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National Programme on Technology Enhanced Learning (NPTEL)

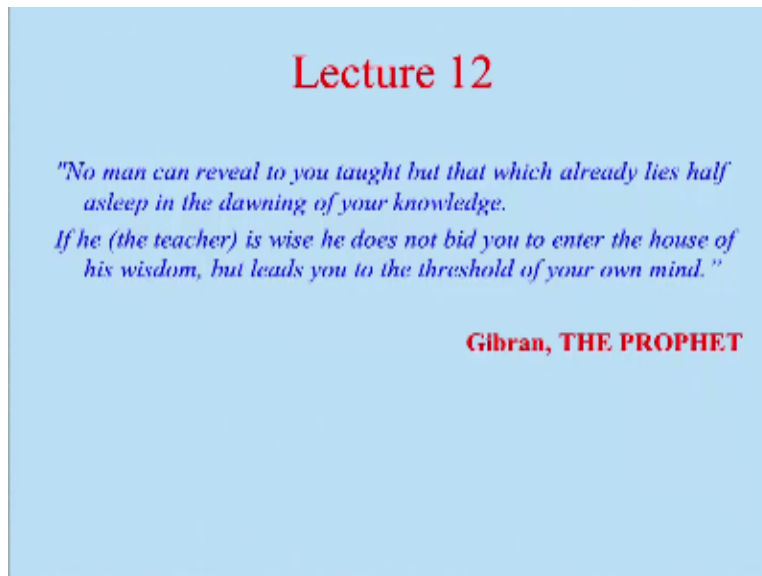
**Course Title
Engineering Thermodynamics**

**Lecture – 12
thermodynamic Properties of Fluids 5**

**By
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So let us start this lecture a thought process from a very great person Gibran.

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And who says that “No man can reveal to you taught but what which already lies have a sleeve in the dawning of your knowledge. This is similar to what the thought process in our Vedas are there the knowledge lies in your mind already. And if he the teacher is wise it does not bead you to enter the house of his wisdom, but leads to you to the threshold of your own mind.” That is a very important statement and then you should keep in mind that we always trust upon our things on the others, but rather we should help people to realize their own potential.

So before you know we will now recall what we learnt in the last lecture we basically looked at, you know data tables for example like superheated steam table and saturated temperature table and saturated pressure table and also seen how to use those data for you know and evaluate it and if it is not available the data, and then we can interpolate using linear interpolation or you can extrapolate also if it is required. And we have looked at if compress you know liquid table for the properties is not available you can use the saturated temperature data table.

And we have looked at all so the equation of state and we discuss in the last lecture like ideal gas which you are familiar with, but we looked at you know range of pressure and temperature under which one can apply it under what condition you should not apply because it will incur error.

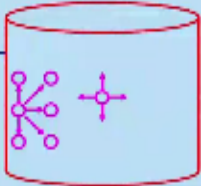
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What do you mean by Real Gas?
Molecular forces of attraction; Molecules have a definite size.
Clausius equation state:
Free volume available for molecular motion = $\hat{v} - b$
b = Measure of volume occupied by gas molecules.

$P(\hat{v} - b) = R_u T$

Van der Waals' Equation of State: (1873)

$$P' - P = \frac{a}{\hat{v}^2}; P' = \left(P + \frac{a}{\hat{v}^2} \right)$$

Wall — 

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

P = observed pressure,
P' = Pressure by gas in absence of attractive force
a and **b** are van der Waals constant.

Now we will look at that other equation of states what people have this thing. Now we need to ask you know like what you call whether this what do you mean by real gas and then because the I earlier that equation of state was basically used for ideal gas. So we know that molecular forces of attraction do exist between among the molecules are between molecules and molecules have a definite size right, and we cannot really neglect those things and particularly at a high pressure and low temperature.

And keeping that in view the Clausius he proposed a equation of state in which case he say that like molecules will be occupying certain amount of volume. So then he proposed he made a correction like that free volume available for a molecular motion in a container or any other

things will be $V - b$ instead of simply V right. And then b is basically a measure of volume occupied by the gas molecules and as it is occupied then the total volume of the container minus that, that will be the, for we you know which will be, you know available for the molecule to move around.

So then he modified the ideal gas law in this form and that is basically known as the what you call the Clausius equation of state this is the Clausius equation of state right. So in later on you know like Van der Waal who proposed another equation of state in 1873, and he modified the pressure term and considering that he assumed that in a container like a in the molecules if it is at the center like here, it will be you know acted upon by other molecule their forces will be in balance you know this molecules.

Whereas if it is nearby to the wall what will happen and that will give me the pressure which will be bumping into the wall, but however these molecules will be attracted by you know by the upper portion any molecule will be there or this portion are also sideways layers whatever it will be the adjacent layers. Of course it is a ideal situation, you know like where they layer we are talking about in real situation you can think of it will be attracted.

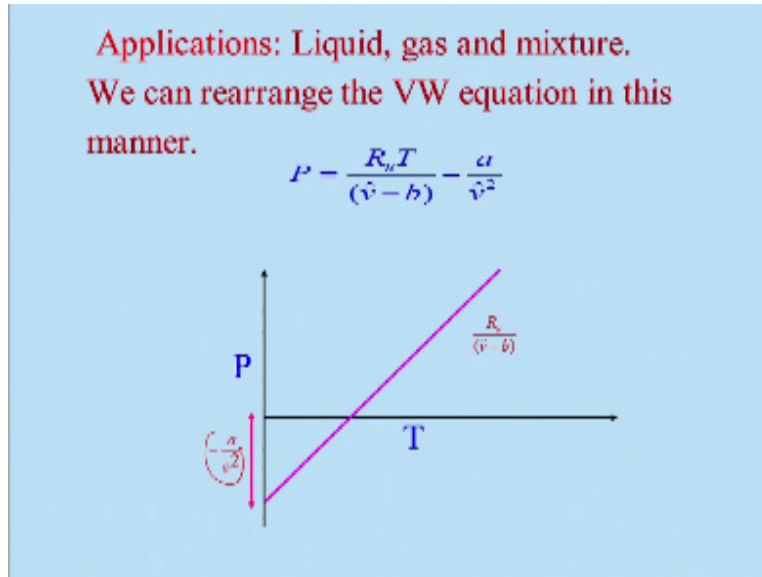
But the other side on the wall there is no attractive because nothing is there near the wall no other molecules of the, you know if you consider any fluid it would not be there, because there is a solid surface. So as a result he says that pressure, you know whatever it is like you will be basically the change in pressure $P' - P$ will be inversely proportional to the specific volume and then he put a constant. And then the pressure what will be acted upon, you know is equal to the, this is the, what you call ideal pressure and this is the correction what he has done.

And then when I apply this thing here in the equation of state I will get a relationship like this which is nothing but $P + (a/v^2)(v-b) = R_u T$. So this equation is basically known as the Van der Waal equation and keep in mind that P' is the pressure of gas in the absence of attractive forces particularly you can think of ideal gas pressure if you know ideal gas law pressure or ideal gas pressure, and P is the actual pressure by the real gas.

So this equation if you look at it is a little complex and question arises how to evaluate this A and V now which are constants Van der Waal gas constants and how to go about it as of course one can conduct experiments and do that we can vary the pressure, you can vary the you know

temperature, particular volume. So if you do that one can really find out is not it. If I take a specific you know, volume particular volume I go on changing the pressure and then temperature will change right and then we can evaluate.

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So and these Van der Waal equations you know can be applied not only for the gas alone, but also for liquid and the mixture of gas and liquid this can be applied. But ideal gas law is only valid for the gas okay. So we can rearrange the Van der Waal equation in the manner like this I can write down p is equal to what we call $R_u T / v - b - a / v^2$ right this is specific volume what I am saying V .

And if I plot this, you know pressure versus what you call the temperature I can get a straight line is not it because if I assume this volume is remaining constant I can conduct experiment and then that what you call this intercept and also the what you call the slope will be nothing but $R_u / v - b$ right sometimes I call this v as v okay new Kappa, Kappa v and the intercept is nothing but $-a / v^2$ if I obtain this thing if I know this R_u of course universal gas constant you know and this volume we are keeping constant in the experiment I can calculate very easily or I can determine the b very easily.

And similarly from this term right I can get this a constant right values because this I will get these values and then I will get this a over here. So I can get those constant and use the equations right.

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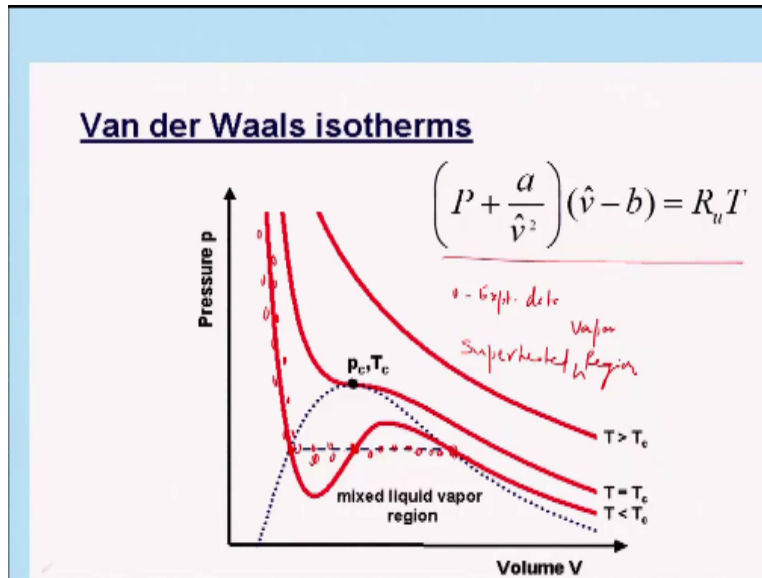
van der Waals Constant (a, b)

Gas	Constant <i>a</i> kPa (m ³ /kmol) ²	Constant <i>b</i> (m ³ /kmol)
Air	135.8	0.0364
NH ₃	423.3	0.0373
CO ₂	364.3	0.0427
H ₂	24.7	0.0265
N ₂	136.1	0.0385

And if you look at this Van der Waal constants are, you know are given here in this table you can note that the air is something 135.8 right, and whereas you look at the ammonia is very high in this case 423 and hydrogen interestingly is very low right. And similarly in this case it is low, but all these values are of course similar or if you look at 0.0364 and then this thing. If you look at this b what did b indicates, b indicates the measure of the volume occupied by the molecules right.

And of course the carbon dioxide is little heavier molecule therefore it is higher right. And if you look at the hydrogen being a lighter gas, you know like if look at is having a low attractive forces A indicates that how much attractive forces you know will be that will be dictated by that and it is low and whereas the ammonia is having a high values.

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So I mean let us look at you know these things Van der Waal equation and in this case what we will be doing, we are basically look at this equation and you can see from this equation that basically the P, you know volume wise it is a cubic you know cubic equations volume wise right. And then if the temperature is greater than T_c it is really you know one kind of things otherwise it will be having this cubic equation here when temperature T is less than T_c it is having you know three values one is here one can think of and then another is here right, if you look at and another is here.

Now that is the prediction for when T is less than T_c , but is it right because that this equation, this line is predicted by Van der Waal equation right. But now if you conduct experiment it would not replicate the values where you know it is this is having it is going down and then, you know pressure again going up and then reach, you know maximum value again going down you know this is basically weight mixtures liquid and vapor mixtures where it is not working.

And if you look at this is a prediction, but actual experimental data will be somewhere, you know like that these are my experimental data you know like you can say that these are experimental you know data. Now it is not so therefore you know the this solution one should not really take this rather wants to take go by the experimental datas and experiment data says that pressure, you know is remaining constant at the pressure at this pressure you know the temperature saturated temperature will be remaining constant, because vaporization process is taking place right.

So therefore one has to, you know careful about using this kind of thing and then from the stability point of view we are not discussing that one can say that this portion of the curve is not really possible in reality right. So therefore we will describe this portion however in this region and this region it is working fine and this is Van der Waal equation will be working in this region well and till up to $T=T_C$ that is isotherm you know like will be working.

And you will also find that in this region I am like you know it won't really work much as you go along we will see but we are in the superheated raise him like this is your superheated region right way were region right so in this it will be what you call doing well so every equation of state must satisfy the following condition.

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Every equation of state must satisfy the following conditions.

- $P \rightarrow 0$; It must reduce to the Ideal Gas Law.
- The critical isotherm must have an inflection point.

What are those that is the when pressure tending towards 0 it must reduce to a ideal gas law right when pressure is very, very small right then ideal gas law should be valid whatever equation of state you see for example we have seen the van der Waals equation of state that is a one condition and we said the critical isotherm must have an inflection point so what is that inflection point if you look at that this is my inflection point you know slope is changing here are you

getting the slope is changing here this is my inflection point the critical point should have an inflection so that should be satisfied and n critical point.

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Every equation of state must satisfy the following conditions.

- $P \rightarrow 0$; It must reduce to the Ideal Gas Law.
- The critical isotherm must have an inflection point.

Critical Point: Highest P & T at which liquid & vapor phases coexist in equilibrium.

$$\left(\frac{\partial P}{\partial v}\right)_{T_c} = 0, \left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c} = 0$$

The highest pressure and temperature at which is liquid and vapor phase coexist in equilibrium that we have seen that means you know in that critical point that you know what will be the condition what has to be valid or what has to be satisfied is ∂P by ∂V see when temperature is constant that is the critical temperature is equal to 0 not only the first gradient rather the second gradient also will be equal to 0 and this condition has to be satisfied you know at the critical point so questionnaire ages we have seen that how you can evaluate.

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Q: How can we evaluate values of a & b?

$$\left(P + \frac{a}{v^2}\right)(v-b) = R_u T \quad \Rightarrow \quad p = \frac{R_u T}{(v-b)} - \frac{a}{v^2}$$

$$\Rightarrow \left(\frac{\partial P}{\partial v}\right)_{T_c} = -\frac{R_u T_c}{(v_c-b)^2} + \frac{2a}{v_c^3} = 0$$

$$\Rightarrow \frac{2a}{v_c^3} = \frac{R_u T_c}{(v_c-b)^2} \dots\dots\dots(1)$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c} = \frac{2R_u T_c}{(v_c-b)^3} - \frac{6a}{v_c^4} = 0$$

$$\Rightarrow \frac{6a}{v_c^4} = \frac{2R_u T_c}{(v_c-b)^3} \dots\dots\dots(2)$$

The you know conduct experiments and then but let us look at how we can evaluate analytically so with the van der Waal equation we can rewrite that in terms of pressure you know just this thing that pressure is equal to $R_u T$ divided as $V - V - a$ by V^2 and then I can what do you call I what you can take a derivative of this expression with respect to the specific volume while keeping the temperature I can get that is ∂P by ∂V at T_C is equal to $- R_u T_C$ divided by $V_c - c - b^2 + 2a / vq$ at of course the critical point we are evaluating.

So therefore I am putting the you know specific volume at critical point and then we can also you know take the second derivative of this things of the pressure and we will answer so from this expression like we can get to a why week ($q_c = R_u T_C / V_C - b)^2$ and what we will do now we will take the second derivative of the pressure and from this expression and we will get is the second derivative of the pressure with respect to the specific volume at constant temperature or the critical temperature.

Is equal to $2R_u T_C / V_C - B$ holds $q - 6ay$ and new for at critical condition is equal to 0 from this expression we can get a relation between the you know $6ay$ new 4 is equal to the $2R_u T_C /$ specific

volume at critical condition - B^3 so from this using this what you call equation one and two we can get the V_c see is nothing but $3v$ right.

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Solving Equations (1) and (2), we can get;

$$\hat{v}_c = 3b$$

By substituting values of \hat{v}_c in equation (1) we get

$$\frac{a}{b} = \frac{27}{8} R_u T_c$$

But we know that,

$$P_c = \frac{R_u T_c}{(\hat{v}_c - b)} - \frac{a}{\hat{v}_c^2} = \frac{R_u T_c}{2b} - \frac{a}{9b^2}$$

That is a very important relationship that specific volume is equal to 3b we are evaluating at the critical condition and by substituting these values in equation 1 we can get a by B is equal to 27 by 8 $R_u T_c$ and but we know that like that p_c the pressure at the critical condition will be nothing but are $R_u T_c / V_c - V - a$ by V_c^2 and what we will do we will basically you know we will use this expression V_c is equal to $3b$ like we can find out that this is nothing but your $3b$ and that became to be and what do I mean that became to be and then in place of this we see I can also use this is nothing but your $9b^2$ and then that will get expression.

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$$p_c = \frac{R_u T_c}{2b} - \frac{a}{9b^2}$$

$$p_c = \frac{R_u T_c}{2b} - \frac{27 R_u T_c}{72b} = \frac{R_u T_c}{8b}$$

$$\frac{a}{b} = \frac{27}{8} R_u T_c$$

$$b = \frac{R_u T_c}{8 p_c} \Rightarrow a = \frac{27 R_u^2 T_c^2}{64 p_c}$$

Note, a & b can be evaluated by measuring P_c & T_c

At the critical point,

$$\frac{P_c v_c}{R_u T_c} = Z_c = \frac{3}{8} = 0.375$$

= Compressibility factor

' Z_c ' is considerably higher than actual value of any substance.

And if you look at we have already seen p_c is equal to this we have already seen that and ab by 27 by $8 R_u T_c$ and then we will use this expression and are you T_c by to be in place of a you know this expression we can use this a be in this we can use a be here and from this expression we can use and I will get basically $27 R_u T_c$ by 7 to be and then when you simplify will get $R_u T_c / 8 b$ and from this expression you know from this I can get b is equal to $R_u T_c / 8 p_c$ and knowing this thing.

And also using this expression ab / b I can get this relationship which is nothing but a $27 R_u^2 T_c^2$ divided by 60 for p_c and if you look at if I know this what you call critical temperature and critical pressure I can evaluate a for a particular substance right and of course if I know this a I can find out also the b right a similar manner and if you look at if I and at the critical point if I know this volume space volume and p_c and T_c if I put these values I will get this we call it as a compressibility factor.

Right which will indicate how much you know it is deviate from the ideal gas law that is nothing but 3 by 8 or 0.375 right this is the condition what will be getting and the Z_c is considerably higher than the actual value of any substance but this will be you know true for that and as it will be this will be deviating from the what you call the values and we'll be discussing more about this compressibility factor whenever we are discussing how to use the ideal gas law and make a correction for this compressibility factor.

So that you can use ideal gas law very easily for real gas beside this there are several number of what we call ideal number of equation of state being device for treating the for dealing with the real gases so one of them is Betty and breathe man equation of state which was being proposed by these two persons in 1928 and that is basically.

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Beattie-Bridgeman Equation of State (1928)

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

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

The constants are given in Table for various substances. It is known to be reasonably accurate for densities up to about $0.8\rho_c$.

If you look at that is p is equal to $R_u T / V^2$ into $1 - C/V$ into T and multiplied by $V + B - a/V^2$ so if you look at in the van der Waals equation there are two constants in this case how many constants there are total three constants a, B, and C capital A, B, and C right and small C so whereas a is equal to $a_0 (1 - AB)$ by new and b is equal to $b_0 (1 - V/V)$ so if you look at now this constant actually the constants are inside constant so therefore total whatever you could see is you know total five constants like.

If you look at B_0, A_0, B and C so there are total basically five constants for this as compared to the van der Waals equation so these constants can be obtained you know like for various substances people have found out and given a tabular form and you can use and this you know equation can be used reasonably you know till the densities up to the point eight of the critical density that means when around critical point you cannot apply this equation right it will be away from the critical point where you can apply this equation and with reasonable accuracy.

So these are the data table one can think of the total you know what you call five constants are being given here and for various substances and these substances will be varying you know.

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Beattie-Bridgeman Equation of State (1928)

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

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

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

Gas	A_0 $\left(\frac{Pa \cdot m^3}{mol^2} \right)$	$B_0 \times 10^6$ (m^3 / mol)	$\alpha \times 10^6$ (m^3 / mol)	$b \times 10^6$ (m^3 / mol)	c $\left(\frac{m^3 \cdot K^2}{mol} \right)$
Air	0.1318	46.11	19.31	11.010	43.40
Ammonia	0.2425	34.15	170.31	19.112	4768.70
n Butane	1.8030	246.20	121.61	94.230	3500.00
CO	0.5073	104.76	71.32	72.350	660.00
Ethane	0.5958	94.00	58.61	19.150	900.00
Helium	0.00219	14.00	59.84	0.000	0.04
Hydrogen	0.0200	20.96	5.06	43.590	5.04
Methane	0.2307	55.87	18.55	158.700	128.30
Nitrogen	0.1362	50.46	26.17	6.910	42.00
Oxygen	0.1511	46.24	25.62	4.208	48.00
Propane	1.2078	181.00	73.21	42.930	1200.00

Like different values for example air is aA_0 is 10.1318 and whereas you know you can get butane which is 1.8 very high values right and of course helium is having a very small value so it varies a lot I am similarly be not also like butane is the having highest value here and here of course 46.11 so one has to be careful about this not only the values and also the what you call their units is very important so that one has to be careful about using this equation of state and let us look at Benedict where Ruben equation of state which was given in 19 you know.

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Benedict-Webb-Rubin Equation of State (1940)

$$P = \frac{R_u T}{\hat{v}} + \left(B_0 R_u T - A_0 - \frac{C_0}{T^2} \right) \frac{1}{\hat{v}^2}$$

$$+ \frac{b R_u T - a}{\hat{v}^3} + \frac{a \alpha}{\hat{v}^6} + \frac{c}{\hat{v}^3 T^2} \left(1 + \frac{\gamma}{\hat{v}^2} \right) e^{-\gamma/\hat{v}^2}$$

Eight constants are given in Table. This equation can handle substances at densities up to about $2.5\rho_{cr}$.

In 1962, Strobridge improved this equation by using 16 constants

Redlich – Kwong Equation of State:

A more accurate and simple equation of state

$$P = \frac{R_u T}{(\hat{v} - b)} - \frac{a}{\hat{v}(\hat{v} + b)T^{0.5}}$$

a and b are evaluated from T_c & P_c

$$a = 0.4278 R_u^2 T_c^{2.5} / P_c \quad b = 0.0867 R_u T_c / P_c$$

40 and this is having a very what you call a little more complex equations and having this so are you if you look at the first term if you look at in each equation will be similar you know are you T by nu plus there is another lot of you know other terms are there and having you know this is the first term and this as the second term and the third term for term fifth terms you know like kind of things and having lot of constants so this 8 constants are given in this you know and this equation can handle substance a dense ease up to 2.5 of the critical density right.

That means this is a little better than the earlier equation of state and of course the 1962 Rubin improved this equation by using 16 constants you not like and there might be several others which are having more number of constants and there is a you know the table which you can see in the textbook and other books also you can use those table I am not expecting that you should remember this equation is not that easy to remember but however you should know how to use and where to use.

That is important and there is another equation which is the rate Hong equation of state and it is more accurate and simple equation of state and it is used very you know what you call profusely by the chemical engineering people to handle the mixtures which is you know simple very simple like if you look at it is similar to that of the van der Waal equation it is the P is $R_u T$ divided by $\eta - b$ and $-a$ divided by V into again multiplied by $b + b$ and $T^{2.5}$ so if you look at it is similar but not same and a and b are evaluated from the you know critical temperature and pressure and this is the relationship what is given here and keep in mind that you need not to remember this thing also a is equal to $0.427R^2$ that is universal gas constant and $T_c^{2.5}/P_c$.

And similarly B is relations are given so if you can note that a B is basically dependent on the P_c and T_c and you can get the table for the critical temperature and pressure and you can evaluate very easily so therefore there is no need to have table. If you know the data for the critical pressure and temperature for a particular substance you know you can evaluate very easily this constant.

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Virial Equation of State:

The equation of state can be expressed in a series form. *Ideal gas law*

$$\frac{P\hat{v}}{R_u T} = 1 + \frac{B(T)}{\hat{v}} + \frac{C(T)}{\hat{v}^2} + \frac{D(T)}{\hat{v}^3} + \dots$$

Where, B, C, D, are known as 2nd Virial constant (VC), 3rd VC etc.

VCs describes how it is different from ideality. The P-v-T data can be improved by including more VCs. The expt. value of 2nd VC for number of gases are available. The value of 3rd VC is not known for several gases. The Virial and ideal equation of state have a strong theoretical base.

So beside this if you look at there is a you know people are always very much what you call interested to have a simpler form of the equation of state similar to the ideal gas law, so they thought that why not you use extend that ideal gas law and people have done that extended the ideal gas law and putting lot of you know what you call series form I am expressing it in a series form and that is the equation what we call $Pv/RuT=1$.

And then there are several you know kind of thing if you look at it similar to your other series which you might have used like your binomial cities or the tailors is not that way but at least series why I am saying so $B(T)/\eta + C(T)$ what you call velocity square and $D(T)$ velocity q and these are all what you call constant which is a function of temperature you need to you know evaluate that or in a tabular form.

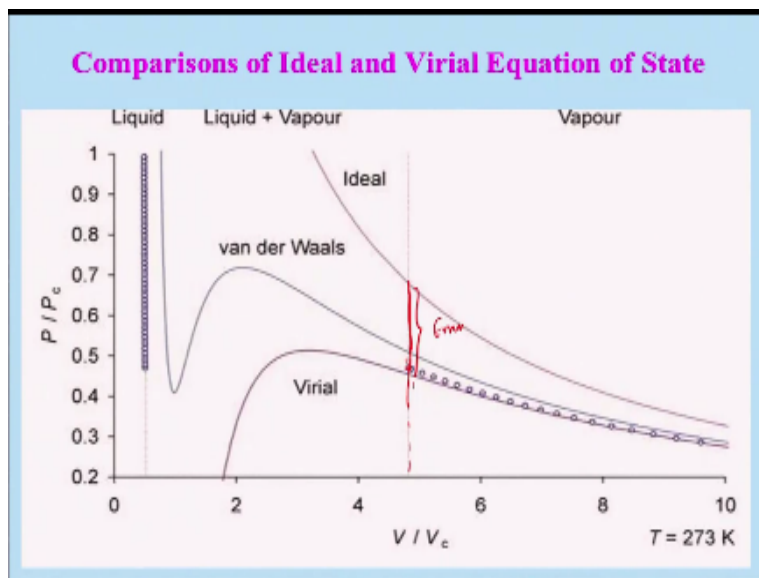
So if you look at if I will you know neglect this terms you know these terms this is this or in other words the first term this term is nothing but what your ideal gas law right, so this is your ideal rest of the things you are doing some my addition so that it will be more correct one or the accuracy will improve as you go for the higher pressure and low temperature gas is standard and where the B and C and D are known as the second you know virial constants and the third and fourth and respectively or like that.

And we see basically this virial constant escape how it is different from ideality because ideal is this one right, and then as you go on and then you know you add the accuracy of that and PVT data can be improved by including more number of this virial constants. But experimental values

for the second virial constant for number of gases are available but the third and fourth one are not available so you know you people are working on that they may having and the virial and the ideal gas law would you know state have a strong theoretical base.

For example like you know whatever the equation i have shown for the real gas except the Van der Waals like your Benedict equations and then Redlich-Kwong equation and Rubin equations and other things they are having know what you call theoretical basis they are a semi empirical relations see what people have done but whereas it is having, so therefore people do use it and to improve because so I just make a comparison how good it is you know.

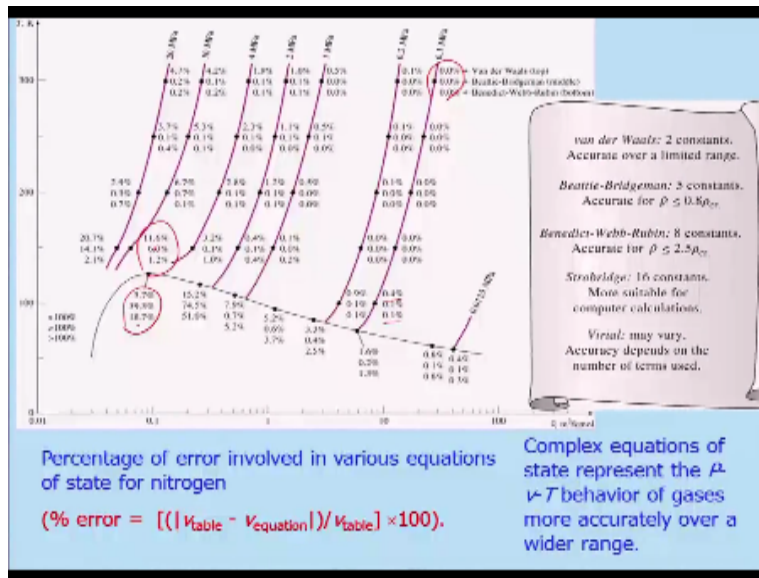
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If you look at that this thing if you look at the virial equation will be here you know when this parted P/P_c V/V_c at a temperature 273 and these are experimental data right, and the venerable equation lying very close you know if you look at a higher this well volume ratios it is almost closed but ideal gas law is far out that means if I consider this one you know error will be too much error will be this much error this will be an error you know when he use the ideal you know gas law instead of actual and because experiments all this and experiment is very close to the virial equation therefore one can think of using that.

But if you are in this resume IAM okay, I am like one can use but little bit error will be there, so therefore one has to be careful when you are using the vertical the gas laws.

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So as I told that van der Waal equations having to constant and accurate over a limited range and betty and breathe man five constant which is accurate you know for when the density is less than the 0.8 critical density and Benedict Webb and Rubin equation 8 constant accurate when the ρ is less than equal 2.5 critical density and Strohbridge is equation16 constant more suitable for computer calculation because hand calculation is difficult you know to add.

And of course the virial equation may vary depending upon how many terms you are taking extra than that of the first terms are the coefficients you are considering and if we look at the that means you know percentage of error involved in various ways one can evaluate table you can use equation instead of a table. You can look at from here you know these are the of course the saturated vapor line and you can see that van der Waal equation you know first one is a very, very low you know like very less percentage and all are giving the good result in this range.

But as you are coming closer to the this saturated line you see that van der Waal is giving something 0.4% you know and whereas these are 0.1. But if you go to the you know this is the low pressure what is happening but if you go towards the higher pressure and this is the critical point here you find that error is very, very high in the van der Waal equation give 11.6% and 6.3% and this is 1.2% you know like that is the Benedict wave and Rubin bottom one.

So similarly you know like there are I am sorry actually so the other way around like you know this point is basically 7.3% give the van der Waal equation because all are evaluated at the what you call critical point whereas the Bearrie and you know Bridgeman will give you 59.3 fifty and Benedict and Rubin is this a very little bit improvement will be there right, if you look at these are the things which you will be talking about.

But however you are nearby you know it gives you know like that you know Van der Waal equation gives more percentage kind of things like for example if you consider this point you know like it gives the 11.6 the van der Waal and Bearrie and Bridgeman is 6.3 and 1.2 it gives the Benedict and Rubin kind of things away from the critical point.

So if you look at one has to see where you know to apply and which condition like and then one can use the equation of state otherwise if where not you know what you call having the resume where you can apply the equation of state either the van der Waal or any other equation of state you need not use rather go for the steam table or the any other table for example refrigeration represent tables are efficient table kind of things.

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Example : 1 kmol of NH_3 is contained in a 0.6 m^3 at
 $T = 200^\circ\text{C}$. Estimate the pressure developed
by the gas by (a) Ideal gas law
(b) Van der Waals equation
(c) Redlich-Kwong equation of state.

Solution: $N = 1 \text{ kmol}$, $V = 0.6 \text{ m}^3$,
 $T = 473.15\text{K}$, $R_u = 8.314 \text{ kJ/kmol K}$

$$P = \frac{R_u T}{\hat{v}} = \frac{8.314 \times 10^3 \times 473.15}{0.6} = 6.5563 \text{ MPa}$$

So now let us take an example just to illustrate this point that which one has to choose, so for example 1 kilo mole of ammonia is contained in point 6m^3 at temperature of 200°C we need to estimate pressure developed by the gas using the ideal gas law and Van der Waal equation and Redlich-Kwong equation of state, so if you look at the number of moles is given one kilo mole and volume is given temperature is given we know the universal gas constant right, so and we can find out pressure very easily right $p=R_u T / \hat{v}$ is nothing but volume per unit mole, so if we substitute these values you are getting 6.55 you know or 6.56 mega Pascal around.

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(b) Van der Waals Equation:

For NH_3 , $a = 423.3 \text{ kPa (m}^3/\text{kmol)}^2$

$b = 0.0373 \text{ m}^3/\text{kmol}$

$$\begin{aligned} P &= \frac{RT}{\hat{v} - b} - \frac{a}{\hat{v}^2} \\ &= \frac{8.314 \times 473.15}{0.6 - 0.0373} - \frac{423.3}{(0.6)^2} \\ &= 5.815 \text{ MPa} \end{aligned}$$

And if I will you know van der Waal equation will use ammonia you know from the table I will get this a is 423.3 kilo Pascal's and b is 0.373m³/kmol and what I will do like I will substitute these values in the van der Waal equation and what you call this is basically are you universal gas constant and temperature I know this universal gas constant and this temperature is given and this is the volume is given and this is the correction for the volume is given that is nothing but your b and this a is known and then this volume is known you will get 5.815 mega Pascal if you look at it is different than the ideal gas law.

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(c) Redlich – Kwong Equation of state:

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

$$\text{where, } a = 0.4278R^2 \frac{T_c^{2.5}}{P_c}$$

$$b = 0.0867 \frac{RT_c}{P_c}$$

$$T_c = 405.6K, P_c = 11.277MPa$$

So let us look at Redlich and Kwong equation of state and we can evaluate you know a values here and we know this T_c we can find out corresponding to the ammonia and so also the P_c and we can this happens to be you know 405.6 kelvin and P_c this thing.

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$$\begin{aligned}
 a &= \frac{0.4278 \times (8.314)^2 \times (405.6)^{2.5}}{P_c} \\
 &= 8687.85 \text{ kPa} \left(\frac{\text{m}^3}{\text{kmol}} \right) \\
 b &= \frac{0.0867 \times 8.314 \times 473.95}{11.27 \times 10^3} = 0.0259 \text{ m}^3 / \text{kmol} \\
 P &= \frac{8.314 \times 473.95}{0.6 - 0.0259} - \frac{8687.85}{0.6(0.6 + 0.0259)(473.15)^{0.15}} \\
 &= 5.7885 \text{ MPa}
 \end{aligned}$$

And when you substitute these values right, you will get the a and b from there and if you find out this 5.7885 mega Pascal see if you look at three different pressures you are getting from using this now one has to also worry about like you know that which one has to be used right so of course in this problem we are not you know worried about what is but I am saying that this pressure evaluated by different equation state is basically is different.

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Compressibility Chart:

Ideal gas law is quite simple and elegant to use.

But it holds good, only for low density of gases.

Z = Compressibility Factor

= (Actual Volume / Volume of Ideal Gas)

$$Z = \frac{\hat{v}_{actual}}{\hat{v}_{ideal}} = \frac{\hat{v}}{(R_u T / P)} = \frac{P \hat{v}}{R_u T}$$

For Ideal gas Z=1(Low Pressure & High Temperature)

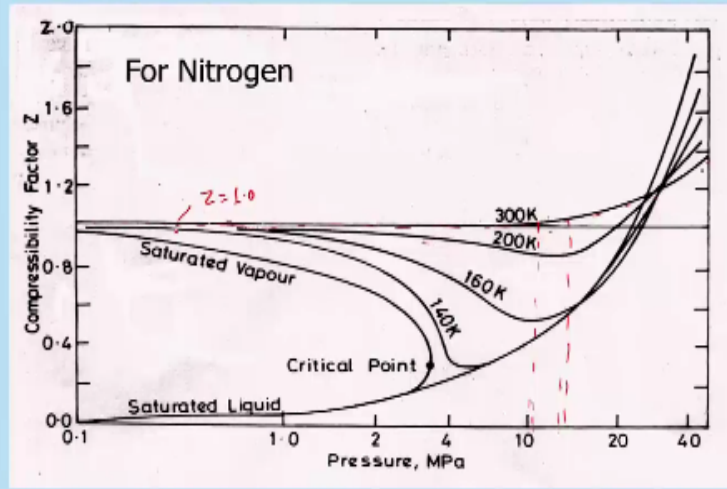
$$Z = f(P, T)$$

So what we have done till now you know like ideal gas law is a you know being used profusely and ideal gas law is being used prophecy because it is quite simple and elegant to use but it holds good only for the low density gases or basically the low pressure or the high temperature gases right. So now as we have defined you know a compressibility factor which is basically the ratio of actual volume divided volume occupied by the ideal gas.

If we assume the gas to be ideal the volume will be occupied that we call it as a you know volume of ideal gas. So if I you know use these factors you know V actual per of course this volume is the per unit mole then this is the ideal I can use this ideal gas law and I will find out Z is nothing but P into $\hat{v} / R_u T$ and this factor if it is equal to 1 what will happen if Z is equal to 1 that means it will be same as that of the ideal gas law and if for a particular you know this thing then you know ideal gas law will be valid. And basically if you look at Z is a function of what pressure and temperature right and what will do.

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Compressibility Chart



We will have to look at that you know compressibility factor if we will plot versus you know pressure and for different temperature let us say nitrogen I have considered right and if you look at if I take this 300 Kelvin you know this line is here and after that it goes on increasing right and if I take this is your saturated vapor line right and this is a critical point this saturated liquid line at different temperature it will be like that you know this goes on.

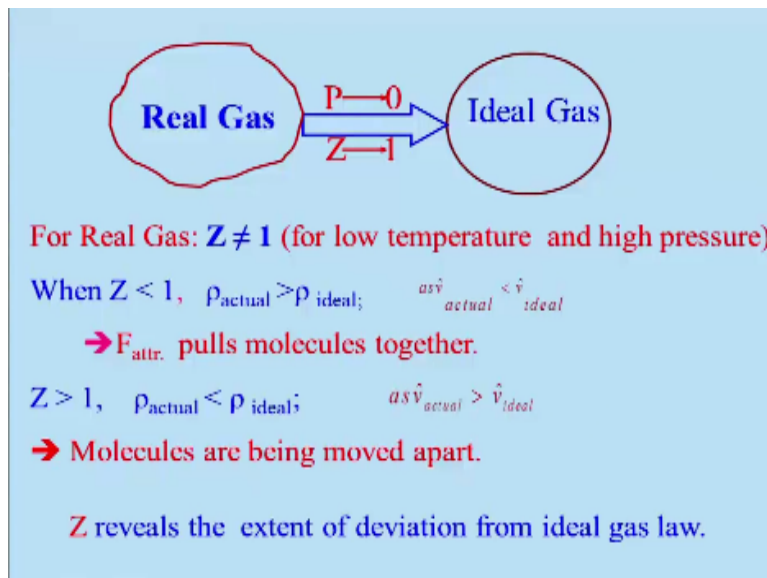
Now from this plot one can say when I can use particularly if you consider nitrogen you know and nitrogen percentage in the air is quite hot you can consider the air will be behaving similar manner that of this compressible chart for nitrogen right from this plot looking at if my temperature is ambient right then at what pressure I can use the ideal gas law can anybody tell me look at this you know chart and tell me the what I will have to do we will have to see that where the Z is you know equal to our closer to one.

For example if I take 300 Kelvin right 300 Kelvin that means I can think of using here very happily you know something around 10 kind of mega Pascal's I can use very happily ideal gas and 300 if I increase the temperature let us say 2000 Kelvin in the combustors in the you know other places it may occur right what will happen I can happily use ideal gas law are you getting my point means 100 atmospheric pressure roughly it is good now if I will have you know I can go little further also maybe till this if it is I am not bother about that much of error let us say you know something around 5% then I can that means safely one can use hundred atmosphere for air at ambient condition.

If it is of course the lower one then one has to worry if I talk about lower temperature you know then you one cannot use it because it can go for a low-pressure for example 200 Kelvin you know it is error if I use your Z will be here somewhere right jade is away from the one and of course if I going towards the lower pressure it is reaching it is reaching this Z is equal to 1 because this is Z is equal to 1 okay.

So therefore at a lower temperature I can I will have to go to the lower pressure and ambient temperature for air or the nitrogen then I can go for the higher pressure around roughly 100 you know atmospheric pressure now this chart will be different you know for the different kind of materials different kind of nitrogen you know what you call oxygen helium hydrogen now how to go about it if we will have to use several chart then it is the problem. So right the real gas will be you know what you call become ideal gas.

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Only when Z is closer to one and as I told for real gas jade is not you know will be different than one when Z is less than one that actual density is greater than the ideal because the specific you know volume of actual is less than the ideal specific volume and when the attractive forces pulls the molecule together right, so that you can have this situation and when Z is greater than one then actual density is less than ideal because the specific volume of actual is greater than the specific volume of ideal.

In this case molecules are moving a part that means molecules are going away from each other. So the Z dribbles basically extent of deviation from ideal gas law like that indicates how far it is from the ideal gas law.

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Law of Corresponding States: All gases when considered at same value of P_R and T_R will have the same value of compressibility factor, Z .

Let us define, reduced parameters

Reduced pressure, $P_R = (P/P_C)$

Reduced Temperature, $T_R = (T/T_C)$

Reduced Volume, $\hat{v}_R = \hat{v}/\hat{v}_C$

where P_C, T_C , and \hat{v}_C are pressure, temp and Sp. volume at critical state.

And as I told that all gases when considered as I told earlier that you know each gases will be having their own compressibility chart then it will be difficult what people have found out that all gases when considered at the same value of the reduced pressure or temperature will have the same compressibility factor what is that reduced pressure reduced pressure is basically what they say that one can think of using the critical condition that is pressure / critical pressure will give me the reduced pressure and the temperature / critical pressure will give me reduced temperature.

And similarly the reduced volume and rate then when they found that all gases are now you know if you are what you call taking with reference to the critical conditions the properties the pressure temperature and volume using the reduced pressure reduced temperature and reduce volume then all these things are coming into one plot, so therefore you know it is this is very important.

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Generalized Compressibility Chart:

$$Z = Z(P_R, T_R)$$

From the Generalized Compressibility Chart

$$Z = 0.27 \text{ at } P_R = 1.0, T_R = 1.0$$

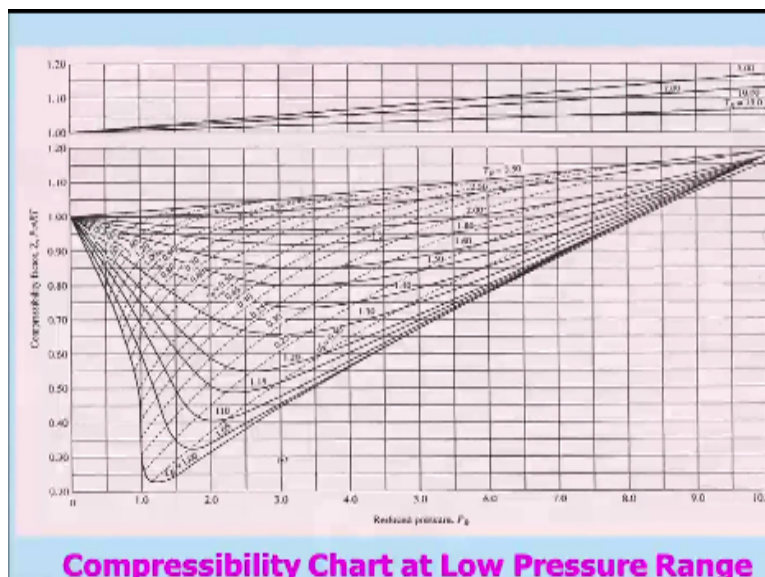
=> $Z_C = 0.27$ for all substance

Z_C of several substance varies from 0.23 – 0.33

Hence it is not very accurate.

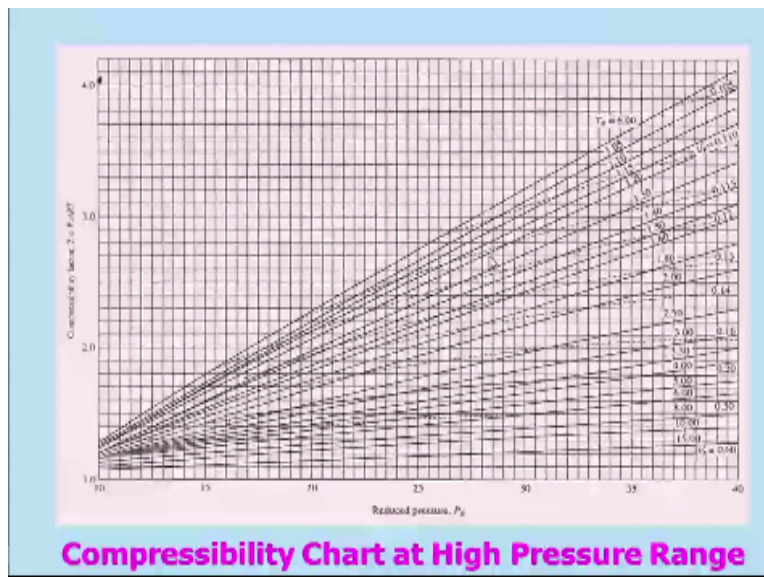
So generally is compressibility chart if you look at Z is equal to basically function of the PR and TR and if you look at Z at PR is equal to one and TR is equal to one Z is around to be 0.27 for all substances right but unfortunately because we are all defining that way with respect to their corresponding critical temperature and pressure but Z values will be varying from 0.23 to 0.33. So therefore there is a deviation in that that means if you is that you will be making some error as well right. So hence it is not very accurate but however if it is it is being used because of its simplicity.

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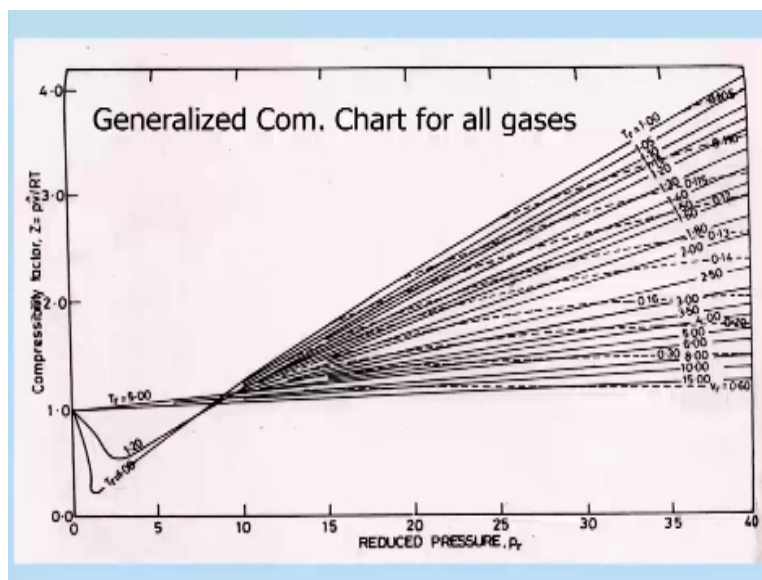
And if you look at the compressibility chart will be looking like that here this is for the low pressure of 10 you know kind of thing reduced pressure is 10 times that of the critical pressure you know actual pressure is 10 times that of the critical pressure you know at different TR values is being plotted you know like these are corresponding to TR values, so this is PR right.

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So these are basically TR values which is being used right and of course at the you know when Z is greater than one this is being so on right and this dashed line is basically the specific volume if you look at this dashed line VR 0.5, 0.253 and other things goes on the ER pseudo space what you call critical or the reduced volume pseudo reduced volume similarly you can get that the higher pressure range and in the tutorial class will be using this you know compressible chart we evaluate the data and finding it out.

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So this is generalized when you combine both low-pressure and high pressure you will be looking like that you know if you look at with the 10 I have magnified you know that portion I have seen this is the low pressure and the high pressure region right you can look like this is a generalized compressible chart for all gases right.

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EX: 1 kmol of NH_3 is filled 0.6 m^3 vessel at 200 $^\circ\text{C}$.
Determine P in the vessel using generalized compressibility chart.

Ans: $T = 200^\circ\text{C} = 473.15 \text{ K}$, $V = 0.6 \text{ m}^3$,
 $n = 1 \text{ kmol}$. We have to find out P.

For NH_3 , $T_C = 405.6 \text{ K}$, $P_C = 11.277 \text{ MPa}$

$T_R = (T/T_C) = (473.15/405.6) = 1.17$

Since P is not known, P_R can not be determined. But we can express P in terms of P_R as;

$$P = P_R P_C = 11.277 \times 10^6 P_R \quad (1)$$

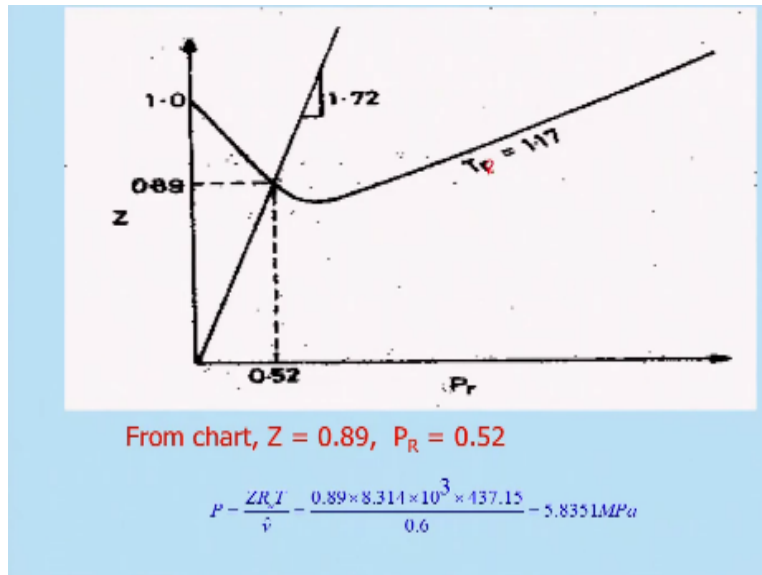
$$Z = \frac{P\hat{V}}{R_u T_C} = \frac{11.277 \times 10^6 P_R \times 0.6}{8.314 \times 10^3 \times 473.15} = 1.72 P_R \quad (2)$$

What we will do we will take one example then we will this thing 1 kilo mole of methane is filled with 0.6 meter cube vessel at 200⁰ degrees Celsius and we need to determine pressure in the vessel using the generalized compressible to chart right, so if you look at the temperature is given. So we can find out very easily the reduce temperature right what is that p but divided by the critical temperature and also a pressure is given but the in the, you know in the example the pressure has to be determined.

So we cannot find out critical pressure okay am I right we cannot find the okay sorry we can find out critical pressure from the data of ammonia but we cannot find out the reduced pressure but however if I do not know the reduce what you call pressure or I do not know the pressure then I cannot find out the reduced volume see this is the problem but let us find out T_R , T_R is basically T by T_C we can get 1.17 very easily and as I told since P is not known P_R cannot be determined but we can express p in terms of P_R right p is equal to p r into p_c so we can get a relationship if you look at if I plot p versus P_R it will be nothing but a straight line right.

So now if you look at I can get another relationship between Z and putting these values and it will be what you call Jade is if I put all these values because you know a specific volume is given R_u given T_C is given then I will get Z is equal to 1.7 to P_R again this is the straight line Z is a function of P_R which is nothing but a straight line.

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So what we will do we will be getting you know TR corresponding to 1.17 right we have already evaluated TR this is basically capital R TR 1.17 then I know that relationship Z is equal to 1.7 to PRI will draw a line here and wherever it will cross I will get this Z values and of course I can get this PR values here directly right and if I know these Z values from here I can calculate what will be P are you getting that means getting this what you call the chart itself can be utilized to find out the pressure by doing this relation.

So this is not a you know very straightforward little bit twisted so I thought that I will show you how you can use chart to do the you know data for using the generalized compressibility chart right and once I know the Z can find out varies in the pressure, so we have seen basically in this lecture how we can handle you know using various equation of state and how handy it is the compressible chart although it may lead to some little bit error but however you know we can use it, so in the next lecture we will be discussing will be starting a new topic and then we will stop over here thank you.

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