Basic Thermodynamics

Prof. S. K. Som

Department of Mechanical Engineering

Indian Institute of Technology, Kharagpur

Lecture - 19

Properties of Ideal Gases

Good afternoon. Last class, we discussed the behavior of ideal gases which obey the equation of state as p into v the pressure and the volume equals to mass into the characteristic gas constant and temperature. In another form, if you express in terms of moles, the amount of the gas then p times v becomes equal to the number of moles times the universal gas constant is constant for all gases and the temperature. Following this equation of state as the first line of the definition of an ideal gas, we derived a number of corollaries; that is enthalpy and internal energy are functions of temperatures.

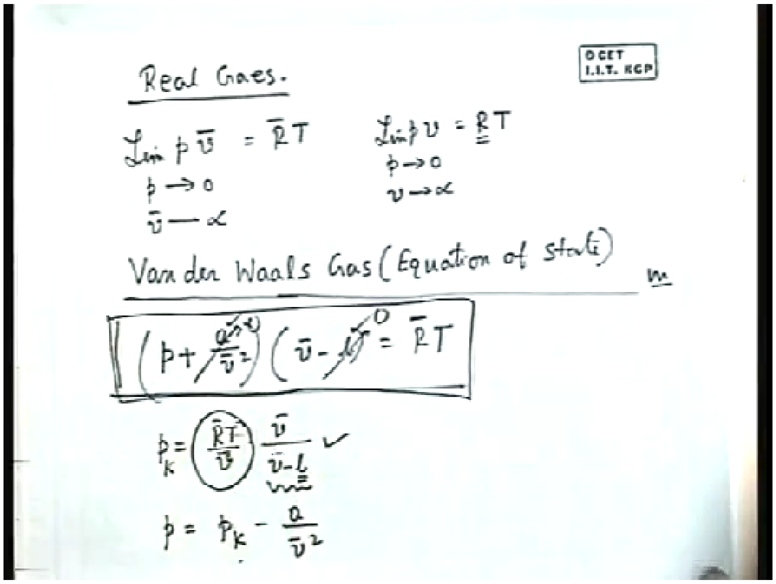
At the same time, we assumed that the specific heat, and constant pressure and volume are constant for an ideal gas. Sometimes, for an ideal gas, we will also tell that specific heat at constant pressure and volume may vary with the temperature, but usually, we assume for an ideal gas, these are constant and those cases, the ideal gases are called calorically perfect gas.

We derived the expression relating to pressure volume, pressure temperature and volume temperature for an isentropic process. With the use of these equations that enthalpy and internal energies or functions of temperatures and the equation of state, we derived certain equations relating to work transfer in the displacement mode or that is pdv and all these things. Also, the entropy change in a process, how it relates the pressures and temperatures at the two equilibrium states executed by an ideal gas in a process.

Today, I will discuss first what are real gases? We also realize that the gases in reality may not always obey the ideal gas states. The ideal gas equations are fairly accurate for all real gases when they are at a extremely superheated or ratified state which can be theoretically stated that the limiting value of the pressure and volume as pressure tends to 0, or volume tends to infinity, becomes equal to R bar T.

For real gases that means the gases in reality, this is rather the equation that p, let us consider the molar volume pv and as p tends to 0 or molar volume tends to infinity. We get R bar T, or in terms of the specific volume, same thing limit pv as p tends to 0 or v tends to infinity is RT, where R is the characteristic gas constant. Therefore, we see under one limiting conditions, this equation that pv is equal to R bar T and pv is equal to RT are valid, but not in all ranges of pressure and temperatures.

(Refer Slide Time: 04:10)



Real Gases.

$\lim\limits_{\substack{p \to 0 \\ \bar{v} \to \infty}} p\bar{v} = \bar{R}T$ $\quad$ $\lim\limits_{\substack{p \to 0 \\ v \to \infty}} pv = \underline{\underline{R}}T$

Van der Waals Gas (Equation of state)

$$\boxed{\left(p + \cancel{\frac{a}{\bar{v}^2}}^{\,0}\right)\left(\bar{v} - \cancel{b}\right)^{0} = \bar{R}T}$$

$$p_k = \frac{\bar{R}T}{\bar{v}} \, \frac{\bar{v}}{\bar{v} - b} \checkmark$$

$$p = p_k - \frac{a}{\bar{v}^2}$$

It has been found from experiments that for real gases where the pressures are very low and it is not at a very high superheated condition, the pressure volume temperature relationship is not followed by that of the ideal gases. At the same time, it has been found experimentally that a unique relationship between pressure, volume and temperature is very difficult to be obtained in a wider range of pressure and temperature. That is why, sometimes it is like empirical equations. When we develop empirical equations for any process, the performance of a system that output parameter has a function of input parameters or operating parameters. These relationships are valid within the range of the experiments, including certain range of operating parameter.

Similarly, different functional relationships of pressure and volume are obtained at different ranges for pressure and volume and temperature for real gases. It is not like that an ideal gas at all ranges of pressure, volume and temperature, we can substantially take that equation of state pv is equal to RT or R bar T depending upon whether it is specific volume or molar volume. But there are equations which are only valid within a range of certain pressure and volume. Usually, in practice, when we deal with real gases and solve for problems relating to work and heating directions in a process, change of entropy in a process, change of internal energy in a process or evaluating enthalpy, we are supplied with the equation of states; within certain range, this equation is valid and within certain range this equation is valid. So, we do not have to remember any equations.

There are different equations proposed by different scientists, which are valid for certain gases. They specify these are the gases within these ranges and thus they obey these equations; that means, you have to know simply that equation of state is a functional relationship between pressure, volume and temperature. It is usually obtained from experiments and these are being supplied if I know this relationship. Then we can apply this equation, just is a mathematical operation, to evaluate all other thermodynamic parameters; the heat work interactions, change in entropy and all these things.

One such equation of state was proposed by a scientist Van Der Waals and this is known as Van Der Waals gas. Van Der Waals gas or Van Der Waals equation of state is a gas which obeys this equation of state. It is beyond the scope of this study that will deal with in details with all types of real gases and what are the probable equations and all these things, because there are plenty of empirical equations in different ranges. but I will tell you that how usually the real gases are being specified in terms of their equation of state.

One very important real gas is Van Der Waal gas. It has been found that in a wider range of pressure and temperature, many real gases follow a particular equation of state. Let me first write this equation of state, then I will explain. The equation of state is like this; if p is the pressure in terms of the molar volume, write p plus a by v square into v minus b is equal to R bar T, where v is the molar volume. R bar is the universal gas constant whose value is same for that of ideal gas, where a and b are parametric constant defining these Van Der Waal equation.

Therefore, we see this relationship between pvT. Even if we draw this curve in a pvT plane as a surface or in pv for different values of T, the parameters a and b are there. That means different gases obeying Van Der Waals equation will have different values of a and b which are typical to the particular gas obeying the Van Der Waals. That means, Van Der Waal gas represents a class of gases over a certain range of pressure, volume and temperature which are being distinguished from one another by the different values of a and b.

This has been verified experimentally and it has been proposed from experimental results, but Van Der Waals initially deduces this equation of state from kinetic theory of matter. The way the ideal gases are developed by the kinetic theory of matter with the assumptions that when the molecules move in a rectilinear path, there is no force of attraction and the volume of the molecules are negligible with respect to the volume of the container in which they exist.

From that he relaxed. Actually, he made the restrictions for these two assumptions; one is the volume of the molecules were taken into account; that is, the volume of the molecules were not considered to be negligible. At the same time, the molecular cohesive forces were taken into account, because in real gases, the molecular cohesive forces will be there. So, he developed in this fashion. I am not going to make a full proof of it that the pressure which is exerted now. Since the volume of the molecules are taken into account, it is not negligible compared to the volume of the container. So, molecules get less space for their movement.

If this be so the number of collisions that the molecules make, for example, if the wall for which we define the pressure as the change of momentum, because of this collisions that number of collisions increases. Therefore, the pressure exerted by a real gas on the wall becomes more than that of the ideal gases. This factor Van Der Waal showed that a part of it is taken to be as a kinetic pressure which showed that it should be proportional to R bar T by v bar is the pressure for an ideal gas. It is proportional to this value, where b is a volume parameter. But b indicates the volume excluding the molecular motions.

If we exclude the molecular motion, what is the volume that is b which means that v minus b is actually the volume that is the restricted volume which is in access to the molecules for its motion and he proved that it is in linear proportion to that. That means, v bar minus b is less restricted volume. Therefore, the kinetic pressure that means the pressure which it should give is equal to this; that means, this is more than the ideal gas values.

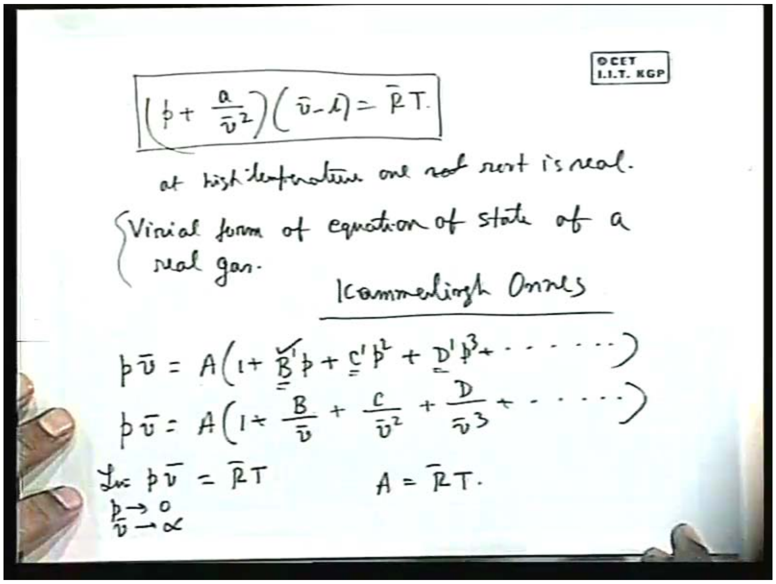
Apart from that actual pressure will be less by this kinetic pressure by an amount which takes care of the molecular cohesiveness. We have read in fluid mechanics that molecules are always being pulled by other molecules; that is, the force of attraction, by its neighboring molecules. That means, if you concentrate our attention on a particular molecule and we will see a molecule on the bulk which is far from the free surface, far from the wall, is being pulled by all neighboring molecules from outside so that a molecule is almost in a balance. But if we go very near to the wall or very near to the free surface, we see there is a misbalanced force. we may know that the molecules are being pulled by more number of molecules.

If we concentrate our attention on a single molecule, by more number of molecules from the bulk of the fluid, because there are very fewer molecules near the free surface or near the wall. Therefore, if we consider a molecule near the wall or near the free surface, there is a net attractive force of the molecule towards the bulk of the system or bulk of the fluid or bulk of the gas. In this case, it causes a reduction; rather, it causes a reduction in the pressure, the way the surface is being stretched. That means always there is a surface in stretched condition. As we have read in fluid mechanics, to create a surface we require energy, because a molecule has to be brought to the surface against the inward attraction of the molecule.

Similar is the case, if a molecule has to be brought to the wall, work has to be done. That means what happens when a molecule comes very close to the wall? Net pull on the molecule is there towards the bulk of the gas for which a reduction in the pressure that is from the kinetic pressure is there. He proved that it is directly proportional to the molar density. By common sense, we can guess the number of moles per unit volume is more, so force will be more so that the pressure will be less. Therefore, it is inversely proportional to the molar volume.

If we substitute p_k we will get a relationship like that. It is not a detailed proof, but thought that this will be sufficient enough to know that the origin or the basic genesis from which this comes. That means a by v square term accounts for the molecular cohesiveness or the molecular cohesive forces which were neglected in case of an ideal gas. b is the parameter or term which takes care of the volume of the molecules. In case of an ideal gas, p plus a divided by v bar square and v bar minus b both are 0 and pv is equal to R bar T. This equation of state is known as Van Der Waals equation. Many real gases obey this Van Der Waals equation of state over a certain range of pressure and temperature.

(Refer Slide Time: 13:51)



$$\boxed{\left(p + \frac{a}{\bar{v}^2}\right)(\bar{v} - b) = \bar{R}T.}$$

at high temperature one rot root is real.

Virial form of equation of state of a real gas.

Kammerlingh Onnes

$$p\bar{v} = A(1 + \underline{B'}p + \underline{C'}p^2 + \underline{D'}p^3 + \cdots\cdots)$$

$$p\bar{v} = A\left(1 + \frac{B}{\bar{v}} + \frac{C}{\bar{v}^2} + \frac{D}{\bar{v}^3} + \cdots\cdots\right)$$

$$\lim_{\substack{p \to 0 \\ \bar{v} \to \infty}} p\bar{v} = \bar{R}T \qquad A = \bar{R}T.$$

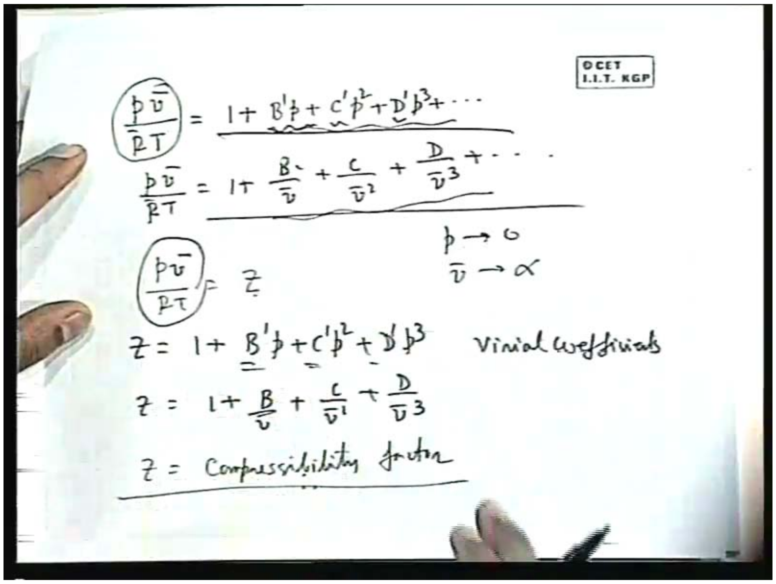
The next thing is that we see the Van Der Waal gas. If we again write this that p plus a divided by v square into v minus b is equal to R bar T. In this case, if we solve for v, v will give three roots. It is cubic in various equations; that means, for a given pressure and temperature, v will be having three roots. But it has been found that if we solve this, amongst these three roots only one root is real at high temperature and at low temperature. There are three real roots, but out of that one root is in a metastable state; only this information will be sufficient.

Another root which is real, but it is not feasible. That root will lie on a curve which gives a negative compressibility. Always, for all substances, if we increase the pressure, volume decreases. Therefore, one of the roots, one is metastable state and another root represents a physically impossible value. Therefore, only if you solve this, we always get one real and physically possible value of v. So, this is mostly all about the Van Der Waals equation.

After that I will tell this virial form of equation of state of a real gas. Like Van Der Waals equation there are number of equations which we can express as I have told for different gases obey at different pressures and temperatures. But one scientist Kamerlingh Onnes is a German scientist. He proposed that all real gases should be expressed in this fashion; some constant A into one plus B dash p plus C dash p square plus D dash p to the power three in an infinite power series. Either these two A's are same, or one plus B divided by bar plus C divided by v bar square plus D divided by v bar cube in an infinite power series. I can use B C D here or dash here doesn't matter this is the usual convention that I am following.

If we can express this in power series then we can closely approximate all real gases by properly evaluating these values of B dash C dash D dash and B C D. Here, we see this A, B dash, C dash and D dash or A, B, C and D are all constants. They are functions of temperatures; that means, at a constant temperature these are giving numerical values. So, A, B dash, C dash and D dash which are the coefficients of this power series; either in p or in v bar, they are functions of temperature. If we recall this limit pv bar as p tends to 0 or v tends to infinity always satisfies this relationship and we get A becomes equal to R bar T.

(Refer Slide Time: 17:47)



$$\boxed{\frac{p\bar{v}}{\bar{R}T}} = \underline{1 + B'p + C'p^2 + D'p^3 + \cdots}$$

$$\frac{p\bar{v}}{\bar{R}T} = \underline{1 + \frac{B}{\bar{v}} + \frac{C}{\bar{v}^2} + \frac{D}{\bar{v}^3} + \cdots}$$

$p \rightarrow 0$

$\bar{v} \rightarrow \infty$

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

$$Z = 1 + B'p + C'p^2 + D'p^3$$ Virial coefficients

$$Z = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3}$$

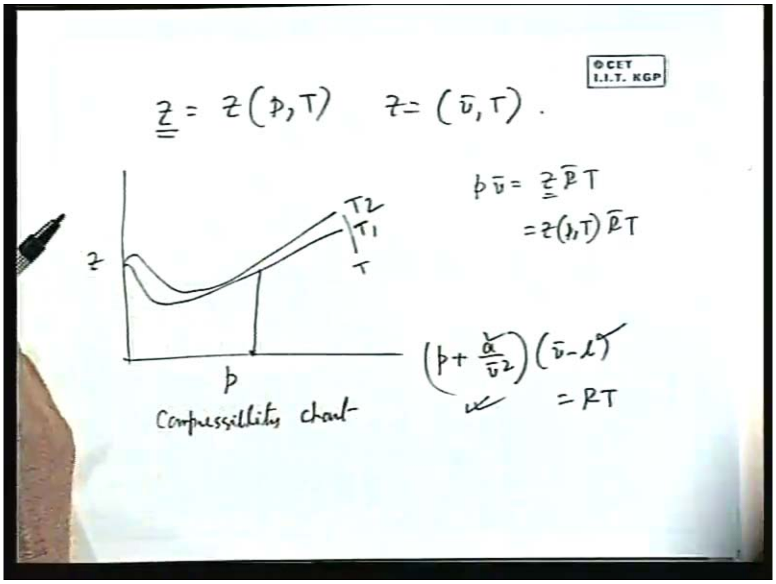
Z = Compressibility factor

Therefore, this equation can be expressed as pv bar R bar T is equal to one plus B dash p plus C dash p square plus D dash p cube plus like that. Similarly, in terms of molar volume, B divided by v bar plus C divided v square plus D divided v cube plus this in finite series. Therefore, we see for an ideal gas, B dash, C dash, D dash B, C, D becomes 0. pv dash by RT if we represent as z then we can write z is equal to one plus B dash p plus C dash p square plus D dash p cube not A B dash C dash is zero sorry I am sorry I have told wrong I am sorry.

For real gas, B dash, C dash, D dash and B, C, D is 0; that is hypothesis that is not wrong what I want to mean is that when p tends to 0 and v tends to infinity, obviously these terms become 0. But for an ideal gas I am correct that these coefficients are 0. This pv bar by RT is known as compressibility factor; this z is known as compressibility factor. This compressibility should not be confused with the compressibility of the fluid mechanics, but this gives almost a same concept physically, why because this is something to do in with the compressible that is the compression.

Here, you see this is known as compressibility factor. First of all, we see mathematically that z is compressibility factor whose value for ideal gas is 1, but for real gases are different from 1. Why it is compressibility factor? Because of the compression, a gas at a ratified state satisfies the ideal gas laws, but when you compress it at high pressure then it deviates from the ideal gas laws. That is why z is defined as the compressibility factor when z is equal to 1 that represents an ideal gas.

(Refer Slide Time: 20:21)



$z = z(p, T) \quad z = (\bar{v}, T)$.

$p\bar{v} = z\bar{R}T$

$= z(p,T)\bar{R}T$

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

Compressibility chart

This compressibility, usually a function of pressure and temperature may be a function of volume and temperature. Let us draw a figure z versus p at different values of T as parameter. I am showing a particular curve like this. At different temperatures T_1, T_2, these are plotted. This is known as compressibility chart; that means, if one can find out at a particular state point, what is the value of z from the compressibility chart?, or compressibility table just like steam table. We know the steam properties at a particular pressure or temperature either saturated state or superheated state and corresponding tables we know all the properties.

Similar way, if we know the compressibility factors then you write the equation of state for any gas at z R bar T, where z is function of p and T. That means this is a multiplying factor; that means, pv bar is equal to z R bar T, where z is equal to 1 for an ideal gas. For a real gas, we have to find out the value of z corresponding to that particular pressure and temperature. z is a function of the state point, because state point will decide how much deviation is there from the ideal gas. This is the definition of the compressibility and this is the compressibility chart.

Similar to the concept of fluid mechanics, as we have seen that it has been found that for a Van Der Waal gas p plus a by v square into v bar minus b is equal to RT. Now, for different values of a and b, it constitutes a different equation of state. Equation of state will vary; the structure is same and functional relation is same. Because they belong to a particular class; Van Der Waals equation of state, but the particular equation will go on varying. If we have got ten gases following, for an example Van Der Waal gas with different values of a and b, we will have to provide compressibility chart; for ten gases ten compressibility charts. Try to understand z as a function of p and T, but if we want to make that for a particular class of gases following a particular type of equation of state by a single equation of state, there will not be any parameter which is distinguishing from gas to gas.

In that case also, we can express the compressibility factor in terms of some normalized dimensionless pressure and dimensionless temperature which will be unique just like following the principle of similarity. For an example, we come to the fluid mechanics. We know that pressure drop is a function of flow rate for a given fluid for a given diameter of the pipe. Pressure drop per unit length, for example, in a parallel flow, the pressure drop per unit length is constant. So, pressure drop per unit length is a function of flow rate for a given fluid; that means, for a given value of row mu and for a given diameter.

If I have to provide a figure, pressure drop versus flow rate then we will have to mention this is valid for a pipe of this diameter for a liquid of this density and this viscosity. If we have to show this similar relationship delta p versus q for different pipe diameters at least for ten diameters, I will have to produce ten curves.

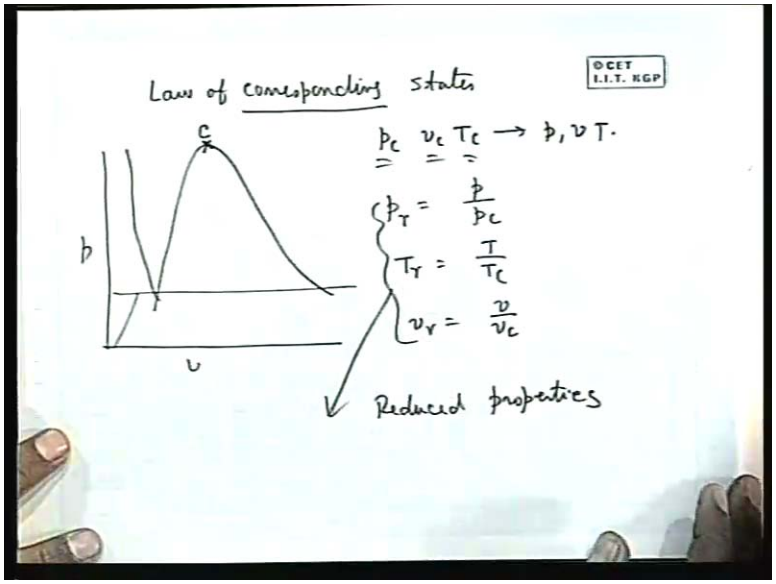
Again, for each diameter, if I have to show the influence of density then I will have to produce so many curves for variation of density. This is the relationship q, but it is not done. Then from the principle of similarity, we have shown also from the theoretical equations, the Navier Stokes equation. It has been found that this phenomena that pressure drop per unit length depends upon the flow rate, depends upon the density, depends upon the viscosity and depends upon the diameter.

All these things clubbed together, we define implicit functional relations of all these variables then apply the Buckingham’s pi theorem and show. Ultimately, this entire physical phenomenon is guided by two governing parameters in non-dimensional forms. They are known as pi terms. 1 is the friction factor and another is the Reynolds number.

So, density, viscosity, diameter and velocity; that means the flow rate in terms of the average velocity of flow is clubbed in one dimensionless term. Reynolds number and the pressure drop is normalized with half row v square is one parameter as the friction factor. So, we give the value of friction factor versus Reynolds number which takes care of pressure drop flow rate curve for all diameters and all fluids in a particular group. What is that group?

Newtonian fluid where in non-Newtonian fluid there is the different relations. Newtonian fluid gives a group homologous series in fluid machines. Also, we will read that machines of similar geometrical shapes are falling on a particular class these are known as homologous series in a particular group. Similarly, here also, a number of gases following the Van Der Waals equation can be expressed in terms of this dimensionless parameter so that one can express one single equation of state. A single compressibility chart to work with all gases of this particular kind with this genesis and theory the concept of law of corresponding states came.

(Refer Slide Time: 26:11)



Law of corresponding states

$\underline{p_c}\ \underline{v_c}\ \underline{T_c} \rightarrow p, v\, T.$

$p_r = \frac{p}{p_c}$

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

$v_r = \frac{v}{v_c}$

Reduced properties

Law of corresponding states, this is very important. In thermodynamics, we tell that this corresponding word is same to the similar points that the similar parameters. To do that, the basic physical concept is taken that pv diagram, because there has to be some sort of similarity. Otherwise, the similarity parameter that is pi parameters cannot be taken. For example, when I compare the two pi flow problems with different diameters or different fluids then I see that there is some similarity in the physics of flow. The two flows are governed by the pressure forces and viscous forces.

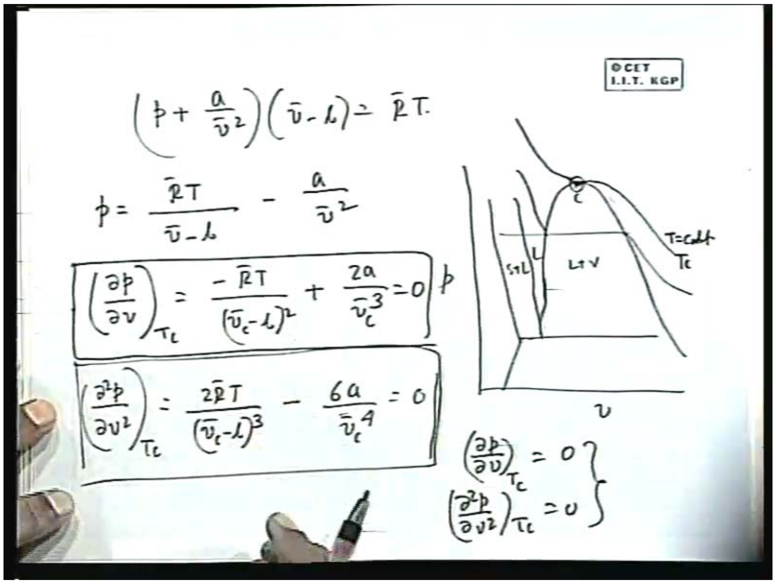
Similarly, when the flow in a surface waves or in a free surface flow, the physics are same. The two flows different situation, different liquids, different geometry are governed by the gravity force and the inertia of forces. Similarly, some common similarity should be there. What is that it has been found that this vapor dome is similar for all substances; that is, there is a similarity in the structure of these vapor dome. That means if you draw the pv diagram, you see their structure is same quantitative value maybe different. There is a critical point and the slope and all these things are similar; that means, they reveal a geometrical similarity on this pv diagram.

Therefore, from this it was thought that similarity parameters can be resorted to make the similarity principle valid there so that we can do what we have told. For that, what we do? This critical point which is different for different gases, even the Van Der Waals gases, there may be number of gases following the same equation of state, but having different a, b values different critical point. Similarly, for ideal gases also all gases are not saying, because their values of R the characteristic gas constant may be differing.

For ideal gases one thing is unique that if we express in terms of the molar volume, they reduce to a single equation. R bar is same for all gases which is not so for the ideal gases. Even if we express in terms of the molar volume a, b parameter, for an example, Van Der Waal gas all gases will be having such parameters; they are not same. Their critical points are also different, but we can use these value p_c, v_c, T_c to normalize the corresponding dimensional parameter p,v,T. We define that dimensionless pressure as p_r is equal to p divided by $p_{c;}$ that means these are used as the reference variable for normalizing the actual dimensional variables.

We define T_r is equal to T divided by T_c and v_r is equal to v divided by v_c and this non-dimensional terms in science of thermodynamics are known as reduced properties. That means p_r is the reduced pressure, T_r is the reduced temperature and v_r is the reduced volume and if you do so, we will see that this equations take a unique form. I just give an example . Let us do it for Van Der Waals gas.

(Refer Slide Time: 29:22)



©CET
I.I.T. KGP

$$\left(p + \frac{a}{\bar v^2}\right)(\bar v - b) = \bar R T.$$

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

$$\boxed{\left(\frac{\partial p}{\partial v}\right)_{T_c} = \frac{-\bar R T}{(\bar v_c - b)^2} + \frac{2a}{\bar v_c^3} = 0}$$

$$\boxed{\left(\frac{\partial^2 p}{\partial v^2}\right)_{T_c} = \frac{2\bar R T}{(\bar v_c - b)^3} - \frac{6a}{\bar v_c^4} = 0}$$

$$\left.\begin{array}{l}\left(\frac{\partial p}{\partial v}\right)_{T_c} = 0 \\ \left(\frac{\partial^2 p}{\partial v^2}\right)_{T_c} = 0\end{array}\right\}$$

Van Der Waals equation is p plus a by v bar square into v bar minus b is equal to R bar T. Along with that, we have to take care of another physical fact that if we draw this pv diagram for example these are liquid vapor as you know I am not drawing all these thing these are known.

So, one thing is that at the critical point, you know these are the isotherms. So, the isotherms at the critical point have a 0 slope and 0 curvature. This is a physical fact, which means mathematically, del p divided by del v; this is for all gases, del p divided del v at the at T_c; that means, the slope of the isotherm that is T is equal to constant which is T_c. Here is the isotherm that at Tc this slope is 0 and del square p divided del v square at T_c is 0; that means, this is almost flat here which has got both a 0 slope and the 0 curvature.

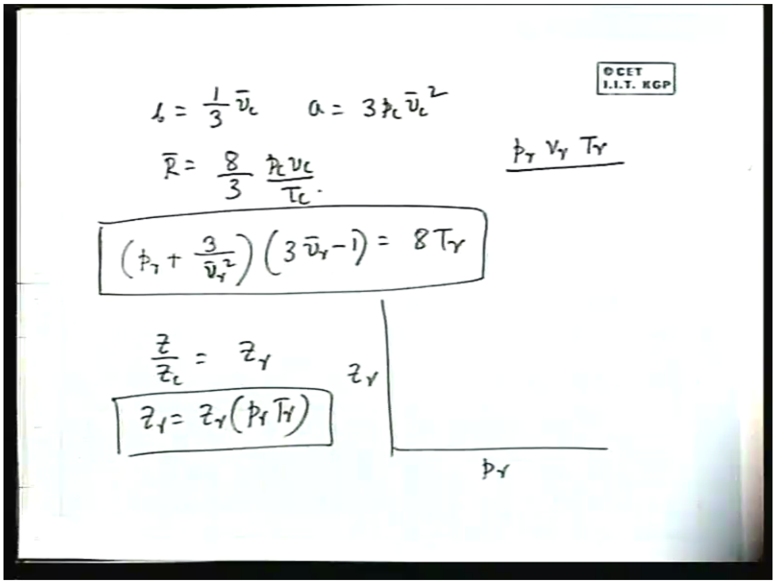
If we use this, we write p is equal to R bar T divided by v bar minus v minus a by v square. Then if we find out del p divided del v at at T_c is equal to minus R bar T by v_c bar minus b whole square plus 2 a divided by v_c bar whole cube. This is one equation; another equation is the second derivative. Then second derivative del square p divided by del v square at T_c

second derivative; that means, again it will be plus 2 R bar T divided by v_c bar minus b whole cube minus 6 a by v_c bar to the power four is 0. So, that is another equation.

If we solve these two equations that I am not doing it here the simple algebra then we get

a, b and R bar in terms of p_cv. This we have done at the school level understand but again it will be recapitulation cannot help.

(Refer Slide Time: 32:15)



$b = \frac{1}{3}\bar{v}_c \qquad a = 3 p_c \bar{v}_c^2$

$\underline{p_r \; v_r \; T_r}$

$\bar{R} = \frac{8}{3}\frac{p_c v_c}{T_c}.$

$$\boxed{\left(p_r + \frac{3}{\bar{v}_r^2}\right)\left(3\bar{v}_r - 1\right) = 8T_r}$$

$\frac{z}{z_c} = z_r$

$$\boxed{z_r = z_r(p_r T_r)}$$

We get b is equal to one-third v_c molar volume at the critical state and a is equal to 3 p_c vc bar square and R bar is equal to 8 by 3 $p_c v_c$ divided by $T_{c;}$ this is z_c that is compressibility at the critical point. If you substitute this in the Van Der Waals equation of state then the equation of state becomes like this; 3 by v_r bar square into 3 v_r minus 1 is equal to 8 T_r. This Van Der Waals equation of state is valid for all gases, following the Van Der Waals equation a, b is eliminated. In that case, if we define z by z_c as I reduce of course z is non-dimensional, but if we scale it with z_c and if we plot z_r as a function of p_r T_r, we get only one equation.

That is a series of curves in z_r, p_r plane with different values of T_r is unique that means this families of curves are unique for all Van Der Waal gases. This is the theory behind the law of corresponding state. This is expressed like that and corresponding states means a state of a system gas. For example, Van Der Waals gas or any gas which are having the same p_r, v_r, T_r are known as corresponding states.

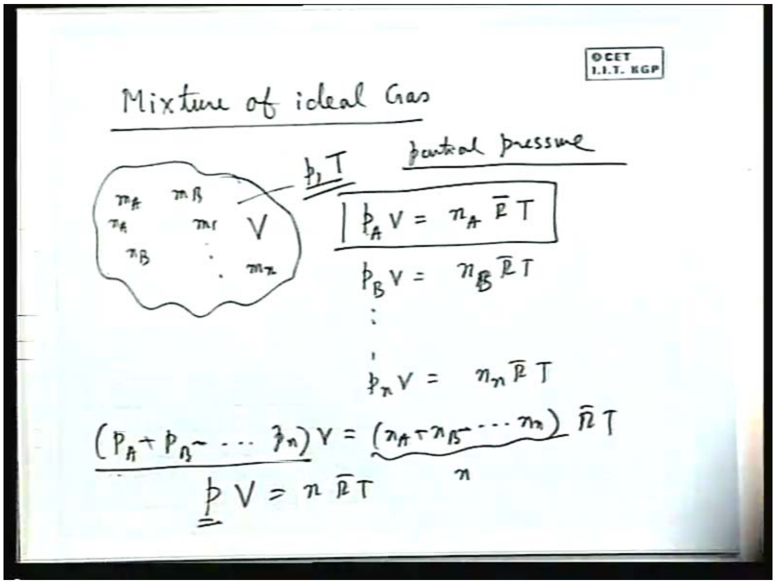
Similar situations in fluid flow; that means the same Reynolds number, in two flows same Froude's number. All these things that means their actual velocity may be different, their actual gravity condition may be different, but they are having the same Reynolds number; that means, the situations are similar.

Here also, the p, v, T maybe different at two states, but for the two gases. If we normalize the p_c, v_c, T_c and if we see the reduced properties are same, then they are told as corresponding states that means states are similar. For corresponding states, we get the same value of z_r. For example, a Reynolds number is fixed; friction factor is fixed, but if we have got a higher velocity then we get a higher pressure drop. If we have got a lower velocity, we get a lower pressure drop. That will be decoded from the friction factor which is unique, because friction factor, if we decode in terms of the pressure drop, we will see automatically, the flow for which velocity is high we will get a more pressure drop; for flow whose velocity is less, there will be a less pressure drop, but Reynolds number is same.

That is if velocity is high, for that case, d may be lower or rho mu may be lower. So, I adjusted that Reynolds number is same. This is the concept of the similarity situations. Similarly, here, the same similarity situations are just replaced by the term in thermodynamic science; that is, the law of corresponding state. So, there is nothing much in the law of corresponding states.

Now after this very simple I will leave you today early do not know how much I can tell.

(Refer Slide Time: 35:43)



Mixture of ideal Gas

p, T partial pressure

$$\boxed{p_A V = n_A \bar{R} T}$$

$$p_B V = n_B \bar{R} T$$

$$\vdots$$

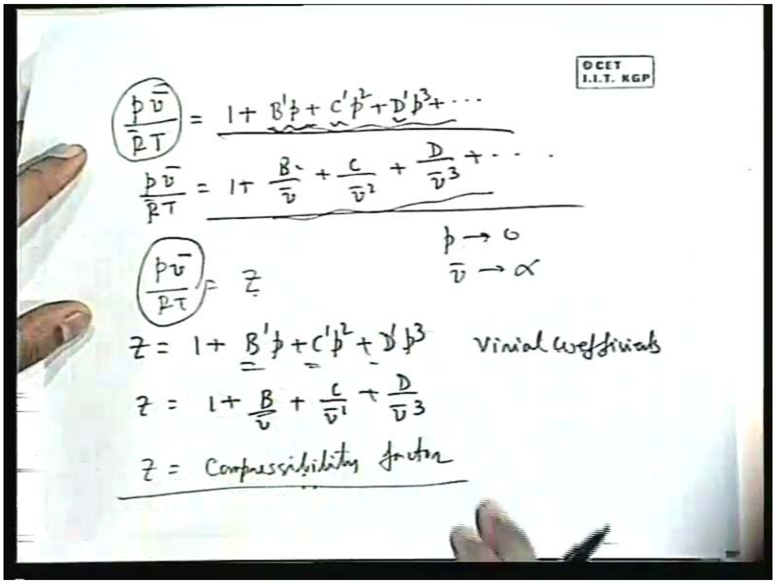
$$p_n V = n_n \bar{R} T$$

$$\underline{(p_A + p_B + \cdots p_n)} V = \underbrace{(n_A + n_B + \cdots n_n)}_{n} \bar{R} T$$

$$\underline{p} V = n \bar{R} T$$

Let us come to mixture of ideal gases. First, I will tell mixture of ideal gases, though mixture of real gases excluded from these syllables for you. Now, again, go back to ideal gas. This is some information about the real gas and especially about the Van Der Waal gas. As an example, how we can reduce it into in terms of the reduced properties and the concept of corresponding states, how you can express the real gas in terms of a virial expansion coefficients.

(Refer Slide Time: 36:21)



OCET
I.I.T. KGP

$$\boxed{\frac{p\bar{v}}{\bar{R}T}} = \underline{1 + B'p + C'p^2 + D'p^3 + \cdots}$$

$$\frac{p\bar{v}}{\bar{R}T} = \underline{1 + \frac{B}{\bar{v}} + \frac{C}{\bar{v}^2} + \frac{D}{\bar{v}^3} + \cdots}$$

$p \to 0$
$\bar{v} \to \infty$

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

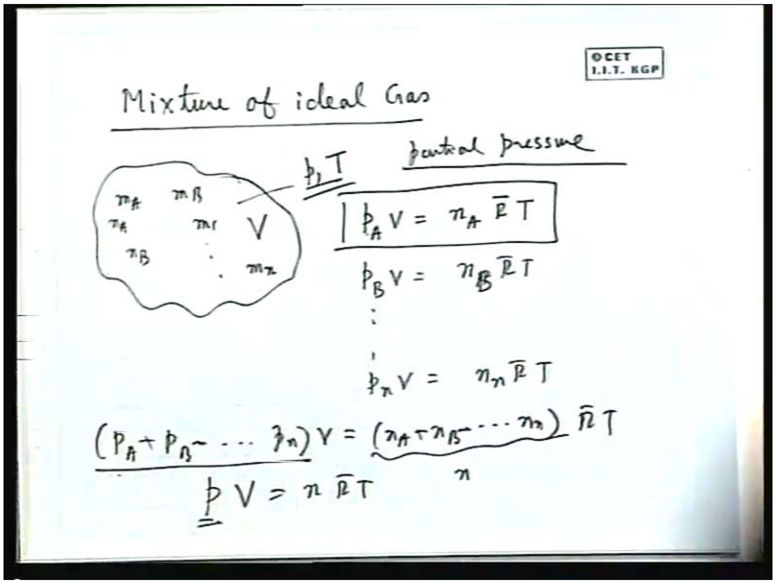
$$Z = 1 + \underline{B'}p + \underline{C'}p^2 + \underline{D'}p^3$$ Virial coefficients

$$Z = 1 + \frac{B}{\bar{v}} + \frac{C}{\bar{v}^2} + \frac{D}{\bar{v}^3}$$

Z = Compressibility factor

There are of course I have forgotten to tell this coefficients b, c, d are known as virial and this expansion is known as virial expansion or virial series. Then the definition of the compressibility and compressibility is 1 in case of an ideal gas and the law of corresponding states.

(Refer Slide Time: 36:40)



OCET
I.I.T. KGP

Mixture of ideal Gas

p, T

partial pressure

$$\boxed{p_A V = n_A \bar{R} T}$$

$$p_B V = n_B \bar{R} T$$

$$\vdots$$

$$p_n V = n_n \bar{R} T$$

$$\underline{(p_A + p_B \cdots p_n)} V = \underbrace{(n_A + n_B \cdots n_n)}_{n} \bar{R} T$$

$$\underline{p} V = n \bar{R} T$$

Let us go back to mixture of ideal gas. In many situations, we have to deal with a mixture of ideal gases; that means, it is not a single component system. For example, air itself is a mixture of ideal gases, but its composition is throughout same that it behaves almost like a single component. That is why it is a pure substance, but somewhere composition may change sometime. However, at any state, mixtures of ideal gases also behave as an ideal gas. This is a hypothesis. This has been found experimentally. This has been proved from kinetic theory of matter; that is, if we assume all the ideal gas is hypothesis then mixture of ideal gases are also ideal gas; that means if a mixture of ideal gas is there, for a fixed composition this gas will behave as an ideal gas the way air does. So, mixture of ideal gases, the first thing is they behave as an ideal gas.

There are certain laws; for example, if we have in a container for example there are number of gases with mass m_A, m_B and $m_{C.}$ There are n number of gases with mass m_A and corresponding number of moles are there n_A $n_{B.}$ Like that there are number of gases. When a mixture of gases is in equilibrium, means what? The pressure and temperature are same. That means the entire system having a pressure p and a temperature T. In this case what happens? When we mix two gases what happens to that ideal gas hypothesis? The molecules do not have any volumes. That means there is an intermolecular diffusion; both the gases diffuse into one another. What happens if there is a fixed container? All the constituent gases occupy the same volume. Therefore what happens?

Each gas is under an expanded state; that means, its pressure is reduced, because it has to expand to its volume. That means it goes in an intermolecular diffusion with the other gases. Therefore, the pressure exerted by each gas individually is less than that of the pressure which the mixture is exhibiting. That pressure is known physically as the partial pressure which means that if any one of the gas, at the same temperature, the temperature of the mixture is allowed to exist alone in that particular volume, because exactly it is occupying the same volume. Then the pressure it could have exerted because other molecules are there of the other constituting component is known as partial pressure.

If we deal with the mole then it will be better. That means I can write if the partial pressure of A is p_A and the volume is V of the container that means the mixture p_AV is equal to number of moles n_A R bar T, where R bar is same for all constituting components ideal gas that is one good thing.

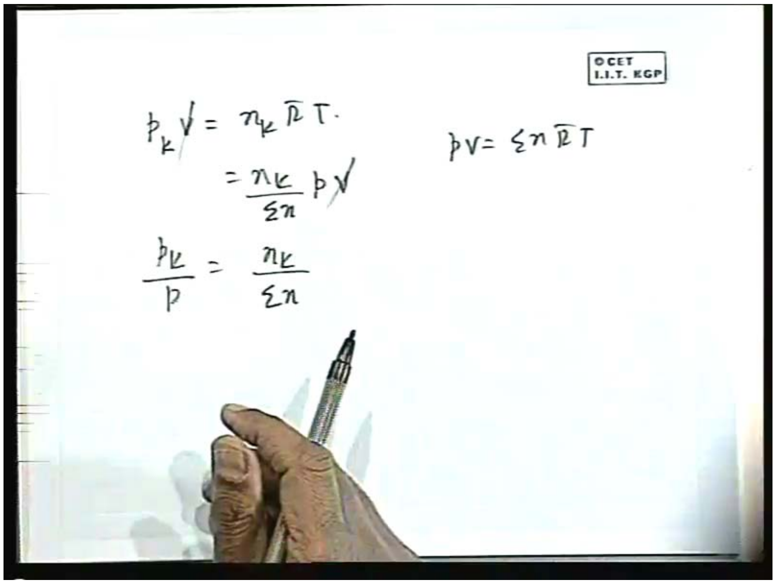
This is the mathematical equation which defines the partial pressure and which I have told just now is the physical concept; how you can conceive the partial pressure of a particular constituting ideal gas in a mixture of number of ideal gases. Therefore, this is the basic equation for the partial pressure. Similarly, if we define the partial pressure for the component B then we get another expression; that is, p_B V is equal to number of moles n_B R bar T.

[Conversation between Student and Professor – Not audible ((00:40:18 min))]

nB am sorry very very very very good and ultimately, all these things can write for the nth component is equal to n_n R bar T. If I add this, we get p_A plus p_B plus dot dot dot upto p_n V is equal to n_A plus n_B plus dot dot dot up to n_n into R bar T. Now, what is n_A plus n_B plus dot dot dot? These are the total number of moles of the gas, because they are the amount of thing. So, amounts are additive. These are the extensive properties and therefore, this for the entire mixture as an ideal gas. I can write its pressure into its total volume of the ideal gas; ideal gas as a whole, I am now considering as a pure substance. Ideal gas as a whole is a pure substance if it has got same composition which does not change. pV is equal to n R bar T. If I compare, the pressure of the mixture that is sometimes known as total pressure is equal to the sum of the partial pressure. Who is the person who first derived developed it?

Dalton is the scientist. That is why it is known as Dalton's law that sum of the partial pressures equals the total pressure. If we see that for a given particular component p_AV is n_A R bar T.

(Refer Slide Time: 41:45)



$$p_k \cancel{V} = n_k \bar{R} T.$$

$$= \frac{n_k}{\Sigma n} p \cancel{V}$$

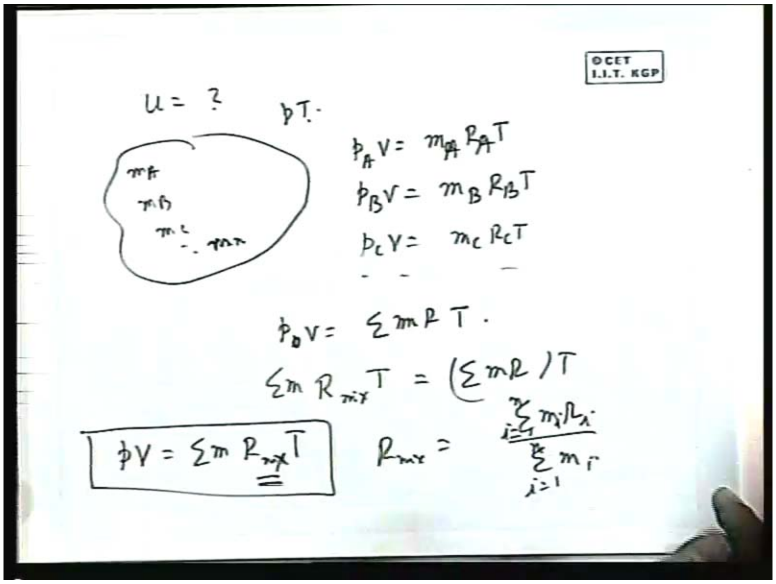
$$pV = \Sigma n \bar{R} T$$

$$\frac{p_k}{p} = \frac{n_k}{\Sigma n}$$

For example, here, If we see for any component kth component, let us write for kth component that is equal to n_k R bar T. If we now substitute R bar T as sigma n like this, that means n_k divided by sigma n pV, then you cancel V. The ratio of the partial pressure to the total pressure is the mole fraction; that means, depending upon the mole fraction its partial pressure will be determined.

Ratio of the partial pressure to the total pressure is the ratio it depends upon the number of moles, what pressure will exist. It will depend upon its number of moles as compared to the total number of moles. This is one equation. Therefore, the sum of the partial pressure is the total pressure for extensive properties. How do you write other properties? For example, what is u? Before that, how do you define the characteristic gas constant? Again refer the same figure.

(Refer Slide Time: 42:52)



$u = ?$ pT.

m_A, m_B, m_C ... m_n

$p_A V = m_A R_A T$

$p_B V = m_B R_B T$

$p_C V = m_C R_C T$

$p_0 V = \Sigma m R T$.

$\Sigma m R_{mix} T = (\Sigma m R) T$

$$\boxed{pV = \Sigma m \underline{\underline{R_{mix}}} T} \quad R_{mix} = \frac{\sum_{i=1}^{n} m_i R_i}{\sum_{i=1}^{n} m_i}$$

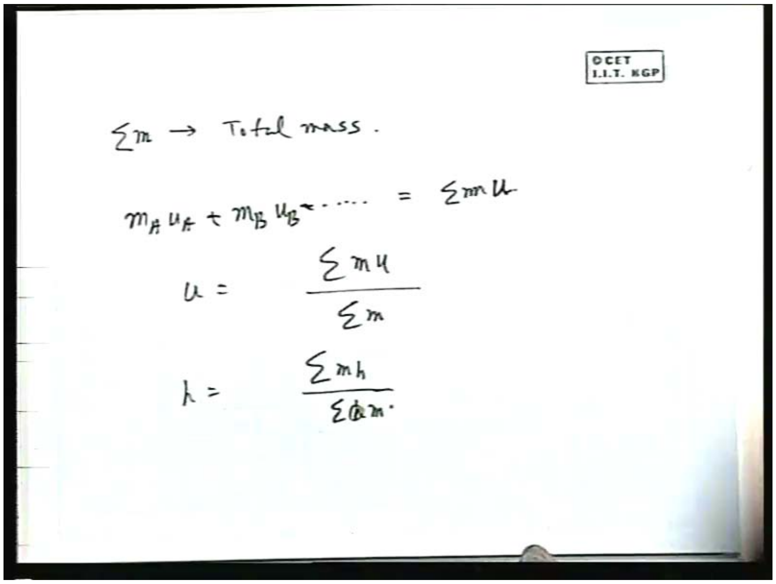
The number of components I am writing the m_A, m_B like this m_C m_n, and p and T. If we write it down, the partial pressure point of view $p_A V$ is equal to m_A $R_A T$, because all are ideal gases. But the equation of stating terms of characteristic gas constant is varying. So, I am giving A sorry capital A sorry.

Similarly, p_B V is equal to that means I am writing in terms of the mass; earlier, I wrote n_A R bar T, now I am writing m_B $R_B T$ like this. If we add it now, we will get p into V sorry I am not writing again because p_A, p_B, p_C, is total pressure you know that is is equal to sigma m R in to T.

What is pV? pV is sigma m R of the mixture; that means, I define the R of the mixture by this equation pV is equal to mixture mass R mixture T, because if that mixture is an ideal gas which is at a pressure p and temperature T then what is the definition of the R mixture? Then we have to use this equation which will define the R mixture. This is the equation which defines the R mixture.

If we write this then we get m R into T that means R mixture is the weighted mean of m_i. For example, we write mi Ri, i is equal to 1. So, I am not writing in that fashion. So, you know this is very simple that means it is a weighted average of m. This way, all other extensive properties can be defined. That means internal energy of an ideal gas, enthalpy of an ideal gas, these are all mass basis.

(Refer Slide Time: 45:03)



$\Sigma m \rightarrow$ Total mass.

$$m_A u_A + m_B u_B + \ldots\ldots = \Sigma m u$$

$$u = \frac{\Sigma m u}{\Sigma m}$$

$$h = \frac{\Sigma m h}{\Sigma m}.$$

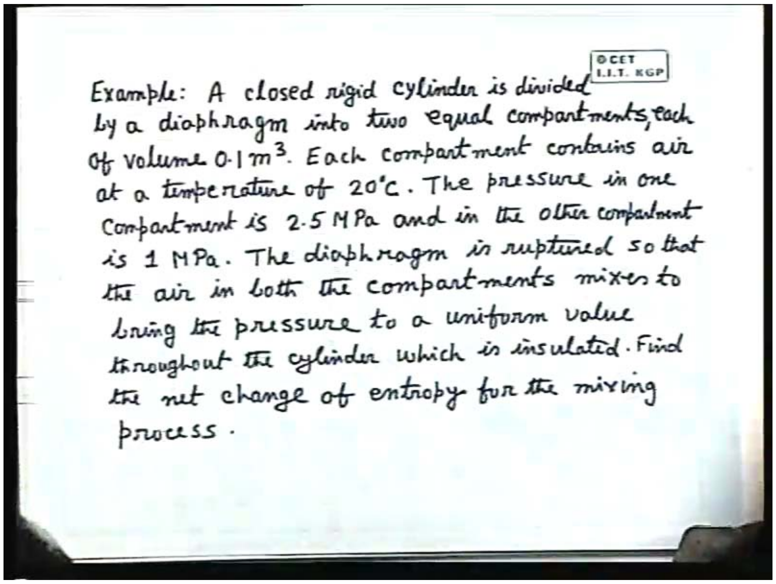
That means if total mass is sigma m then specific internal energies are defined; the total internal energy will be m_A u_A plus m_B u_B dot dot dot is equal to total mass sigma mu is specific internal energy. That means per unit mass that is c_v into T. Therefore, u is sigma mu divided by sigma m. Similarly, uh is equal to sigma mh by sigma m. So, all extensive properties can be written as weighted average very simple mass basis. That means total energy is the contributed energy, but specific internal energy is c_v into T.

[Conversation between Student and Professor – Not audible ((00:46:01 min))]

Oh sorry very good am in a little don't know in a hurry all right so today have to finish it the number of classes.

I will solve certain examples first. I think this one will be very much appreciated I do first this now The change of entropy in a mixture of ideal gases that will not describe in terms of this nomenclature. These are very simple; just a school level thing the recapitulation, but will solve this problem and then you will see how interesting it is. Probably, you know these things already.

(Refer Slide Time: 46:44)

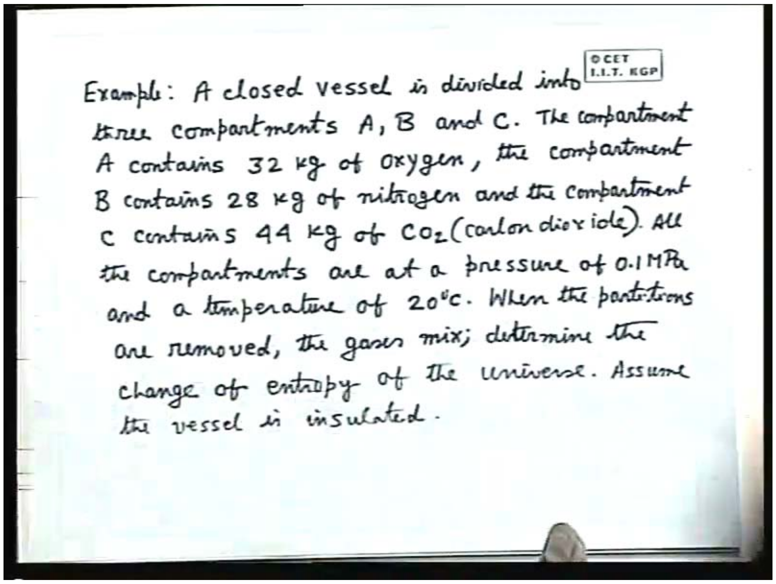


©CET I.I.T. KGP

Example: A closed rigid cylinder is divided by a diaphragm into two equal compartments, each of volume $0.1 m^3$. Each compartment contains air at a temperature of 20°C. The pressure in one compartment is 2.5 MPa and in the other compartment is 1 MPa. The diaphragm is ruptured so that the air in both the compartments mixes to bring the pressure to a uniform value throughout the cylinder which is insulated. Find the net change of entropy for the mixing process.

How to calculate the change in entropy when a mixing of different gases take place which is a very important thing, which makes the definition that how do you define the entropy of a mixture of ideal gas? Let us consider this example. A closed rigid cylinder is divided by a diaphragm into two equal compartments each of volume 0.1m cube. Each compartment contains air no I am sorry will not go this this is a simple example but later what I told let us first sorry I am sorry.

(Refer Slide Time: 47:25)

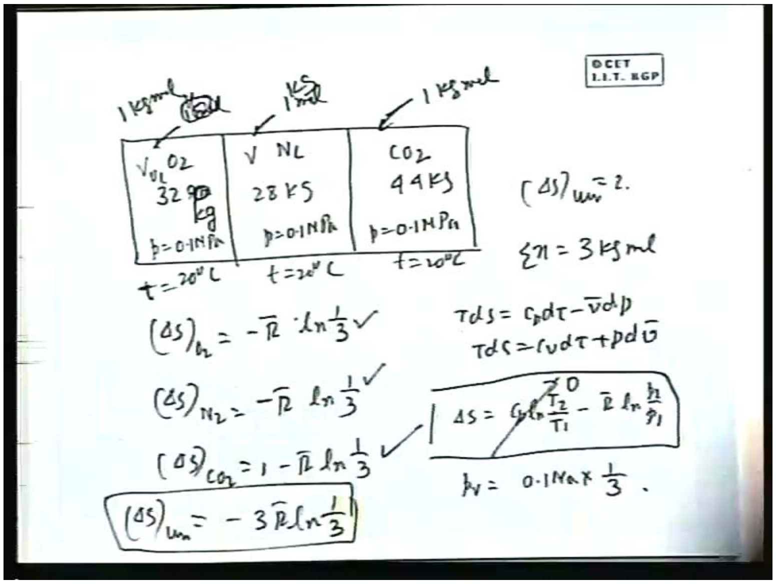


© CET
I.I.T. KGP

Example: A closed vessel is divided into three compartments A, B and C. The compartment A contains 32 kg of oxygen, the compartment B contains 28 kg of nitrogen and the compartment C contains 44 kg of CO_2 (carbon dioxide). All the compartments are at a pressure of 0.1 MPa and a temperature of 20°c. When the partitions are removed, the gases mix; determine the change of entropy of the universe. Assume the vessel is insulated.

A closed vessel is divided into three compartments A, B and C. The compartments A contains 32 kg of oxygen, the compartment B contains 28 kg of nitrogen and the compartment C contains 44 kg of $CO_{2.}$ We can understand from masses that there are one mole carbon dioxide. All the compartments are at a pressure of 0.1M Pa same pressure the atmospheric pressure and at a temperature of 20 degree Celsius. When the partitions are removed, the gases mix. Determine the change of entropy of the universe. Assume the vessel is insulated.

(Refer Slide Time: 48:17)



$(\Delta s)_{mix} = 2.$

$\Sigma n = 3$ kg mol

$(\Delta s)_{O_2} = -\bar{R} \ln \frac{1}{3}$ ✓

$(\Delta s)_{N_2} = -\bar{R} \ln \frac{1}{3}$ ✓

$(\Delta s)_{CO_2} = 1 - \bar{R} \ln \frac{1}{3}$ ✓

$\boxed{(\Delta s)_{mix} = -3\bar{R} \ln \frac{1}{3}}$

$T ds = c_p dT - \bar{v} dp$

$T ds = c_v dT + p d\bar{v}$

$\boxed{\Delta s = \cancel{c_p \ln \frac{T_2}{T_1}}^{\,0} - \bar{R} \ln \frac{p_2}{p_1}}$

$p_2 = 0.1\text{MPa} \times \frac{1}{3}.$

Problem is like this; there are three compartments: one contains 32 kg of oxygen, another contains 28 kg of Nitrogen and the other contains 44kg of CO_2. Pressure for all these compartments p is same; that is, p is equal to 0.1MPa and temperature is also same that is t is equal to 20 degree Celsius.

If I rupture this diaphragm, all these gases are in mechanical and thermal equilibrium. What is the definition of thermodynamic equilibrium? Three equilibriums have to be maintained; mechanic, thermal and chemical. So, what process is going on? There is no work transfer process, there is no heat transfer process, but are they in chemical equilibrium. Any two? No, because there is the difference in chemical potential which we can visualize simply by the concentration gradient. In this compartment nitrogen concentration is 0, whereas oxygen concentration is 100; reverse is the case here. Therefore, there is a concentration gradient. Thermodynamic potentials are different.

Thermodynamics of multi-component systems are not being taught. That is why we cannot understand what is thermodynamic potential, but at least, you can conceive. When they are ruptured, the gases will mix. There will be intermolecular diffusion which is a process defined by the gradient of thermodynamic potential or concentration gradient. That means if we have two gases at different chambers, if we remove and if there is a concentration gradient that flows, just as I explained in the last class that a water vapor flows, because water vapor from a surface it flows into the surrounding. Because surrounding water vapor is less, there is a less concentration, whereas water vapor concentration is more here, and that is why it flows. There is a molecular diffusion. So, they diffuse and they mix. So, there is a process which may not incur work transfer or heat transfer, but there is a process, intermolecular diffusions because of this chemical non-equilibrium to be existing there.

My problem is that how to find out the delta s universe; that means, we will have to find out in that case delta s O_2, delta s N_2, and delta s CO_2 and all of them contain one mole.

Oh kilo mole very good. One not kilo mole last class told that you do not call it kilo mole many book tell kilo mole one kg mole. When they mixed total mixture is 3 kg mole. Now you tell me first that when there is an entropy change of the oxygen, what property of the oxygen is changing, for which entropy change is there, there is no change in temperature.

[Conversation between Student and Professor – Not audible ((00:51:32 min))]

Volume of the oxygen is changing from one volume, but I do not know the volume divisions. Any other parameter you think here that is correct; that is, the volume is changing, oxygen is expanding from this volume to the total volume, but can you take any other parameter?

[Conversation between Student and Professor – Not audible ((00:51:54 min))]

Pressure, because we have got equations of entropy change relating to both volume and pressure, because we have Tds is equal to c_pdT minus vdp or Tds is $c_v$dt plus pdv. If we use this equation, we write the molar volume or the total whatever way we write. Then if we use this equation then you get delta s is $c_p$ln T_2 divided by T_1, T_1 is the initial state minus R bar into ln p_2 divided by p_1, where 2 and 1 are the final and initial state.

If we use this, we will get c_v here plus R bar ln v_2 by v_1. But if I use this one then for this case, for all gases this part is 0, but all gases starting from an initial pressure of point 1MPa is attending a final pressure which is the respective partial pressure in the mixture.

When the equilibrium mixing state is there, after mixing equilibrium state all gases have got their individual partial pressures and that partial pressure is nothing but 0.1MPa into 1 by 3. Therefore, this term is 1 by 3. Therefore, delta s of O_2 is minus R bar into ln 1 by 3

[Conversation between Student and Professor – Not audible ((00:53:25 min))]

Minus very good because this is minus so this will be plus so in both the cases there is a increase of entropy. Therefore delta s of N_2 is minus R bar into ln 1 by 3 and delta s of CO_2 is minus R bar into ln 1 by 3, because there is one mole for each. So, R bar into 1 R bar into 1. If the values are different, we have to calculate dividing by the molecular weight what are the number of moles number of moles, then sum up these and then find out the mole fractions.

For each gas, the ratio of the final to initial pressures may change. To make the calculation simple, I have made this data so that it is easier to calculate. Concept is the same. Here all one mole. So, everywhere it is 1 by 3. So, if we do it, delta S is minus 3 R bar into ln 1 by 3.

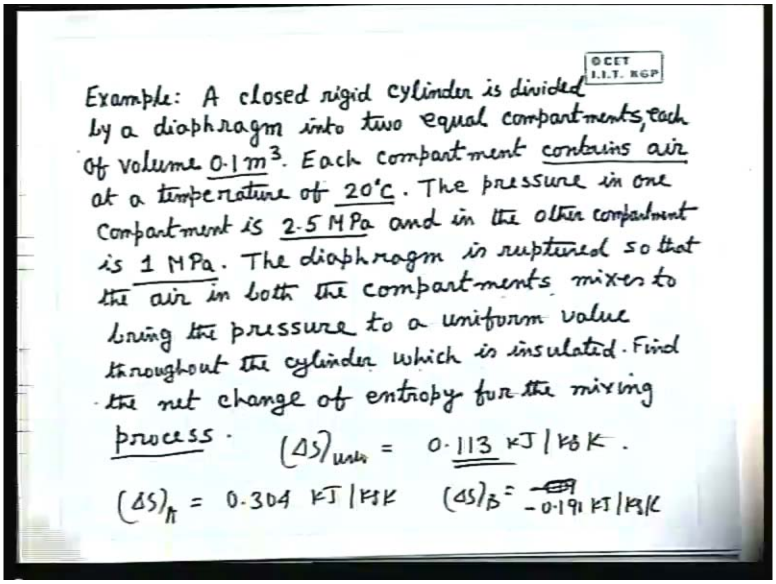
[Conversation between Student and Professor – Not audible ((00:54:12 min))]

It is the one mole one mole one mole. The pressure temperature is same, volume will be same, but we do not have to consider the volume. We can find out the volume, of course that is another thing that you can tell that when the moles are same, pressure temperature same, volume is same, that is good thing and then you can use that three; that is also correct.

[Conversation between Student and Professor – Not audible ((00:54:44 min))]

So then another problem, time is up but this problem you solve this is a given as the your task homework I will give you the answer also this is a homework its not there in the tutorial sheet you take it.

(Refer Slide Time: 54:56)



Example: A closed rigid cylinder is divided by a diaphragm into two equal compartments, each of volume 0.1 m^3. Each compartment contains air at a temperature of 20°C. The pressure in one compartment is 2.5 MPa and in the other compartment is 1 MPa. The diaphragm is ruptured so that the air in both the compartments mixes to bring the pressure to a uniform value throughout the cylinder which is insulated. Find the net change of entropy for the mixing process.

$(\Delta S)_{univ} = 0.113$ kJ/kgK.

$(\Delta S)_A = 0.304$ kJ/kgK $\quad (\Delta S)_B = -0.191$ kJ/kgK

A closed rigid cylinder is divided by a diaphragm into two equal compartments each of volume point 0.1m cube; that means the volume is same. Each compartment contains air. This is not a mixture different components same component air at a temperature of 20 degree Celsius. The pressure in one compartment is 2.5 MPa and in other compartment is 1MPa; that means there is a difference of pressure. They are in mechanical disequilibrium, but the partition is strong enough to sustain that pressure difference so that no work transfer is taking place. The diaphragm is now ruptured. So, there will be a work transfer in between so that the air in both the compartment mixes to bring the pressure to a uniform value throughout the cylinder.

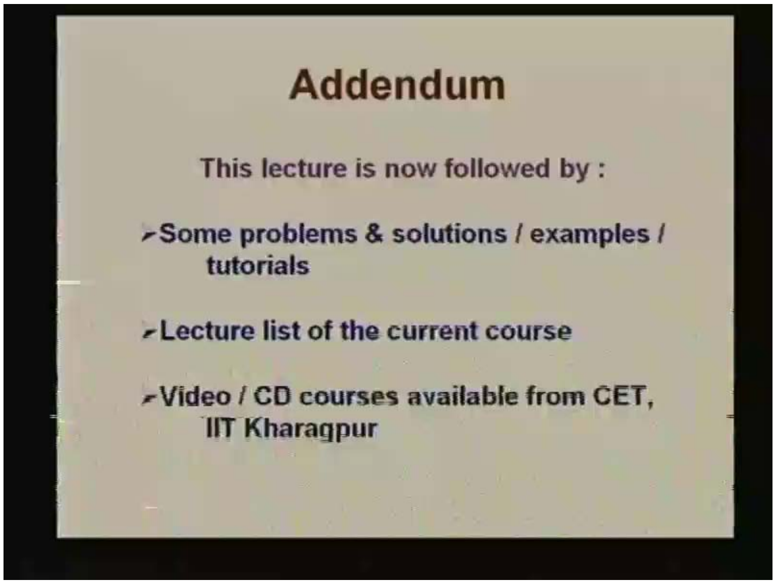
When they mix final state will represent to unique value of the pressure. Equilibrium state means what? All properties will be uniform and constant throughout the cylinder which is insulated; that means entire cylinder is insulated. There is a partition. Earlier problem also, the vessel was insulated. There are two partitions and three compartments similarly insulated. Find the net change of entropy for the mixing process. We have to find, here before calculating this, we have to calculate what the final pressure is.

We use the equation of state for finding out the pressures and accordingly by the same procedure, you can find out delta s A delta s B. Finally, I tell you the delta $S_{universe}$ is equal to

0113 kilo Joule per kilogram kelvin. Delta s A you take it for your homework it will come as 0.304 kilo Joule per kilogram kelvin. Here, the situation is little different; delta s B will be negative that is minus 0.191 kilo Joule per kilogram kelvin so that the algebraic sum of this two gives this one.

Then thank you for today. So attendance will take so next class will start the cycles the vapor power cycles and the

(Refer Slide Time: 57:31)

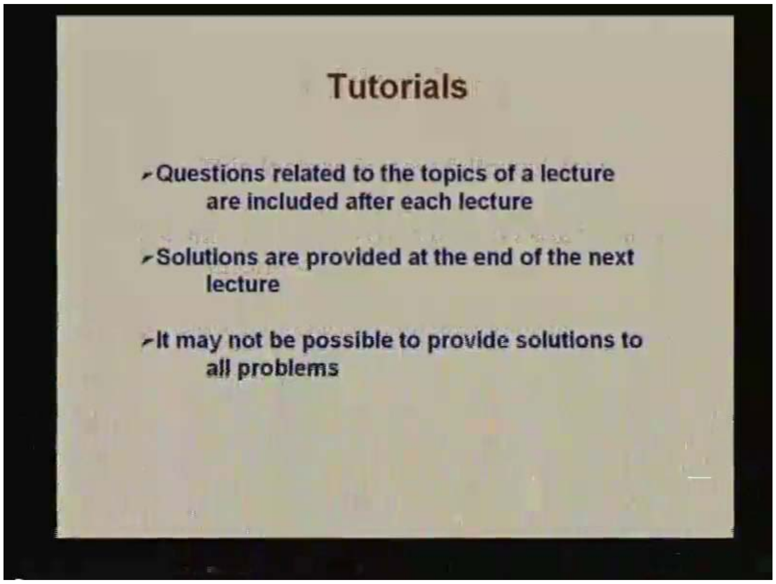


Addendum

This lecture is now followed by :

- Some problems & solutions / examples / tutorials
- Lecture list of the current course
- Video / CD courses available from CET, IIT Kharagpur

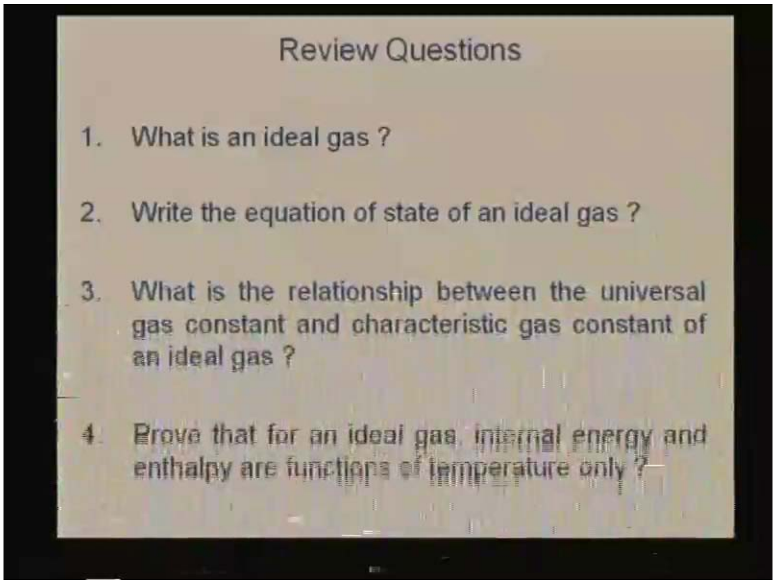
(Refer Slide Time: 57:44)



Tutorials

- Questions related to the topics of a lecture are included after each lecture
- Solutions are provided at the end of the next lecture
- It may not be possible to provide solutions to all problems

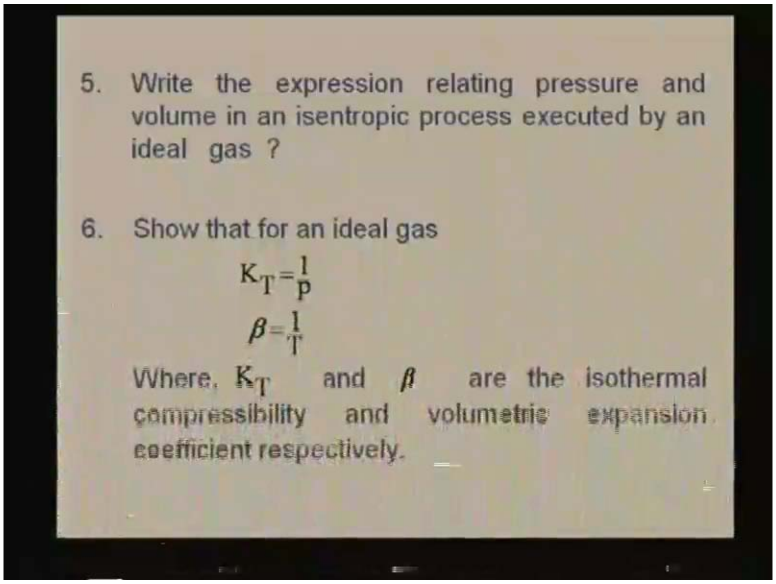
(Refer Slide Time: 57:57)



Review Questions

1. What is an ideal gas ?
2. Write the equation of state of an ideal gas ?
3. What is the relationship between the universal gas constant and characteristic gas constant of an ideal gas ?
4. Prove that for an ideal gas, internal energy and enthalpy are functions of temperature only ?

(Refer Slide Time: 58:16)



5. Write the expression relating pressure and volume in an isentropic process executed by an ideal gas ?

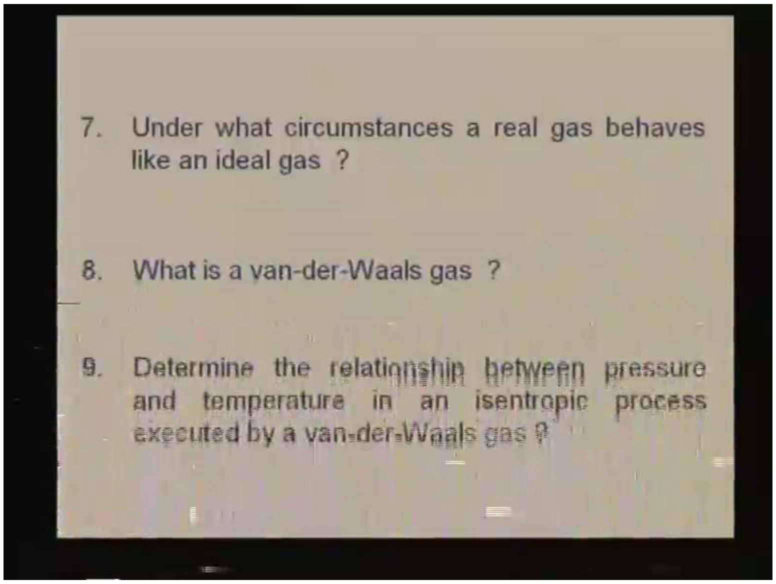
6. Show that for an ideal gas

$$K_T = \frac{1}{p}$$

$$\beta = \frac{1}{T}$$

Where, K_T and β are the isothermal compressibility and volumetric expansion coefficient respectively.

(Refer Slide Time: 58:35)

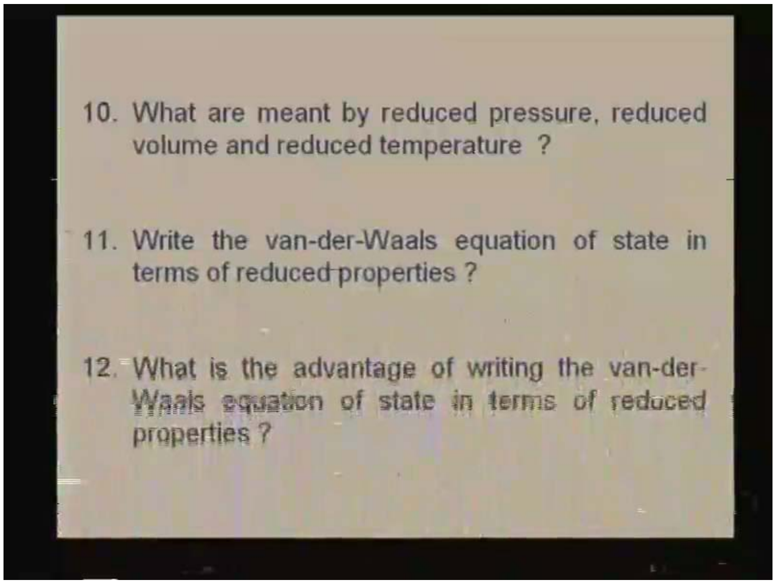


7. Under what circumstances a real gas behaves like an ideal gas ?

8. What is a van-der-Waals gas ?

9. Determine the relationship between pressure and temperature in an isentropic process executed by a van-der-Waals gas ?

(Refer Slide Time: 58:54)



10. What are meant by reduced pressure, reduced volume and reduced temperature ?
11. Write the van-der-Waals equation of state in terms of reduced properties ?
12. What is the advantage of writing the van-der-Waals equation of state in terms of reduced properties ?