Applied Thermodynamics for Engineers
Dipankar N. Basu
Department of Mechanical Engineering
Indian Institute of Technology - Guwahati

Lecture – 10
Properties of Pure Substances

Hello friends, welcome to the third lecture of this week where we are looking to wrap up this topic of properties of pure substances. Over last two lectures, we started with the definition of pure substance where by now, we know that here by the term pure substance, we are actually talking about a substance which is having uniform chemical composition throughout the domain of our interest.

And then we have discussed about different characteristics of the pure substance particularly, in relevance with the phase change processes. Now, primarily a substance can have three kinds of phases: solid, liquid and gaseous. However, liquid to gaseous or gaseous to liquid phase change is the most relevant one in relation with the thermal and fluid industries. And therefore, we have discussed about different possible phases, different kinds of physical states that we can identify in relation with a liquid to vapour or vapour to liquid phase change.

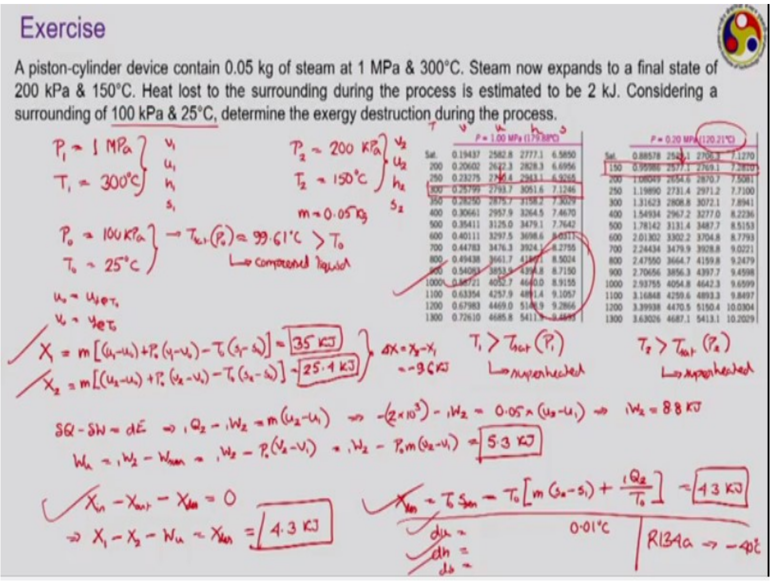
Thereby primarily, identifying three different regimes: a compress liquid regime, a super-heated vapour regime and a liquid-vapour mixture regime. In the previous lecture, we have discussed about the use of thermodynamic property tables to identify or calculated properties in relation with each of the three regimes, how we can identify a substance or a state belong to which kind of regime, just from the knowledge of its pressure and temperature or any other relevant properties.

Or as per the phase rule, if we know any of the two independent intensive properties then, with the use of these two property values and in conjunction with the property tables, how can we identify the regime. And then once you identify the regime, how we can get the values of the properties using the tables that we have discussed in detail. And we have also solved numerical problems on that. We have also talked about two most important state points in relation with this liquid-vapour phase change.

One is a critical point, which serves as some kind of distinction between condensable and non-condensable phases of the vapour state. Whereas, we have also talked about the triple point which refers to a situation where all the three phases can be in equilibrium with each other. Today to start, with we shall again be solving another numerical problem, we have already solved quite a few in the previous lecture but I would like to solve another one which is a quite involved one, particularly, involving concept of exergy.

As during the first module, during the review of thermodynamic principles, we have not solved any problem related to exergy which involves a pure substance, so I would like to do this one.

(Refer Slide Time: 03:06)



Exercise

A piston-cylinder device contain 0.05 kg of steam at 1 MPa & 300°C. Steam now expands to a final state of 200 kPa & 150°C. Heat lost to the surrounding during the process is estimated to be 2 kJ. Considering a surrounding of 100 kPa & 25°C, determine the exergy destruction during the process.

$P_1 = 1$ MPa, $T_1 = 300°C$ } v_1, u_1, h_1, s_1

$P_2 = 200$ kPa, $T_2 = 150°C$ } v_2, u_2, h_2, s_2

$m = 0.05$ kg

$P_0 = 100$ kPa, $T_0 = 25°C$ } → $T_{sat}(P_0) = 99.61°C > T_0$ ↳ compressed liquid

$u_0 = u_f @ T_0$

$v_0 = v_f @ T_0$

T	v	u	h	s
	P = 1.00 MPa (179.88°C)			
Sat.	0.19437	2582.8	2777.1	6.5850
200	0.20602	2622.3	2828.3	6.6956
250	0.23275	[illegible]	2943.1	6.9265
300	0.25799	2793.7	3051.6	7.1246
350	0.28250	2875.7	3158.2	7.3029
400	0.30661	2957.9	3264.5	7.4670
500	0.35411	3125.0	3479.1	7.7642
600	0.40111	3297.5	3698.6	8.0311
700	0.44783	3476.3	3924.1	8.2755
800	0.49438	3661.7	[illegible]	8.5024
900	0.54083	3853.9	4394.8	8.7150
1000	[illegible]	4052.7	4640.0	8.9155
1100	0.63354	4257.9	[illegible]	9.1057
1200	0.67983	4469.0	[illegible]	9.2866
1300	0.72610	4685.8	[illegible]	[illegible]

	P = 0.20 MPa (120.21°C)			
Sat.	0.88578	[illegible]	2706.3	7.1270
150	0.95986	2577.1	2769.1	7.2810
200	1.08049	2654.6	2870.7	7.5081
250	1.19890	2731.4	2971.2	7.7100
300	1.31623	2808.8	3072.1	7.8941
400	1.54934	2967.2	3277.0	8.2236
500	1.78142	3131.4	3487.7	8.5153
600	2.01302	3302.2	3704.8	8.7793
700	2.24434	3479.9	3928.8	9.0221
800	2.47550	3664.7	4159.8	9.2479
900	2.70656	3856.3	4397.7	9.4598
1000	2.93755	4054.8	4642.3	9.6599
1100	3.16848	4259.6	4893.3	9.8497
1200	3.39938	4470.5	5150.4	10.0304
1300	3.63026	4687.1	5413.1	10.2029

$T_1 > T_{sat}(P_1)$ ↳ superheated

$T_2 > T_{sat}(P_2)$ ↳ superheated

$X_1 = m[(u_1-u_0)+P_0(v_1-v_0)-T_0(s_1-s_0)] = \boxed{35\ kJ}$

$X_2 = m[(u_2-u_0)+P_0(v_2-v_0)-T_0(s_2-s_0)] = \boxed{25.4\ kJ}$

$\Delta X = X_2 - X_1 = -9.6\ kJ$

$\delta Q - \delta W = dE \Rightarrow {}_1Q_2 - {}_1W_2 = m(u_2-u_1) \Rightarrow -(2\times10^3) - {}_1W_2 = 0.05\times(u_2-u_1) \Rightarrow {}_1W_2 = 8.8\ kJ$

$W_u = {}_1W_2 - W_{surr} = {}_1W_2 - P_0(V_2-V_1) = {}_1W_2 - P_0 m(v_2-v_1) = \boxed{5.3\ kJ}$

$X_{in} - X_{out} - X_{des} = 0$

$\Rightarrow X_1 - X_2 - W_u = X_{des} = \boxed{4.3\ kJ}$

$X_{des} = T_0 S_{gen} = T_0\left[m(s_2-s_1) + \frac{{}_1Q_2}{T_0}\right] = \boxed{4.3\ kJ}$

$du =$

$dh =$

$ds =$

0.01°C

R134a → −40°C

And this also will show you the use of different kind of property tables as usual. So, just read the problem carefully; here we are talking about the piston cylinder device which is containing 0.05 kg of steam. Now one term you have to be careful here we are using the term steam, it may refer to the liquid phase, or it may refer to the vapour phase. Similarly, if we use the term water that can also refer to the liquid phase or vapour phase.

Generally, the term steam is used in relation is super-heated vapour but not necessarily and similarly, if we are using just water that does not mean it is liquid. It can be the vapour phase also because the chemical composition is as same that is H_2O only. Now, here the initial state is 1 MPa and 300 ^{0}C, so let us summarise:

$P_1 = 1$ MPa

$T_1 = 300$ ^{0}C

Ideally, you would like to convert this one to SI units but most of the thermodynamic tables actually list the temperature in terms of Celsius so, we can stick with this 300 ^{0}C. The steam now expands to a final state of 200 kPa and 150 ^{0}C so your state 2 involves:

$P_2 = 200$ kPa

You have to be very careful about this unit. In first case it is mega Pascal, in second case it is kilo Pascal.

$T_2 = 150$ ^{0}C

Heat loss to the surrounding during the process estimated to be 2 kJ. So, as the steam is expanding from state 1 to state 2, 2 kJ of heat is being lost or being transferred from system to the surroundings. Considering a surrounding of 100 kPa and 25 ^{0}C, determine the exergy destruction during the process. So, during the process, we have these as your reference state; 100 kPa and 25 ^{0}C.

But before going to the reference state, let us look at the 2 states. State 1 is 1 MPa and 300 ^{0}C. Now, which regime this should belong to compress liquid or superheated vapour or maybe a mixture? That we can identify by using these two values. Now, how to do that? You know this, like, if we just fix of the pressure for 1 MPa, we have to identify the corresponding temperature.

So, here I have the glimpse of the corresponding superheated vapour table corresponding to 1 MPa and there you can see the corresponding saturation temperature is 179 ^{0}C or 179.80 ^{0}C.

$$T_1 > T_{sat}(P_1)$$

So your T_1 is greater than T_{sat}, corresponding to P_1 that means, it is superheated. So, we are dealing with superheated vapour. So, you need to make use of the superheated vapour table. So, this is a table for 1 MPa and temperature is 300 ^{0}C. So, this is the block that we are talking about. Here, of course the headers are missing but I can summarise the header, here it is temperature in Celsius, this is your specific volume, this is internal energy, this is enthalpy, this is entropy or specific enthalpy and specific entropy. All in here, u and h are in kJ, s in kJ/kgK, and specific

volume, v is in m^3/kg, the basic SI unit. So, here you have the all the related property values at state 1; v_1, u_1, h_1, s_1, all you can note from here. So, we have v_1, u_1, h_1 and s_1.
Similarly for state 2; this is your state 2; 200 kPa and 150 ^{0}C. So, in the first case from the use of the term steam, we can still identify here we are talking about probably either a super-heated vapour or at the most saturated vapour but the second phase, we do not do anything about it. Also, nothing is given about the nature of the process.

So, let us check 200 kPa and corresponding saturation temperature. So, corresponding 200 kPa or 0.2 MPa, the saturation temperature is 120.21 ^{0}C. So, your T_2, is again greater than the saturation temperature corresponding to P_2, so incidentally this phase 2 is also, at state point 2 is also a superheated one, so 0.2 MPa or 200 kPa, 150 ^{0}C, so similarly this is the data sets that we are talking about.

So, from here you can get all the properties for state 2 as well, so we have v_2, u_2, h_2 and s_2, all are known to us. And it is also given the mass of the steam is 0.05 kg and from the language that is used in the question, we can easily say that we are dealing actually a closed system, so that the mass remains constant. So, now we have to look at the surrounding, which is 100 kPa and 25 ^{0}C.

The surrounding is generally taken as a different state while dealing with exergy calculations. So, we can identify this:
$P_0 = 100$ kPa
$T_0 = 25$ ^{0}C
Now which state this one should belong to? If you are having your water at this particular condition, which state they should belong? 100 kPa is quite closely the atmospheric pressure; atmospheric pressure is 101.3 kPa. So, 100 kPa, you can easily say that this corresponding saturation temperature definitely give you higher than 25 ^{0}C. Actually, the saturation temperature T_{sat} corresponding to this P_0 is roughly equal to 99.61 ^{0}C, which is greater than this T_0. So which state this one belong to? Here the temperature is lower than the saturation temperature corresponding to the pressure, so you are talking about compressed liquid.

So, corresponding to compressed liquid state, we can get all the relevant properties like corresponding

$u_0 = u_{f@T0}$

$v_0 = v_{f@T0}$

Similarly, we can get h_0 and s_0 as well. So, we now know all the properties, property value at state 1, property value at state 2 and also the property value corresponding to the reference condition of 100 kPa and 25 ^{0}C.

Now, you have to determine the exergy destroyed during the process, now how much will be the exergy corresponding to state 1? You can easily calculate that:

$$X_1 = m[(u - u_0) + P_0(v - v_0) - T_0(s - s_0)]$$

where

X_1 belongs to the total exergy of state 1

if you can remember the relation it is fine otherwise, you can refer to our first week of the module 1. The fourth lecture of module 1 or you can refer to the textbook, here we are talking about a closed system.

You have all the property values here means, for state 1 and state 2, I have already shown the table for state, for the reference state you can get it from any standard data base. And if you do the calculation, your X_1 is going to be coming approximately 35 kJ. So,

$$X_1 = 35\ kJ$$

Similarly, how much will be X_2? Your X_2 will be again mass into the same we can calculate the exergy for state 2. For state 1 actually we have to put the subscript; v_1, u_1 and s_1. Similarly, for state 2, it will be:

$$X_2 = m[(u_2 - u_0) + P_0(v_2 - v_0) - T_0(s_2 - s_0)]$$

and that will be coming to be equal to 25.4 kJ. So,

$$X_2 = 25.4\ kJ$$

So, ΔX, the change in exergy of the system over the process should be equal to:

$$\Delta X = X_2 - X_1 = -\,9.6\ kJ$$

So, exergy of a system is decreased during the process. But we are talking about exergy destruction and not exergy decrease, to get the exergy destruction now, we have to calculate the total amount of work done by the system during the process. Now, how much is the work that has been done by the system? How can you calculate that? We know, we have information about state 1 and 2 and you also know about the heat transfer.

Then, we can use of the first law of thermodynamics, i.e.,:

$$\delta Q - \delta W = dE$$

for any general system, general closed system. So, for in this particular case, heat is being lost to the surrounding or we can write:

$$_1Q_2 - {_1W_2} = m\,(u_2 - u_1)$$

assuming to be a stationary system. No information is given about the changes in kinetic and potential energy of the system, so we are assuming it to be a stationary one.

In this particular case, therefore, $_1Q_2$ is how much? 2 kJ but that is negative because heat is lost to the surroundings. So,

$$= -\,(2\times10^3) - {_1W_2} = 0.05 \times (u_2 - u_1)$$

From that if you do the calculation, your W_{out} during the process will be coming to:

$$W_{out} = 8.8 \text{ kJ}$$

So, this is the work produced by the system. Let us stick to our standard conventions, so during the process, $W_{out} = 8.8$ kJ is the amount of work produced during the process. Now how much is the corresponding useful work output? Because there will be something lost to the surrounding, the system is expanding, there is change in the volume and therefore, there will be some amount of surrounding work. Therefore, useful work W_u will be equal to:

$$W_u = {_1W_2} - W_{surr} = {_1W_2} - P_0\,m\,(v_2 - v_1) = 5.3 \text{ kJ}$$

So, this is a useful work that you are getting from the system.

And in this process, these are the exergy values. This is your initial exergy that is supplied to the system, these are final exergy the system is retaining, and in the process, this is the amount of useful work output that you are getting. Then, how much is exergy destruction? If you write an exergy balance equation now, we can always write:

$$X_{in} - X_{out} - X_{des} = 0$$

for a system under steady state condition like in this particular case.

where

X_{in} is Exergy in

X_{out} is exergy out

X_{des} is exergy destroyed, this has minus sign because exergy is always destroyed

So, in this particular case, we can write:

$$X_1 - X_2 - W_u = X_{des}$$

you can put the numbers here and this should be coming to:

$$= 4.3 \text{ kJ}$$

So, this is the final amount of exergy destruction that we are getting for this particular process.

Actually, this problem we could have solved using the concept of entropy as well because we know that:

Exergy destruction = T_0 × entropy generation

and if we want to calculate that way, your exergy destruction will be:

$$X_{des} = T_0 \left[m(s_2 - s_1) + \frac{{}_1Q_2}{T_0} \right]$$

where

$s_2 - s_1$ is the change in entropy of the system

${}_1Q_2$ is the heat loss to the surrounding by T_0

and if you put the numbers, again this one also should give you:

$$= 4.3 \text{ kJ}$$

Essentially, proving that we can solve the process following either this approach or following this approach. So, this is a very good problem where we have been used probably all the concept of thermodynamics that we have talked about, the concept of entropy generation, the concept of exergy and also the use of thermodynamic property tables.

Now, there are two points that I would like to emphasise here, point number 1 that you may try to compared two different data tables or I should say the same data table taken from two different sources and occasionally, you may find there are some differences in the values that are given here, all these values, there may be small differences in this. The reason for this is actually for calculating these values, some reference has to be chosen.

If you just think about what we discussed in the second module, where we develop the thermodynamic property relations, you can remember that we always develop relation as du equal to something, dh equal to something or ds equal to something. This means, we are always talking about the change in the properties. In any kind of cycle analysis or process relation also, we always have to be bothered about the changes in this properties.

And hence there is always some reference that has to be chosen while providing this absolute numbers. Now, the common choice for which this tables has been derived in the or developed in the book of Cengel and Boles for what are the common choice of temperature is 0.01 ^{0}C and common pressure is an atmospheric pressure. Now, did you read something this particular temperature value? 0.01 ^{0}C: it is the triple point of water.

So, commonly we take this triple point temperature as a reference. However, if someone develops a table, choosing some other temperature as reference, there will be some difference in this values. Similar data tables are always available for any other substances as well, here we have discussed everything and solve all the problems in relation to water but you could have solved in terms of any other property also.

They have their own choice of reference for example, if you are talking about R134a that uses a reference of −40 ^{0}C. Similarly everything as a reference temperature of their own and the choice of reference may vary from one source to another source for the same table leading to small changes in numbers. However, the difference between like if you see the expressions X_1 and X_2, here we are always calculating $(u_1 - u_0)$ and thereby negating the effect of the choice of reference for this.

So, the absolute value may change but our choice of reference being the same, we hardly have to bother about the choice of reference in practical thermodynamic calculations. So that is one of the aspect and the other aspect where I would like to take you back to the very objective of having this particular module. What is the need of discussing about all these tables or learning the use of these tables?

Because in the previous module, we have developed this general relations: du, dh, ds etc. And we know that once you have the PvT relationship for a given substance, then you can easily calculate the changes in these properties during a particular process. But the problem is that in most of the situations, the PvT relationship is not known or may be too complicated to perform any kind of mathematical manipulation and that is why we have to go for this deductive of the thermodynamic property tables.

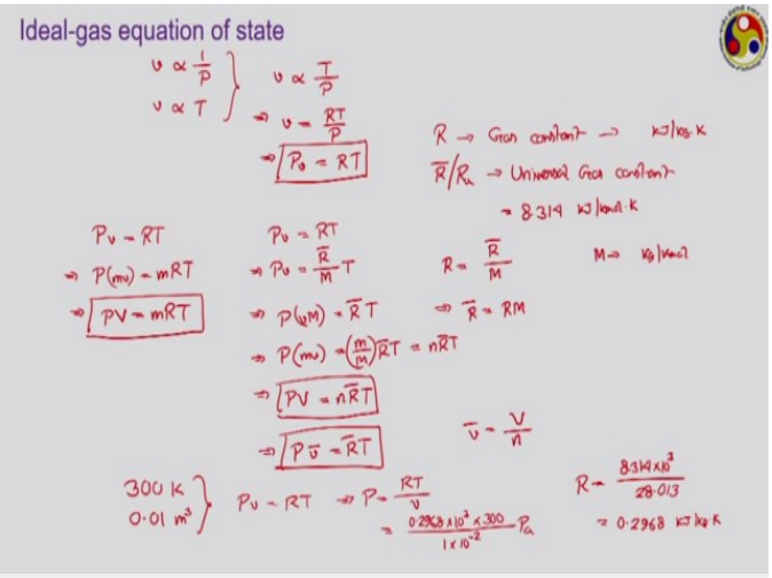
Now, as long as you are dealing with the compressed liquid or saturated mixture states that is fine. But for superheated vapour state, the use of the tables sometimes is quite inconvenient. Because you have seen that for every pressure, we may have a different table for the superheated vapour, like couple of them are already shown on the screen here, for 1 MPa and 0.2 MPa. Similarly, for every pressure we can have a different thermodynamic table.

And you may encounter a situation where you may have 200 kPa and 400 kPa tables available but no table for 300 or 350 kPa, but you actually need to calculate the properties corresponding to 350 kPa. Then you may have to either approximate something, take the average for two tables or may have to go for some kind of interpolation between the 200 and 400 kPa values, which again will have error problem.

So, for the gaseous part is particularly at least the superheated vapour state, it would have been much easier, if we can find some suitable PvT relationship to work with. And that is why we quite often; of course, the tables are available with us but even when the tables are available, we may go for devising some kind of equation of state to check whether these equations are capable of giving values comparable with the table.

If they are able to give, then there is a no replacement for the equation of states, we can just avoid using such bulky tables and directly use the small equations. And the simplest possible equation of state that you can have for the gases is the ideal gas equation of state. Now, ideal gaseous equation of state is very well known to you, you must have heard about the experiments performed by Robert Boyle.

(Refer Slide Time: 21:50)



Ideal-gas equation of state

$$\left.\begin{array}{l} v \propto \frac{1}{P} \\ v \propto T \end{array}\right\} \quad v \propto \frac{T}{P}$$

$$\Rightarrow v = \frac{RT}{P}$$

$$\Rightarrow \boxed{Pv = RT}$$

R → Gas constant → kJ/kg.K

$\bar{R}/R_u$ → Universal Gas constant

= 8.314 kJ/kmol.K

$$Pv = RT$$

$$\Rightarrow P(mv) = mRT$$

$$\Rightarrow \boxed{PV = mRT}$$

$$Pv = RT$$

$$\Rightarrow Pv = \frac{\bar{R}}{M}T$$

$$\Rightarrow P(vM) = \bar{R}T$$

$$\Rightarrow P(mv) = \left(\frac{m}{M}\right)\bar{R}T = n\bar{R}T$$

$$\Rightarrow \boxed{PV = n\bar{R}T}$$

$$\Rightarrow \boxed{P\bar{v} = \bar{R}T}$$

$$R = \frac{\bar{R}}{M}$$

$$\Rightarrow \bar{R} = RM$$

M → kg/kmol

$$\bar{v} = \frac{V}{n}$$

$$\left.\begin{array}{l} 300\ K \\ 0.01\ m^3 \end{array}\right\} \quad Pv = RT \Rightarrow P = \frac{RT}{v} = \frac{0.2968 \times 10^3 \times 300}{1 \times 10^{-2}}\ Pa$$

$$R = \frac{8.314 \times 10^3}{28.013} = 0.2968\ kJ/kg\ K$$

Centuries back, when he observed that at low pressure level as we approach vacuum, the pressure of any substance, or if write it as a specific volume is inversely proportional to pressure.

$$v \propto \frac{1}{P}$$

Similarly, the experiment of J. Charles and J. Gay Lussac have shown that at low pressure levels at least specific volume is directly proportional to the absolute temperature.

$$v \propto T$$

So, if these two are combined, then we can write as:

$$v \propto \frac{T}{P}$$

Or introducing a constant of proportionality,

$$v = \frac{RT}{P}$$

where

R is the constant of proportionality

or

$$PV = RT$$

the very well celebrated form of the ideal gas equation of state. This is called the ideal gas equation of state because this is actually a very much idealisation when the gas density is quite low, then the gases is follow this one quite accurately. Certain gases like hydrogen, oxygen, nitrogen, all the inert gas etc., under common atmospheric conditions follow these within 1% accuracy.

However, substances like high pressure steam, carbon dioxide, etc they hardly follow this one under normal atmospheric condition and that is why we this one may not be most accurate for those kinds of scenarios. Now, there are several alternative forms for this equation also available. But here it is important to note that this R is gas constant which is a characteristic of every gaseous substance.

Every substance has its own value of R, whereas R bar occasionally also written as R_u is the universal gas constant which is a universal constant. Now what is the value of the universal gas constant? It is equal to 8.314 kJ/kmol.K. Whereas the SI unit for R is kJ/kg.K. Be very careful about this units, for universal gas constant, it is kilo mol in the denominator whereas kg in the denominator for the gas constant.

Now, what is the relation between the two? R is defined as:

$$R = \frac{\bar{R}}{M}$$

where

M being the molecular weight.

What is a unit of molecular weight? Molecular weight for us to the mass of the substance which contains number of molecules equal to the above addressed number. Now, what is the unit of this? Here, we are talking about a mass i.e., kg/kmol is the unit for M, from where we derived this unit for R.

$$R = \frac{\bar{R}}{M}$$

Accordingly every substance has its own values, you know the value of *R bar*, so once you know the molecular weight of a substance, you can easily calculate the value of the gas constant for that substance. And using this solution, we can develop several alternative forms of this equation state as well. Like suppose, we have:

$$Pv = RT$$

if we multiply both sides with mass i.e., we write

$$P\,(mv) = m\,RT$$

So, what is (mv)? That is total volume. So,

$$PV = mRT$$

another quite common form of the ideal gas equation of state. Another form is sometimes used where we use the universal gas constant, we know that:

$$\bar{R} = RM$$

Now, if we use the relation for this here,

$$Pv = RT$$

that is

$$P(vM) = \bar{R}T$$

where

M is the molecular weight

R bar is the universal gas constant.

But instead of using this way, if we multiply this equation of both side of this equation with mass again, so we are writing:

$$P(mv) = \frac{m}{M}\bar{R}T$$

where

m is the mass of the substance

M is the molecular weight which is mass per unit mole,

then what this one will be?

This will be

$$= n\bar{R}T$$

where

n is the number of moles involved, i.e.,

$$\boxed{PV = n\bar{R}T}$$

So, this is another alternate form of the ideal gas equation of state written in terms of the universal gas constant. So all these three forms which I have surrounded in the square brackets, they are equivalent to each other and you can use any one of them. Fn fact, sometimes we also write in another alternate form where we express this one as:

$$P\bar{v} = \bar{R}T$$

where

v bar is V/n that is the molar specific volume; specific volume per unit mole.

Like commonly, we define specific volume as volume per unit mass, but here we are talking about volume per unit mole. This $\bar{v}$ bar symbol that we have to use in subsequent slides that is why I am introducing it here. So this is ideal gas equation of state, a very simple form, very easy to use and if it is applicable for any substance, then just from the knowledge of pressure and temperature, we can easily calculate the volume of that or vice versa.

Say for example, if we take the example of nitrogen. Let us say, I have given you nitrogen at a condition of 300 K and the corresponding volume is 0.01 m^3. Then you have been asked to calculate the pressure of nitrogen at this condition. Then how can you do it? Using the ideal gas relation, we have:

$$Pv = RT$$

or

$$P = \frac{RT}{v}$$

now T and v are given here.

T = 300 K, you have to always remember this is ideal gas equation of state, this T is absolute temperature.

Like in the previous thermodynamic tables, we are using T in Celsius but here you have to use T in absolute unit that is in Kelvin as per as SI unit. Now, T is 300 K,

$v = 0.01$ m^3

and what is R for nitrogen?

now R for nitrogen will be R *bar* which is:

$$\bar{R} = \frac{8.314 \times 10^3}{molecular\ weight\ of\ nitrogen}$$

The molecular weight of nitrogen is approximately 28 okay, let me check from the table, I have the table with me.

So, the same table that I showed in the previous class, and here also I am showing snapshot of this table only. So, for nitrogen, its exact molecular weight is 28.013 kg/kmol. So, if we calculate this then, R for nitrogen will be coming to be

= 0.2968 kJ/kgK

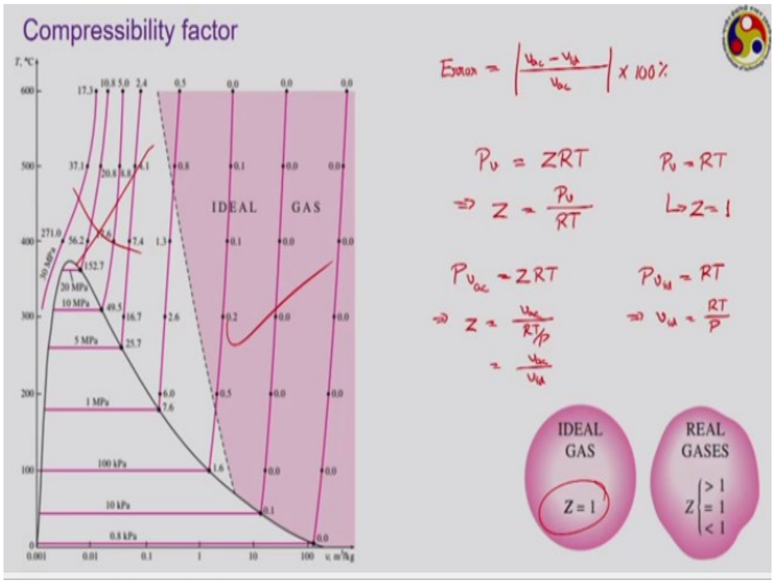
So, the pressure will be

$$P = \frac{0.2698 \times 10^3 \times 300}{1 \times 10^{-2}} Pa$$

where 1 $\times 10^{-2}$ is the specific volume.

Because we have converted everything to SI unit, now you can do the calculation, you can check whatever numbers you are getting for this. This way we can easily use the ideal gas equation of state. But the problem is that as I have mentioned this is found to be more or less accurate only when you are dealing with very low-density gases. As the gas density keeps on increasing since we are moving to higher pressures or low temperatures, it starts to deviate.

(Refer Slide Time: 30:14)



Compressibility factor

$$Error = \left| \frac{v_{ac} - v_{id}}{v_{ac}} \right| \times 100\%$$

$$Pv = ZRT \qquad Pv = RT$$

$$\Rightarrow Z = \frac{Pv}{RT} \qquad \hookrightarrow Z = 1$$

$$Pv_{ac} = ZRT \qquad Pv_{id} = RT$$

$$\Rightarrow Z = \frac{v_{ac}}{RT/p} \qquad \Rightarrow v_{id} = \frac{RT}{P}$$

$$= \frac{v_{ac}}{v_{id}}$$

IDEAL GAS

$\boxed{Z = 1}$

REAL GASES

$$Z \begin{cases} > 1 \\ = 1 \\ < 1 \end{cases}$$

Means, as long as density is low that means pressure is low or temperature is high, ideal gas equation of state has been found to be quite accurate. But in other condition that is not the case that is even better understood by following this table. Here, on this table we are showing a Tv diagram, it is a very standard Tv diagram for water. So, you can see all the horizontal constant pressure lines are shown, these pink lines are constant pressure lines which are horizontal inside the dome, but then they keep on increasing. Like, this is for 100 kPa, this is for 5 MPa, this way we have several constant pressure lines. And whatever values shown at the corresponding different nodal points like 20.8 here, this 0.01 here, these actually are the error, if we use the ideal gas equation or here these values, this error that has been calculated here is:

$$Error = \left|\frac{v_{actual} - v_{ideal}}{v_{actual}}\right| \times 100\%$$

This is the error, these numbers are shown like the 17.3 here, 6.0 and 7.6 here etc.

Now, look at this table carefully or all these error values. Here error values are all shown for a given pressure starting from the saturated vapour state to very high temperature levels. Like for 100 kPa, if we follow the 100 kPa line, these are saturated vapour state, where you can say, there is a 1.6 % error. As we are moving up here, we are having around 200 ^{0}C, we are having an error of 0.5 % and as we are moving up at 500 ^{0}C, the error is 0.1 %.

So, as we are moving to higher temperature, the error is reducing, so it is more logical to use the ideal gas equation of state. Similarly, if we follow any other lines say, for 1 MPa, so error is about 7.6 and 6 % at the saturated; 7.6 % at the saturated vapour state and 6 % with small increase in temperature. But once we go to that 500 ^{0}C, it is only 0.8 %. So if at the 500 ^{0}C, if you are using the ideal gas equation to estimate the property or specific volume of water vapour using ideal gas equation of state that we introduced < 1 % error.

That means for the pink zone shown here on right-hand side of the dotted line here the error being quite low, this is a zone for which we can use the ideal gas equation of state even for water vapour as well for estimating it’s property, specific volume. However, if we are operating on the left-hand side of the same diagram, the errors are quite high, errors can be in the range of 20 %, 17 %, even 56 % so, extremely large errors we are talking about. And therefore, you should not use the ideal gas equation of state in this particular zone.

Now, where is the error most largest? If you observe carefully, I have mentioned in previous slide for low density cases, we can go for ideal gas equation of state. Low density means low pressure, high temperature and following any constant pressure and we can see as we are going to higher temperatures, error is reducing.

Like for 600 ^{0}C, error becomes actually 0 for these pressure levels. However, when you are moving to say, we have gone to a pressure level of 10 MPa, then you can say at even at 600 ^{0}C also, the 10 MPa line shows a 5% error in the value of specific volume which is quite larger error.

So, as we are moving to higher pressures, we are getting very poor result with the use of ideal gas equation. So, we should not use ideal gas equation state in this zone but we definitely can use in this particular site. So, we can use the ideal gas equation of state in terms only when we are dealing with a very low-density gas i.e., at high temperature and low pressure. But high temperature means, exactly how much high? And a low pressure means, exactly how must low? That is something that we have to quantify.

And also, this is shown here for water vapour but the same is applicable for any kind of gaseous substance. Like common non condensable gases like hydrogen and oxygen, to much common refrigerate and vapours etc. We have to define some kind of common criterion, and to define that criterion, we use something known as the compressibility factor. To define the compressibility, we define a modified equation of state as:

$$Pv = ZRT$$

or

$$Z = \frac{Pv}{RT}$$

This Z is called the compressibility factor. Now, if we compare this only the ideal gas equation of state when we had:

$$Pv = RT$$

now for this case, how much is your Z?

Definitely $Z = 1$, so when you know $Z = 1$, we are talking about an ideal gas equation of state and so, if at a particular state point if the value of Z is quite close to 1, you can use ideal gas equation of state for that substance.

But if Z is far away from 1, it is not logical to use that. There is an alternative definition for Z also we can use like, if we write these two equations properly, we should write:

$$Pv_{actual} = ZRT$$

and

$$Pv_{ideal} = RT$$

or

$$v_{ideal} = \frac{RT}{P}$$

So,

$$Z = \frac{v_{actual}}{RT/P}$$

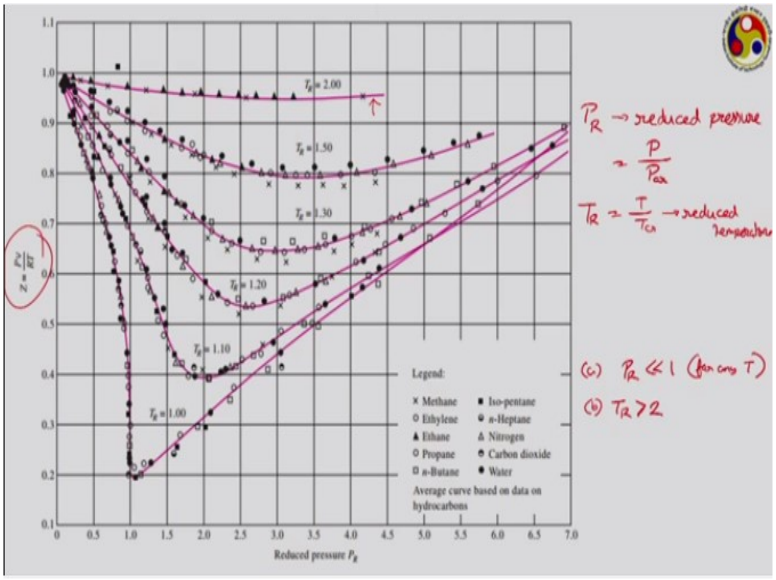
or

$$Z = \frac{v_{actual}}{v_{ideal}}$$

when $Z = 1$, the actual specific volume is reasonably close to ideal specific volume or specific volume calculated following the ideal gas equation of state.

But when Z is varying away from 1, this actual specific volume also keeps on changing rapidly from that ideal value for this. So, we can easily say that for ideal gas, $Z = 1$, for real gases which do not truly follow the ideal gas equation of state, your Z can be both greater than 1 or lesser than 1. And in some very, very restricted cases can be quite close to 1, where we can blindly go for the ideal gas equation of state.

(Refer Slide Time: 36:50)



But when should we use this ideal gas equation of state and when not? That we identify and for that we are using something known as the generalised compressibility chart. The chart shown here is called the generalised compressibility chart. Because this chart has been prepared not only for water but for all the substances that are listed here.

Before going to the description of the chart, I would like to define two parameters; one is P_R; this is called the reduced pressure. And it is defined as:

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

where

P is the he prevailing pressure

P_{cr} is the critical pressure of that substance

Similarly, we can define the reduced temperature T_R as:

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

Again, it is the reduced so, both pressure and temperature at a given state point have been divided by the corresponding critical values, basically to non-dimensional themselves because P_R and T_R will be non-dimensional. And from there, we are going to find some kind of generalisation; generalised behaviour.

Look at this chart, you have Z on the vertical axis, here:

$$Z = \frac{Pv}{RT}$$

this v is v_{actual}.

and you have reduced pressure in the horizontal axis, and each of this pink lines that are shown each of them corresponds to one particular value of T_R. Like the one that I circled that is specific $T_R = 2$, this equal to T_R for 1.2, this is for $T_R = 1$. This way we can get different kind of lines and we can come below $T_R = 1$ as well, if required.

Now, look at the values, if your system or here is the gaseous substance is following the ideal gas equation of state, then what should be the value of Z? Z should be = 1, so this is your $Z = 1$, that means, if the line is following or if your substance with change in pressure is following this particular line, then it is quite close to the ideal gas behaviour. But that is not happening under certain condition which is reasonably close to that.

But under certain condition is far for away from this, like this ranges, they are having extremely small z values far away from 1. And therefore, if we suppose, put a criterion that as long as z is restricted up to 0.9 then, we can use the ideal gas equation of state. Then you can see we are having that limit that $z > 0.9$ only for extremely low value of this reduced pressure, for a very, very low value of reduced pressure, it is quite close to that 1. Means, only in this particular group, it is reasonably close to 1, where the reduced pressure is extremely small compared to the critical pressure.

So, we can find there are two situations actually, we can identify, we can use an ideal gas equation of state. Your case number one, say case (a), where this reduced pressure is approaching 0, which is extremely small or if instead of approaching, so if we write the reduced pressure is extremely small compared to the critical pressure. Then, there is the situation we are getting where the z is quite close to 1, independent of whatever temperature.

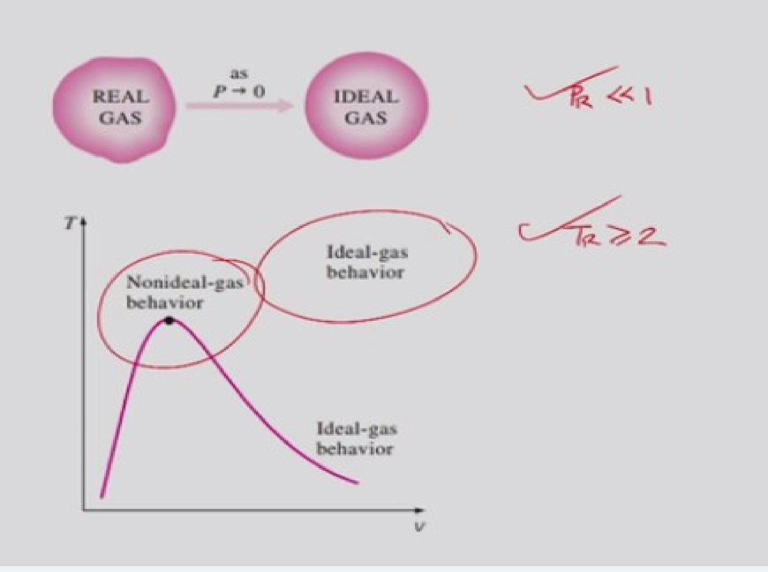
(a) $P_R << 1$

The second criterion, say case (b), is based upon the temperature, you can see, when the $T_R = 2$, the entire lines which I am talking about this particular line, the entire graph is reasonably close to 1. Even for small to large pressure values, I do not think the Z is ever increasing below 0.95. So, throughout this entire pressure range, specific volume values quite close to the ones calculated following ideal gas equation of state. So, when the temperature or T_R is very high, then there is a possibility, then we can use the ideal gas equation of state. So, second criterion is T_R greater than 2 or maybe we can say greater equal to 2. Say,

(b) $T_R > 2$

So, P_R greater equal to; or P_R very small that is much, much less than 1, this is true for any temperature, whereas T_R greater equal to 2 that more or less true for any kind of pressure values. So, these are the two situations for which we can use the ideal gas equation of state but if a state point is varying away from that. This is not suggested to use the ideal gas equation of state rather it will be better to identify something else.

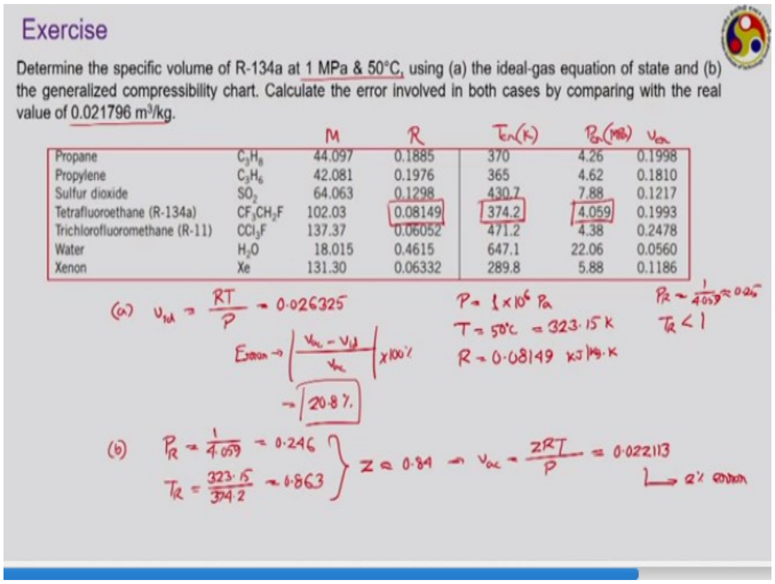
(Refer Slide Time: 41:38)



So, this is a condition that I have summarised as the pressure keeps on reducing that is the number of gas molecules available in a given volume keeps on reducing, the weight approaches ideal gas behaviour which is the criterion that we have identified where $P_R << 1$for any temperature, the second criterion is this where the temperature is very high like it is in this particular range T_R, generally greater equal to 2, we can use this.

But the largest deviations if we just quickly go back to the previous slide, you can see the largest deviations are happening around this particular line, i.e., when $P_R = 1$. And again, that among the temperature lines, the one showing the larger deviation is at $T_R = 1$. So the deviation is the largest close to the critical point, so when you are far away from the critical point and you are just been satisfying this criterion, you can use the ideal gas equation of state. But when you are reasonably close to the critical point somewhere here then, you should not use ideal the ideal gas equation of state. Then what to use? One option is to make use of the generalised compressibility chart that is from the generalised compressibility chart, we can calculate the values as shown in this diagram, we can calculate the z values and we can compare with the measured values.

(Refer Slide Time: 43:05)



Exercise

Determine the specific volume of R-134a at 1 MPa & 50°C, using (a) the ideal-gas equation of state and (b) the generalized compressibility chart. Calculate the error involved in both cases by comparing with the real value of 0.021796 m³/kg.

		M	R	T_{cr}(K)	P_{cr}(MPa)	v_{cr}
Propane	C_3H_8	44.097	0.1885	370	4.26	0.1998
Propylene	C_3H_6	42.081	0.1976	365	4.62	0.1810
Sulfur dioxide	SO_2	64.063	0.1298	430.7	7.88	0.1217
Tetrafluoroethane (R-134a)	CF_3CH_2F	102.03	$\boxed{0.08149}$	$\boxed{374.2}$	$\boxed{4.059}$	0.1993
Trichlorofluoromethane (R-11)	CCl_3F	137.37	0.06052	471.2	4.38	0.2478
Water	H_2O	18.015	0.4615	647.1	22.06	0.0560
Xenon	Xe	131.30	0.06332	289.8	5.88	0.1186

(a) $v_{id} = \frac{RT}{P} = 0.026325$

$P = 1\times10^6$ Pa

$T = 50°C = 323.15$ K

$R = 0.08149$ kJ/kg.K

$P_R = \frac{1}{4.059} \approx 0.25$

$T_R < 1$

Error $\rightarrow \left|\frac{v_{ac} - v_{id}}{v_{ac}}\right| \times 100\%$

$\rightarrow \boxed{20.8\%}$

(b) $\left.\begin{array}{l} P_R = \frac{1}{4.059} = 0.246 \\ T_R = \frac{323.15}{374.2} = 0.863 \end{array}\right\} Z \approx 0.84 \rightarrow v_{ac} = \frac{ZRT}{P} = 0.022113$

$\hookrightarrow$ 2% error

Like here, in the exercise I am talking about R134a, the specific volume R134a has to be determined for this condition of 1 MPa and 50 ^{0}C using the ideal gas equation of state and also using the generalised compressibility chart. The real value is given to be this much, we have to check how much error both of the approaches are giving. Now, this is a table that I have copied again, an any part of the table.

Here, this is your molecular weight, this is the value of R, this is critical temperature, this is critical pressure and this is specific volume corresponding to the critical point, which is not required for our case. So, for R134a you have this as critical temperature 374.2 K. Here critical temperature is given in Kelvin and critical pressure in mega Pascal, it is 4.059 MPa. So, we have to calculate following either of the approaches. So, if we follow approach number 1; specific volume following ideal gas equation of state will be:

$$v_{ideal} = \frac{RT}{P}$$

Here, your

$P = 1 \times 10^6$ Pa

$T = 50\ ^0C$

we should convert that SI unit which will coming as 323.15 K

R = 0.08149 kJ/kgK, from the table

So, if you put the numbers here, I have pre-calculated the value for you, here your ideal value will be coming as:

$$v_{ideal} = \frac{RT}{P} = 0.026325$$

but actual one is 0.021796. So, corresponding error will be:

$$Error = \left|\frac{v_{actual} - v_{ideal}}{v_{actual}}\right| \times 100\%$$

it will be somewhere in the range of 20.8%.

So, very, very large error that we are talking about and if we compare this in terms of criterion, you can see the temperature that you are talking about that is actually in this case, your T_R is <1 and we need to have $T_R > 2$. So and what about P_R? Here your P_R is 1/4.059 so, roughly around 0.25, not that small as well. So, neither of the criterion are being satisfied, so you should not use the ideal gas equation of state. And even if we use, you can see it is inducing such large amount of error. Then what about the compressibility chart? So, we calculate P_R as I have just done there; 1/4.059 actually, I have the number calculated here that is 0.246. T_R = 323.15 /374.2 and this is coming to be something like 0.863 so, if you put them in the generalised compressibility chart that have shown, your Z will be coming roughly 0.84 correspondingly,

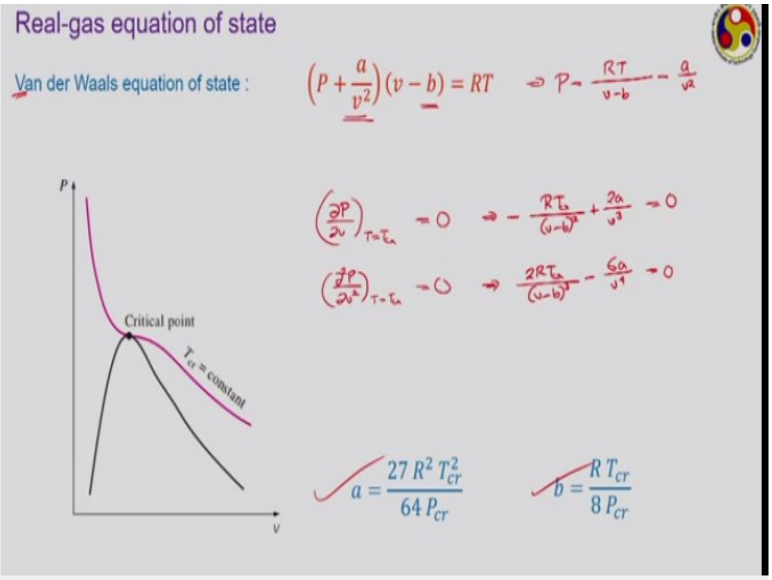
$$v_{actual} = \frac{ZRT}{P}$$

And final value will be coming as 0.022113.

We can compare this one to the real value given which will be giving you approximately 2% error. So, a significant reduction in the error value by choosing the compressibility factor Z. So this is one of the approaches by which we can calculate the actual specific volume using the generalised compressibility chart but here again, we are using a chart.

Then the second approach that is possible is to develop a real gas equation of state which takes care of all the shortcomings of the ideal gas equation of state. And thereby making it directly integratable to apply the generalised thermodynamic property relations. So, there are several real gas equations of state defined, you can say theoretically infinite number of such equations exist, we shall be talking only about three of them here very quickly.

(Refer Slide Time: 48:18)



Real-gas equation of state

Van der Waals equation of state : $\left(P+\frac{a}{v^2}\right)(v-b)=RT \Rightarrow P=\frac{RT}{v-b}-\frac{a}{v^2}$

$\left(\frac{\partial P}{\partial v}\right)_{T=T_{cr}}=0 \Rightarrow -\frac{RT_{cr}}{(v-b)^2}+\frac{2a}{v^3}=0$

$\left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_{cr}}=0 \Rightarrow \frac{2RT_{cr}}{(v-b)^3}-\frac{6a}{v^4}=0$

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

The first term of them that you already know the Van der Waal’s equation of state. Truly speaking, I should have written this V to be small v because that is the way they write, the Van der Waals equation of state, you know the form is a standard format:

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

It takes care of two important shortcomings of the ideal gas equation of state, one is ideal gas equation of state completely neglect the intermolecular forces.

This a/v^2 square, a being a constant is a term which is used to encounter the inter molecular forces somehow. And secondly, the ideal gas equation of state neglects the volume of the gas molecules itself, that has been compensated here by this term small *b*. Now just think about the conditions for which the ideal gas equation of state can be applicable, very low pressure; very low pressure means the number of molecules will be extremely small compared to the volume that you are dealing with.

And therefore, we can actually neglect the volume of the molecules and also, the intermolecular attraction. The same thing is applicable when we go to very high temperatures. However, when you are not operating at these conditions that is P_R extremely small and $T_R > 2$, then this, they should be considered which is done in these Van der Waal's equation of state.

Now, how to get the value of this a and b? There is a mathematical way of doing this, this graph I have shown earlier also. You know that on the Pv plane, the isotherm correspond to the critical temperature shows a point of inflection at the critical point, such that we can write:

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

and even its second derivative is also 0, i.e.,

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

these two equations can be used to develop the values of this a and b for a given state point.

Like from here, we can write:

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

if we use this, suppose, if we differentiate this one:

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

then what you are going to get? We have:

$$\frac{RT_{cr}}{(v-b)^2} + \frac{2a}{v^3} = 0$$

Similarly, if we differentiate this for once more:

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

Then it will be:

$$\frac{2RT_{cr}}{(v-b)^3} - \frac{6a}{v^4} = 0$$

So, if we combine these equations and eliminate specific volume from here then actually, you are going to get these two expressions for a and b:

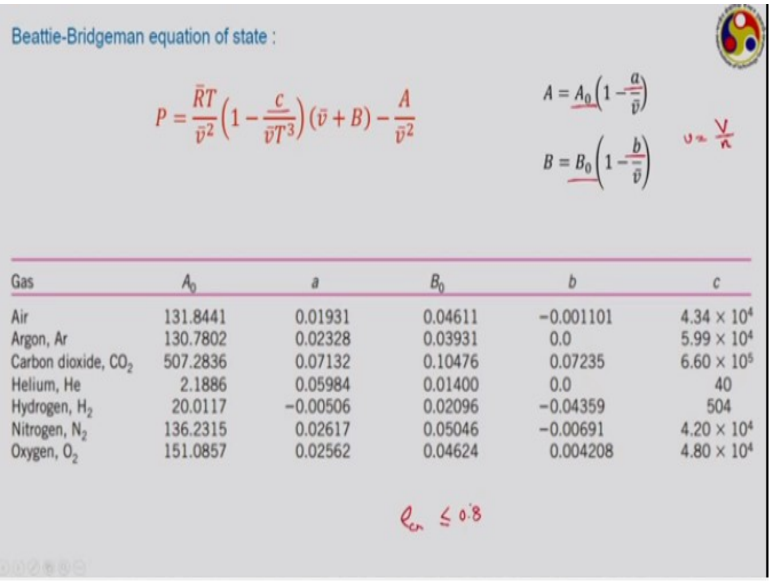
$$a = \frac{27\, R^2 {T_{cr}}^2}{64\, P_{cr}}$$

$$b = \frac{RT_{cr}}{8\,P_{cr}}$$

where we are using ideal gas equation or ideal gas values. Here, one important thing is; I am leaving it to you to develop the mathematical relation. Please try to develop the relations for *a* and *b*. One hint is that you have to remove specific volume from here, somehow introduce the pressure corresponding to the critical point.

So, you will be getting the expressions for *a* and *b* like this where the critical point pressure and temperature values are involved and also, the value of *R*. So, this way once you know the critical point values, you can easily calculate the value of *a* and *b*. Now, Van der Waal's gas equation of state that is not the very accurate as well definitely, more accurate compared to the ideal gas equation of state but it has its own inconsistencies leading to the development of more advanced relations like this one.

(Refer Slide Time: 52:07)



Beattie-Bridgeman equation of state :

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

$$A = \underline{A_0}\left(1-\frac{a}{\bar{v}}\right)$$

$$B = \underline{B_0}\left(1-\frac{b}{\bar{v}}\right)$$

$v = \frac{V}{n}$

Gas	A_0	a	B_0	b	c
Air	131.8441	0.01931	0.04611	−0.001101	4.34×10^4
Argon, Ar	130.7802	0.02328	0.03931	0.0	5.99×10^4
Carbon dioxide, CO_2	507.2836	0.07132	0.10476	0.07235	6.60×10^5
Helium, He	2.1886	0.05984	0.01400	0.0	40
Hydrogen, H_2	20.0117	−0.00506	0.02096	−0.04359	504
Nitrogen, N_2	136.2315	0.02617	0.05046	−0.00691	4.20×10^4
Oxygen, O_2	151.0857	0.02562	0.04624	0.004208	4.80×10^4

$\rho_{cr} \leq 0.8$

The Beattie Bridgeman equation of state is one of the most popular one, this is the format shown for this:

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

where A and B leads to two further equations here.

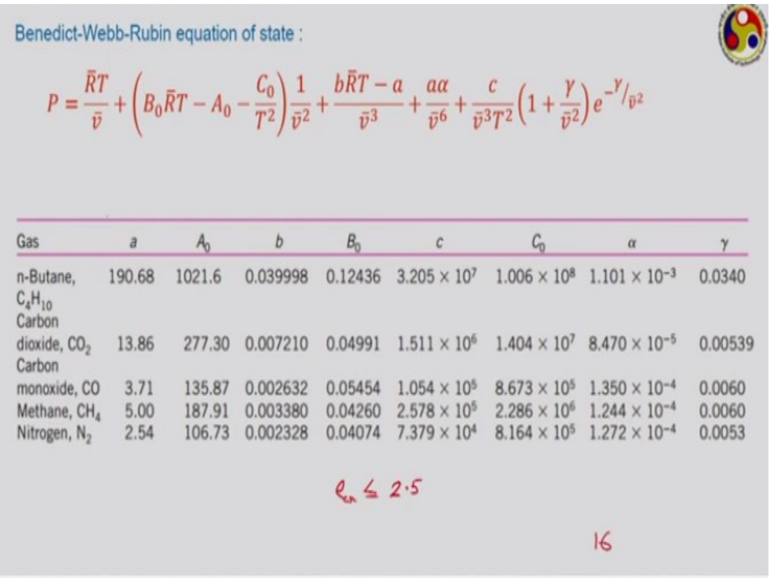
$$A = A_0\left(1-\frac{a}{\bar{v}}\right)$$

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

Note this ῡ, this ῡ is the total volume divided by number of moles. So, how many constants you can identify in this? like in the van der Waal's equation of state, you have two; a and b, how many you can see here?

We have a *c* here, then we have *a*, *b*, A_0 and B_0, five constants involved here. And this is one of the examples of the constants for different gas is shown here. Where this Beattie Bridgeman equation of state is quite accurate at least as long as the density, ρ_{cri} is less than or equal to 0.8, this is quite accurate.

(Refer Slide Time: 53:03)



Benedict-Webb-Rubin equation of state :

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

Gas	a	A_0	b	B_0	c	C_0	α	γ
n-Butane, C_4H_{10}	190.68	1021.6	0.039998	0.12436	3.205×10^7	1.006×10^8	1.101×10^{-3}	0.0340
Carbon dioxide, CO_2	13.86	277.30	0.007210	0.04991	1.511×10^6	1.404×10^7	8.470×10^{-5}	0.00539
Carbon monoxide, CO	3.71	135.87	0.002632	0.05454	1.054×10^5	8.673×10^5	1.350×10^{-4}	0.0060
Methane, CH_4	5.00	187.91	0.003380	0.04260	2.578×10^5	2.286×10^6	1.244×10^{-4}	0.0060
Nitrogen, N_2	2.54	106.73	0.002328	0.04074	7.379×10^4	8.164×10^5	1.272×10^{-4}	0.0053

$\rho_{cr} \leq 2.5$

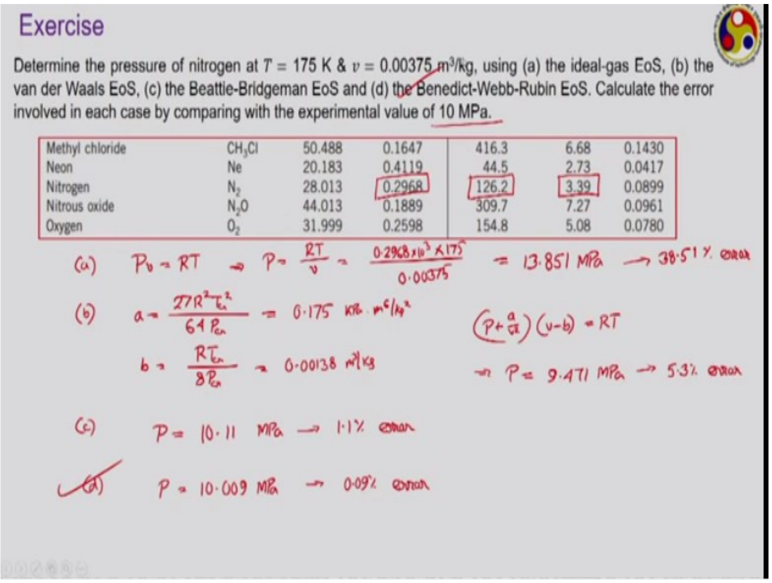
16

And even more accurate equation of state can be this, Benedict-Webb-Rubin equation of state where the form is this:

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

which involves eight constants like this table is showing. It is found to be accurate for ρ_{cri} upto 2.5, so it is a very large range of temperature we are talking about, temperature and pressure for this. And of course, it is much more complicated like there are several others also, we can talk about the Strobridge equation of state which actually involves 16 constants.

(Refer Slide Time: 53:41)



Exercise

Determine the pressure of nitrogen at T = 175 K & v = 0.00375 m^3/kg, using (a) the ideal-gas EoS, (b) the van der Waals EoS, (c) the Beattie-Bridgeman EoS and (d) the Benedict-Webb-Rubin EoS. Calculate the error involved in each case by comparing with the experimental value of 10 MPa.

Methyl chloride	CH_3Cl	50.488	0.1647	416.3	6.68	0.1430
Neon	Ne	20.183	0.4119	44.5	2.73	0.0417
Nitrogen	N_2	28.013	0.2968	126.2	3.39	0.0899
Nitrous oxide	N_2O	44.013	0.1889	309.7	7.27	0.0961
Oxygen	O_2	31.999	0.2598	154.8	5.08	0.0780

(a) $Pv = RT \Rightarrow P = \frac{RT}{v} = \frac{0.2968\times10^3\times175}{0.00375} = 13.851$ MPa → 38.51% error

(b) $a = \frac{27R^2T_{cr}^2}{64P_{cr}} = 0.175$ kPa$\cdot$m^6/kg^2 $\quad (P+\frac{a}{v^2})(v-b) = RT$

$b = \frac{RT_{cr}}{8P_{cr}} = 0.00138$ m^3/kg $\quad \Rightarrow P = 9.471$ MPa → 5.3% error

(c) $P = 10.11$ MPa → 1.1% error

(d) $P = 10.009$ MPa → 0.09% error

That is therefore very difficult for manual calculation, but very suitable for computerised calculation. We would like to close of this module, by checking one example of using this equation of state. So, here our condition is, where you have to calculate the pressure of nitrogen at T = 175 K and specific volume is given, using the ideal gas equation of state, the Vander Waals equation of state, Beattie Bridgeman equation of state and the Benedict Webb Rubin equation of state.

And it has been found that the experimental measured value is 10 MPa, so you have to compare for each of the cases. Now, this is a situation for the nitrogen, you have this as the value of R for nitrogen, critical temperature 126.2 K, critical pressure 3.39 MPa. So let us calculate following the first approach. For ideal gas equation of state:

$$Pv = RT$$

$$P = \frac{RT}{v}$$

$$= \frac{0.2968 \times 10^3 \times 175}{0.00375} = 13.851\,MPa$$

Your calculation will be giving you 13.851 MPa, but the true value is supposed to be 10 MPa, a humongous amount of 38.51% error and that is logical also. You can see critical temperature is 126 K and this temperature 175 K, so we are not talking about a very large value of T_R; T_R is only just above 1. If we follow the Van der Waal's equation of state now, for this you have to compute the, *a* and *b* first. So,

$$a = \frac{27\, R^2 {T_{cr}}^2}{64\, P_{cr}}$$

$$b = \frac{RT_{cr}}{8\, P_{cr}}$$

So, you can calculate the values if you put them the numbers, we get, $a = 0.175$ and $b = 0.00138$ m^3/kg. Now *b* has a unit of specific volume only because we know that:

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

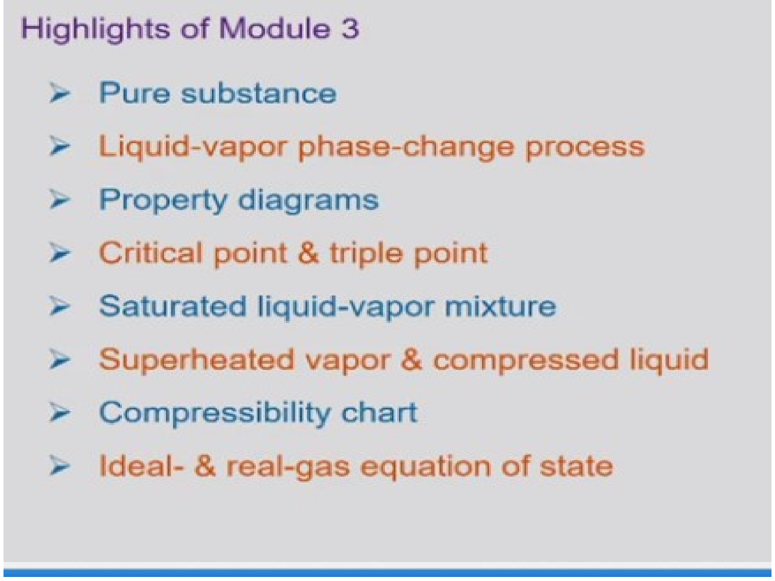
So, *b* and *v* has giving the same unit of specific volume but what will be the unit of this *a*? The unit for a should be: a/v^2 should have the unit of pressure, so unit should be equal of Pv^2 i.e., if you expand this, it will be coming as $kPa.m^6/kg^2$. By expanding it or you can write it in terms of pressure unit as well. So if you calculate following this, your P will be coming roughly to be:

$$P = 9.471 \text{ MPa}$$

So it is coming lower than the true value. But still a less amount of error approximately, 5.3% error. The constants required for the Beattie Bridgeman equation of state and the Benedict Webb Rubin equation of state are given in the previous slides for nitrogen. You can put the numbers there and try to calculate, I am giving you the final result for the Beattie Bridgeman equation of state, your P will be coming to be a merely 10.11 MPa. So how much is the error? This extremely small, you have only 1.1% error. Whereas, if you use the third one; the Benedict-Webb-Rubin, then in this case your P will be coming to be 10.009 MPa. That means we are talking about something in the range of 0.09% error. So definitely this one or I should say this Benedict-Webb-Rubin equation of state is much more accurate compared to the others but again that is much more complicated as well because it involves 8 constants for this.

This way you can find a few other equations of states as well in your textbooks, for there are several specific equations developed for specific applications for specific substances as well. But the ones that I have discussed here the Van der Waals equation of state, the Beattie Bridgeman equation of state and the Benedict-Webb-Rubin equation of state are generally applicable for a wide variety of gases.

(Refer Slide Time: 58:44)



Highlights of Module 3

- Pure substance
- Liquid-vapor phase-change process
- Property diagrams
- Critical point & triple point
- Saturated liquid-vapor mixture
- Superheated vapor & compressed liquid
- Compressibility chart
- Ideal- & real-gas equation of state

So that takes us to the end of our module number 3, where we discussed about the pure substance and the liquid-vapour phase-change processes involved with your substance, from where we develop the property diagrams, *Pv* and *Tv* diagrams then, we involve the solid phase into that as well to get the idea of the triple point and the critical point, then we talked about the calculation of the properties using the tables for saturated liquid-vapour mixtures and superheated vapour and compressed liquids and solved several numerical problems. And then today, we discussed about the use of the generalised compressibility chart to calculate the specific volume of gaseous states, when the ideal gas equation of state is not applicable. We have also derived the condition for which we can develop or we should use the ideal gas equation of state and the conditions for which we should not.

And finally, we discussed about different types of real gas equation of state and there we have seen that the Benedict-Webb-Rubin equation of state is much accurate compared to the others discussed here. So that is it for the third module of our course, you are now in a position to identify the properties of any substance because in the second module, we develop generalised relation for calculation of properties.

And in this third module, we have learned about the use of both equation of states and the general property tables to calculate or to get the values of relevant thermodynamic properties. So, with this background now, in the next week, we shall be going to the discussion of relevant thermodynamic cycles, till then you do your exercise, repeat or revise the lectures and if you have any query, please write back to me. Thank you.