.495.

Now, if you substitute that alpha value, a value, b value, and also molar volume here in this equation at that particular temperature, what should be the pressure you can easily calculate there by this SRT equation and it is finally coming as 89.8 atmosphere. So, this is your basic equation how to calculate the pressure and volume by this SRK equation. Another important aspect of non-ideal gas behavior is whenever there are more than one real gas will be there in a mixture, how then that their reduced temperature and reduced pressure will be changing.

So, in that case, that also to be calculated and accordingly that compressibility factor of that mixture of gases will be different. So, once you know that mixture of gases that compressibility factor, then what should be the pressure and volume from that non-ideal behavior or non-ideal gas equation, you can calculate those pressure and volume.

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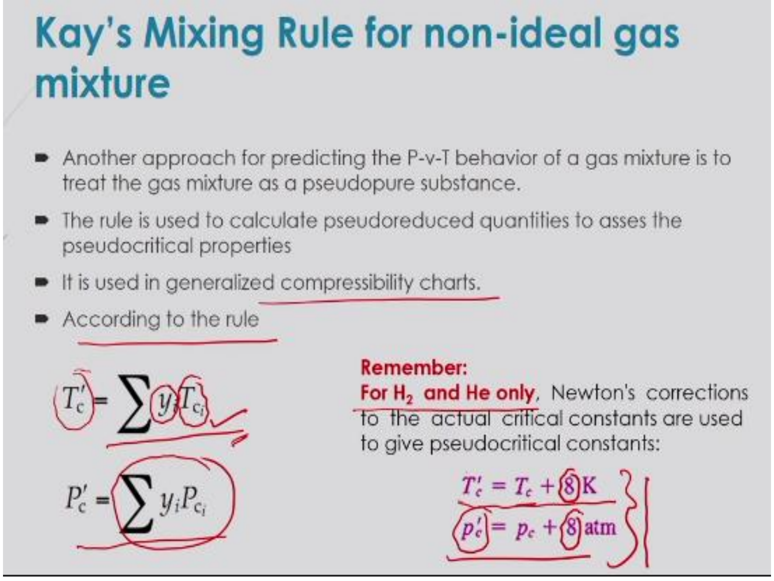

Kay's Mixing Rule for non-ideal gas mixture

- Another approach for predicting the P-v-T behavior of a gas mixture is to treat the gas mixture as a pseudopure substance.
- The rule is used to calculate pseudoreduced quantities to asses the pseudocritical properties
- It is used in generalized compressibility charts.
- According to the rule

$$T_c' = \sum y_i T_{c_i}$$

$$P_c' = \sum y_i P_{c_i}$$

Remember:
For H_2 and He only, Newton's corrections to the actual critical constants are used to give pseudocritical constants:

$$T_c' = T_c + 8\,\text{K}$$

$$p_c' = p_c + 8\,\text{atm}$$

Now, if you have that mixture of gases, then your critical temperature and critical pressure will be represented by pseudo reduced quantities of those gases to assess the pseudocritical properties. Now, it is used in generalized compressibility charts. So, according to the rule of Kay's, it is called Kay's mixing rule. So, this pseudocritical temperature will be regarded as what is the summation of Yi into Tci, i is for individual component of that gases.

Suppose there are 2-3 gases in a mixer, so each gas components will be represented by i and its molar fraction will be is equal to Yi and Tci is the individual gas components at critical temperature. So, summation of all this Yi into Tci will give you that pseudocritical temperature of that mixer of gases and also what is that pseudocritical pressure of the mixture of the gases similarly you can have the summation of Yi into Pci.

But in this case you have to remember that sometimes this hydrogen and helium gas does not follow this particular critical temperature, this pseudocritical temperature and pseudocritical pressure just by that individual gas component, it is critical temperature and pressure. It is seen that at this critical condition, this hydrogen and helium gases will give you the pseudocritical condition if you add it to some factor there with that critical temperature.

Similarly, if you add some factor with that critical pressure, you will see that pseudocritical temperature and pressure will be there. So, remember that for only hydrogen and helium, this pseudocritical temperature will be is equal to Tc + 8 K, here only this value of 8 it will be added to this critical temperature. Similarly, for pressure also you have to add this 8 for the critical pressure to get pseudocritical constants here Pc dash. So, for hydrogen and helium that you have to remember this equation to calculate further.

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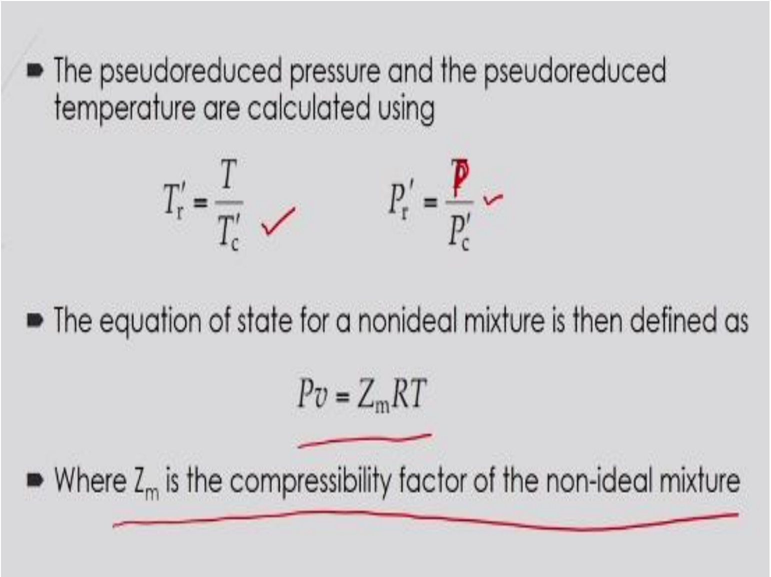

- The pseudoreduced pressure and the pseudoreduced temperature are calculated using

$$T'_r = \frac{T}{T'_c} \checkmark \qquad P'_r = \frac{P}{P'_c} \checkmark$$

- The equation of state for a nonideal mixture is then defined as

$$Pv = Z_m RT$$

- Where Z_m is the compressibility factor of the non-ideal mixture

Now the pseudoreduced pressure and the pseudoreduced temperature are calculated using by this equation here Tr dash will be equal to T divided by Tc dash, Pr dash will be is equal to P by Pc dash. The equation of state for a non-ideal mixture is then defined as Pv will be is equal to ZmRT. What is Zm, Zm is the compressibility factor of the non-ideal gas mixture, so m is for you know mixture.

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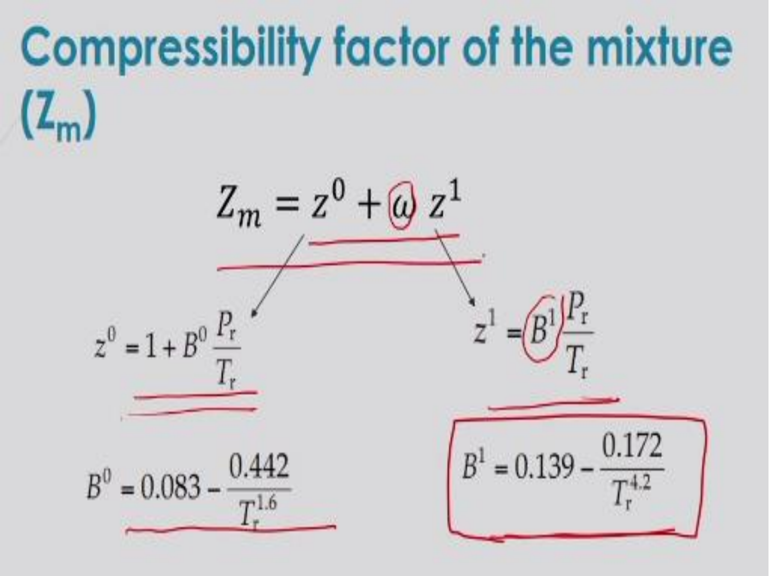

Compressibility factor of the mixture (Z_m)

$$Z_m = z^0 + \omega z^1$$

$$z^0 = 1 + B^0 \frac{P_r}{T_r} \qquad z^1 = B^1 \frac{P_r}{T_r}$$

$$B^0 = 0.083 - \frac{0.442}{T_r^{1.6}} \qquad B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

Now compressibility factor of the mixture, then you can calculate in this way. This Zm will be is equal to Z0 + omega into Z1, where Z0 is defined as 1 + B0 into Pr by Tr, where B0 is defined by this correlation which is a function of reduce temperature and Z1 is another factor that is a function of ratio of reduced pressure and reduced temperature, whereas this B1 is coefficient, that coefficient is a function of reduced temperature which can be calculated from this correlation.

So, once you know this Z0 by this equation and Z1 from this equation and if you know the acentric facto, then you can easily calculate what should be the mixture compressibility factor.

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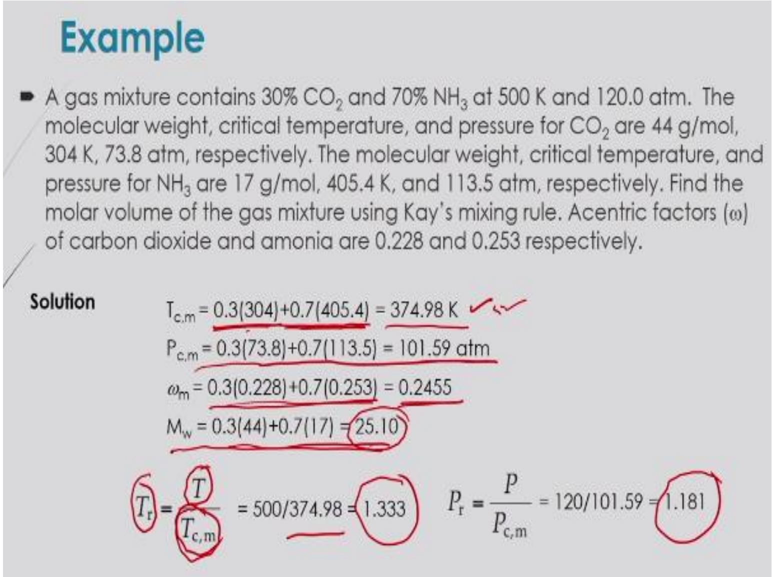

Example

- A gas mixture contains 30% CO_2 and 70% NH_3 at 500 K and 120.0 atm. The molecular weight, critical temperature, and pressure for CO_2 are 44 g/mol, 304 K, 73.8 atm, respectively. The molecular weight, critical temperature, and pressure for NH_3 are 17 g/mol, 405.4 K, and 113.5 atm, respectively. Find the molar volume of the gas mixture using Kay's mixing rule. Acentric factors (ω) of carbon dioxide and amonia are 0.228 and 0.253 respectively.

Solution

$T_{c,m} = 0.3(304)+0.7(405.4) = 374.98$ K

$P_{c,m} = 0.3(73.8)+0.7(113.5) = 101.59$ atm

$\omega_m = 0.3(0.228)+0.7(0.253) = 0.2455$

$M_w = 0.3(44)+0.7(17) = 25.10$

$T_r = \frac{T}{T_{c,m}} = 500/374.98 = 1.333 \qquad P_r = \frac{P}{P_{c,m}} = 120/101.59 = 1.181$

Let us do an example here. Suppose a gas mixer is given to you and that will contain 30% carbon dioxide and 70% ammonia and it exists at 500 Kelvin and 120 atmosphere in container. The molecular weight, critical temperature and pressure for that carbon dioxide and ammonia are given here and also the molecular weight, critical temperature and pressure for the ammonia also given. Find the molar volume of the gas mixture using the Kay's mixing rule?

Here acentric factors of the carbon dioxide and ammonia are given as 0.228 and 0.253 respectively. So, you have to find out here what should be the molar volume of that gas mixture. So, to find out here what should be the, first calculate what would be the Tc.m for that mixture. For that mixture Tc since here molar fraction is 30% and 70%, then you just simply multiply that molar fraction as here 0.3 into 304 + 0.7 into 405.4.

Here 304 is, it is given that critical temperature of the carbon dioxide and 405 is the critical temperature of the ammonia gas and their corresponding mole fraction for carbon dioxide is 30% whereas ammonia gas is 70%. So, total mixture critical temperature will be just based on this equation, it will be coming as 374.98 Kelvin. Similarly, critical pressure of the mixture, simply you have to multiply with that mole fraction and then add it up for all components and it will be coming as 101.59 atmosphere.

Here acentric factor also you have to calculate in the same way of what is the mole fraction, you have to multiply that acentric factor with that respective mole faction and then add it up for all the gas components, then you get this acentric factor of your as per problem here it is

0.2455. Similarly, mixture molecular weight has to be calculated based on that molar concentration here, so it will be as 25.10. Next you have to calculate for the reduced temperature, it is defined as simply T by Tc.m.

T is the temperature at a certain condition it is kept, this is I think 500 K and Tc.m it is calculated earlier, that is it is coming 374.98. If you divide it this 500 by 374.98, you will get this 1.333, it is simply reduced temperature. Similarly, you can get the reduced pressure as 1.181. So, in this way, you can calculate what would be the reduced temperature and reduced pressure.

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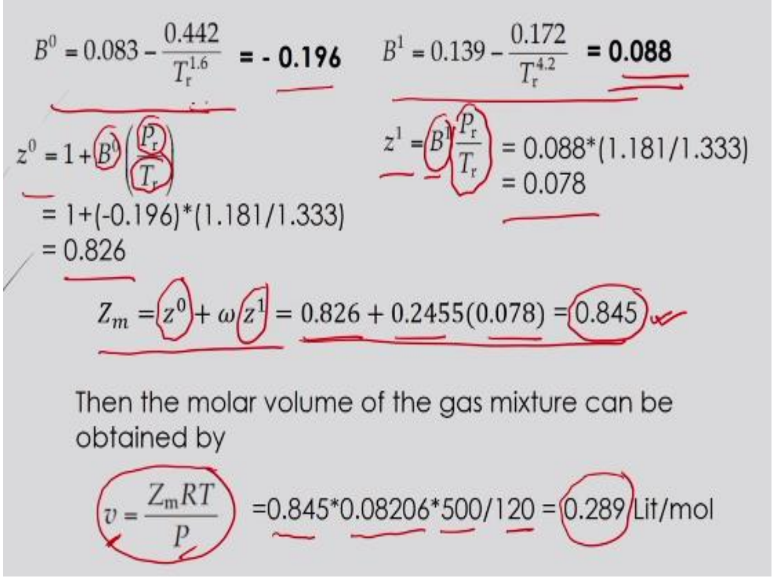

$B^0 = 0.083 - \frac{0.442}{T_r^{1.6}}$ **= - 0.196**

$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$ **= 0.088**

$z^0 = 1 + B^0 \left(\frac{P_r}{T_r}\right)$

= 1+(-0.196)*(1.181/1.333)

= 0.826

$z^1 = B^1 \frac{P_r}{T_r}$ = 0.088*(1.181/1.333)

= 0.078

$Z_m = z^0 + \omega z^1$ = 0.826 + 0.2455(0.078) = 0.845

Then the molar volume of the gas mixture can be obtained by

$v = \frac{Z_m RT}{P}$ =0.845*0.08206*500/120 = 0.289 Lit/mol

After that, you have to calculate that all coefficients given here like B0 and then B1. You know the Tr that is reduced temperature and reduced pressure if it is required, I think in this equation only reduced temperature is required. So B0 will be is equal to this. Similarly B1, it is also a function of only reduced temperature. So, you can calculate this value based on that reduced temperature. Now z0 is a function of reduced pressure and reduced temperature.

If you substitute this value of B0 and this Pr and Tr here, you can simply get this value of z0 as 0.82 m and similarly you need to calculate that z1. This, what is that, this is B1 into Pr by Tr, Pr and Tr here and B1 already you have calculated. So, if you substitute those B1, Pr and Tr here, you can get this z1 value. Now, since this mixture compressibility factor is a function of this z0 and z1, then you can have this mixture compressibility factor after substitution of this value of z0 here whatever you have calculated and z1 whatever you have calculated, but acentric factor of that mixture also you have calculated here, it is why.

So, after simplification, you can get this value of 0.845. So, this is your compressibility factor of the mixture. Then what should be the molar volume of the gas mixture? That can be obtained from this non-ideal gas equation, that is general form of that non-ideal gas equation, that will be is equal to v that will be is equal to ZmRT by P. So, here Zm already you have calculated and then R is even there and T is 500 and what is that P is here 120 K. So, finally, you can get it what will be the value, it is 0.289 liter per mole.

So, in this way, how this case rule of mixing you can apply for that mixture of non-ideal gas to calculate its mixture molar volume, so you have to follow this equation.

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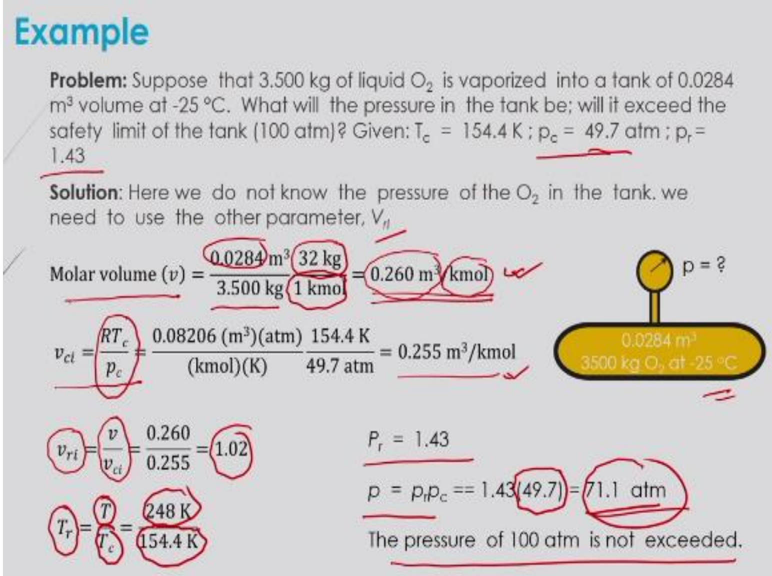

Example

Problem: Suppose that 3.500 kg of liquid O_2 is vaporized into a tank of 0.0284 m^3 volume at -25 °C. What will the pressure in the tank be; will it exceed the safety limit of the tank (100 atm)? Given: T_c = 154.4 K ; p_c = 49.7 atm ; p_r = 1.43

Solution: Here we do not know the pressure of the O_2 in the tank. we need to use the other parameter, V_{ri}

$$\text{Molar volume } (v) = \frac{0.0284\ m^3}{3.500\ kg}\frac{32\ kg}{1\ kmol} = 0.260\ m^3/kmol$$

$$v_{ci} = \frac{RT_c}{p_c} = \frac{0.08206\ (m^3)(atm)}{(kmol)(K)}\frac{154.4\ K}{49.7\ atm} = 0.255\ m^3/kmol$$

$$v_{ri} = \frac{v}{v_{ci}} = \frac{0.260}{0.255} = 1.02$$

$$T_r = \frac{T}{T_c} = \frac{248\ K}{154.4\ K}$$

P_r = 1.43

$p = p_r p_c == 1.43(49.7) = 71.1$ atm

The pressure of 100 atm is not exceeded.

Another example. Suppose that a container or you can say the tank contains 3.5 kg of liquid oxygen, which is to be vaporized in that tank of 0.0284 meter cube here and this will be vaporized at this at about this temperature of minus 25 degrees Celsius. Now, what will be the pressure in the tank will be and will it exceed the safety limit of the tank what is actually to be maintained at 100 atmosphere. In this case, given that the critical temperature of that gases is 154.4 Kelvin and critical pressure of that gas here oxygen is given 49.7 atmosphere and reduced pressure is here 1.43.

So, based on this condition, you have to find out what will be the pressure inside the tank. Now, here this case, we do not know the pressure of the oxygen in the tank. Now, we need to use the other parameter like here Vri that means for a particular component what should be its reduced molar volume? So, to calculate that, first of all you have to calculate molar volume of that gases. So, molar volume is coming that its volume is given is 0.0284 of the container and mass of that gas is given 3.5 kg.

So meter cube per kg to be 0.0284 by 3.5 and if you convert it to this meter cube into again into mole, what is that you can get it to the mole just by multiplying it with this molecular weight. So, in this way, you can calculate that this will be this meter cube per kilomole. So, this tank will be having this volume of 0.260 meter cube per kilomole of that oxygen. Now, what will be the Vci, critical molar volume of that component? So, it will be RTc by Pc.

So, accordingly if you substitute that R value, Tc value and Pc value, you can get it this 0.255 meter cube per kilomole. Again this what will be the reduced molar volume of that component, to be simply that v by vci,v is already you have calculated and vci also you have calculated. If you divide this, you will get 1.02, and what would be the reduced temperature, this is T by Tc. If you substitute that T value and then substitute the Tc, you can get this Tr value.

Then what should be the Pr, Pr will be is equal to 1.43, it is given to you. Then P will be is equal to what, P will be is equal to Pr into Pc, Pr is given to you, Pc also to be calculated, and then Pc is coming here, it is also given 49.7, then it will be coming a 71.1 atmosphere. So, at this condition, the pressure of tank is 71.1 atmosphere, whereas at its safety level, the pressure will be maintained as 100 atmosphere, but it is coming as 71.1. So, we can say that it is in safe condition.

So, in this way, you can calculate based on that critical temperature and pressure and how to calculate that molar volume and also add critical condition how to calculate the molar volume of this component in a particular tank and also what should be the reduced molar volume for that particular components in the tank and based on which you can easily calculate what should be that this pressure simply from this reduced pressure and critical pressure there.

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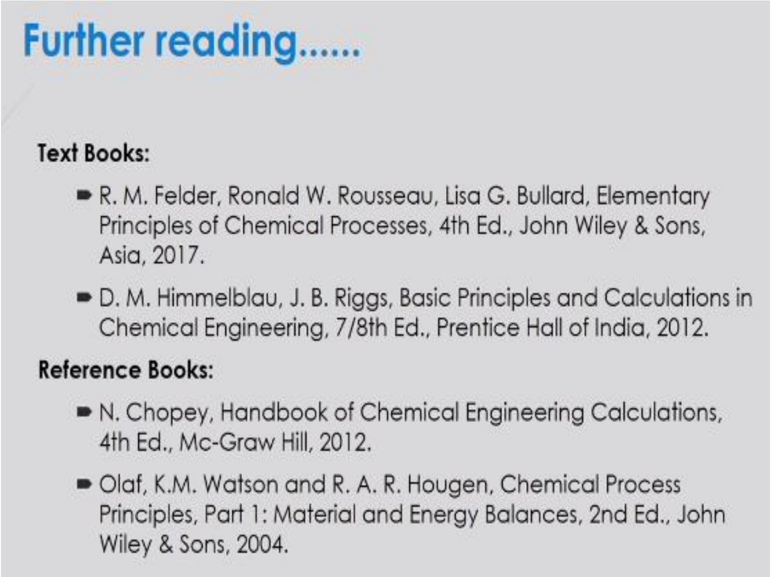

Further reading......

Text Books:

- R. M. Felder, Ronald W. Rousseau, Lisa G. Bullard, Elementary Principles of Chemical Processes, 4th Ed., John Wiley & Sons, Asia, 2017.
- D. M. Himmelblau, J. B. Riggs, Basic Principles and Calculations in Chemical Engineering, 7/8th Ed., Prentice Hall of India, 2012.

Reference Books:

- N. Chopey, Handbook of Chemical Engineering Calculations, 4th Ed., Mc-Graw Hill, 2012.
- Olaf, K.M. Watson and R. A. R. Hougen, Chemical Process Principles, Part 1: Material and Energy Balances, 2nd Ed., John Wiley & Sons, 2004.

So, we have discussed in the lot of theories, how to calculate the pressure and volume of non-ideal gases based on that Van der Waals equation, even RK equation, even you can say that SRK equation, even other equations also are shown there to calculate that non-ideal behavior at a different temperature, even at different pressure and volume what should be the other specific property of the gases and also in a mixture how to calculate that compressibility factor by case rule that we have discussed here.

So, I think you have understood this matter how to calculate that non-ideal behavior by this equation of state if you know the compressibility factor. So, I would suggest you to go this textbook thoroughly and also try to practice some other example problems given in the textbook, so that you can easily understand, also you can further solve the problem based on this concept there. So, I thank you a lot for your kind attention here. In the next lecture, we will try to discuss more about gas system or other system.

In that case, the separate module will be considered, in the separate module, we will discuss something more that multiphase systems and how they actually lies in an equilibrium condition and what are the different laws to express that equilibrium condition will be discussing in the next lecture. Thank you.