Thermodynamics
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Lecture No 28
Ideal Gas - Part 2

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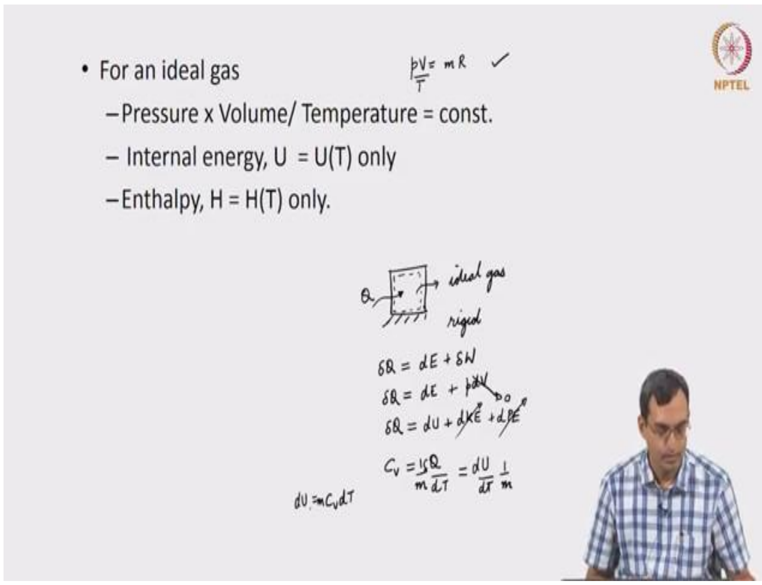

Figure 1.

In the previous lecture, we saw that, for an ideal gas, $pV = mRT$. If we have a system consisting of ideal gas, then mass of the gas m is constant. Then, $\frac{pV}{T} = mR = constant$, because R is a specific gas constant. As long as the composition does not change, R is constant. A consequence of this is that the internal energy U and the enthalpy H of an ideal gas are only a function of temperature.

Consider a rigid container consisting of ideal gas as shown in Fig. 1. It is our system. Add heat Q to this system. There are no changes in kinetic and potential energy of the system as it is not moving or getting lifted. The first law for this system can be written as $\delta Q = dU + \delta W$ (we are writing dE as dU as there are no changes in kinetic and potential energy). Since it is a simple compressible system, $\delta Q = dU + pdV$ (we are considering only the expansion or contraction work). Since the system is rigid, dV = 0. Hence, $\delta Q = dU$, i.e., heat transferred changes the internal energy of the system.

Let's define specific heat for a system. It is defined as the amount of heat needed to raise the temperature of unit mass of a system by unit value. Specific heat can be represented as C_p (specific heat at constant pressure) or C_v (specific heat at constant volume). In the example of the system considered above, $C_v = \frac{1}{m}\frac{\delta Q}{dT} = \frac{1}{m}\frac{dU}{dT}$. Hence, $dU = mC_v dT$. For a system, m is fixed. If C_v is also constant, then U is a function only of temperature.

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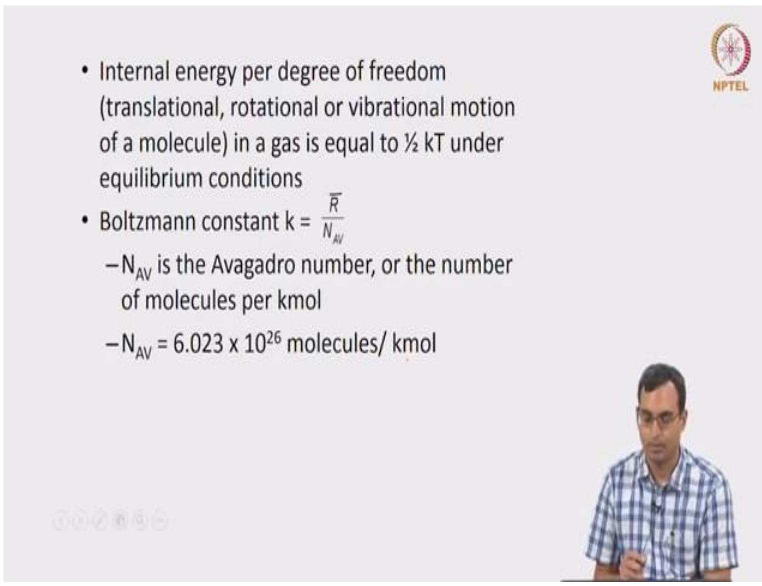

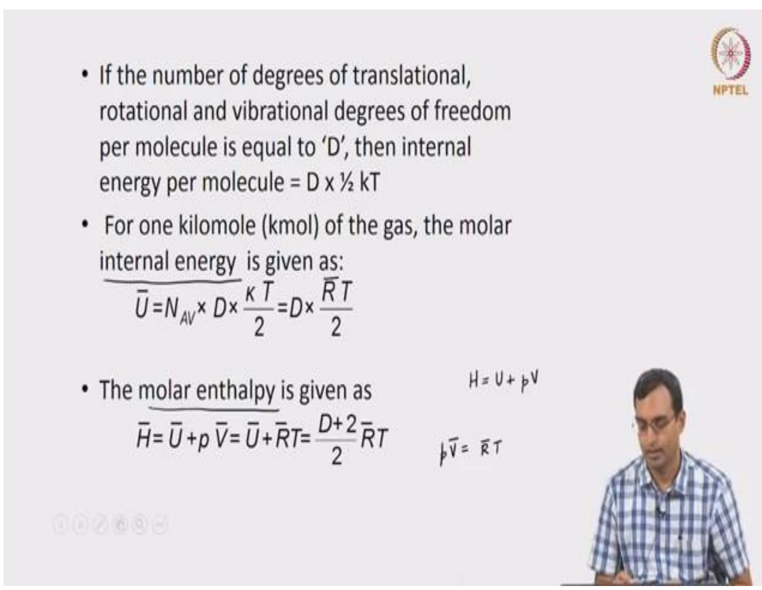

According to the kinetic theory of gases, if the number of translational, rotational and vibrational degrees of freedom per molecule is equal to ‘D’, then internal energy per molecule = $D \times \frac{1}{2}\, kT$, where k is the Boltzmann constant ($k = \frac{\bar{R}}{N_{AV}}$, where $\bar{R}$ is the universal gas constant, N_{AV} is the Avogadro’s number which is 6.023×10^{26} molecules per kilomole). The degree of freedom refers to the number of ways in which the molecule is free to move.

For 1 kilomole of the gas, the molar internal energy is given as $\bar{U} = N_{AV} D \frac{kT}{2} = D \frac{\bar{R}T}{2}$.

Similarly, molar enthalpy $\bar{H} = \bar{U} + p\bar{V}$, where $\bar{V} = \frac{V}{n}$ = specific molar volume (n is number of moles). We know that $pV = n\bar{R}T$. Hence, $p\bar{V} = \bar{R}T$. Thus, $\bar{H} = \bar{U} + \bar{R}T$. Substituting the expression for $\bar{U}$, $\bar{H} = \frac{D+2}{2} \bar{R}T$.

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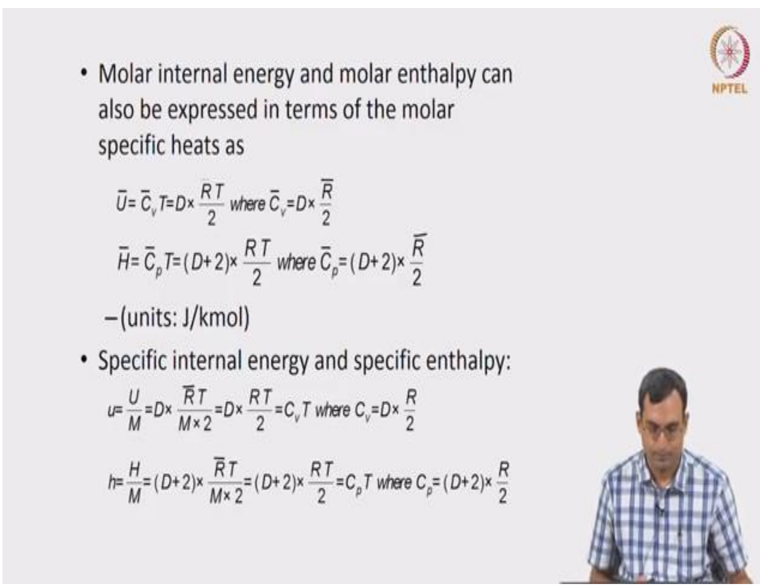

Molar internal energy can also be expressed as follows: $\bar{U} = \bar{C}_v T = D \frac{\bar{R}T}{2}$, where $\bar{C}_v$ is the molar specific heat and $\bar{C}_v = \frac{D\bar{R}}{2}$. Similarly, molar enthalpy can be expressed as $\bar{H} = \bar{C}_p T = (D+2) \frac{\bar{R}T}{2}$, where $\bar{C}_p = (D+2) \frac{\bar{R}}{2}$. The unit of $\bar{U}$ and $\bar{H}$ is J/kmol.

The specific internal energy can be represented as $u = \frac{\bar{U}}{M}$, where M is the molecular weight of the gas. Substituting for $\bar{U}$, $u = D\frac{\bar{R}T}{2}\frac{1}{M} = D\frac{RT}{2} = C_v T$, where $R\left(\frac{\bar{R}}{M}\right)$ is the specific gas constant. Similarly, the specific enthalpy is expressed as $h = \frac{\bar{H}}{M} = (D+2)\frac{\bar{R}T}{2}\frac{1}{M} = (D+2)\frac{RT}{2} = C_p T$.

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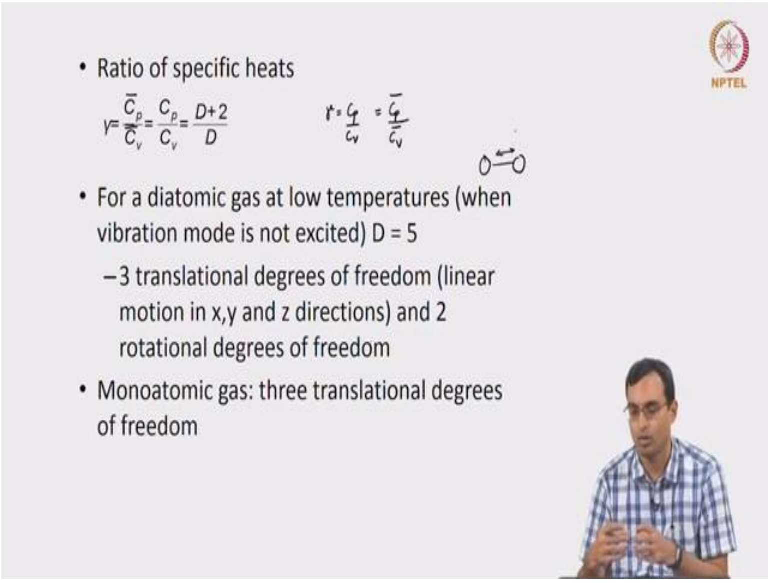

The ratio of specific heats is usually termed as gamma and expressed as $\gamma = \frac{\bar{C}_p}{\bar{C}_v} = \frac{C_p}{C_v} = \frac{D+2}{D}$.

A diatomic molecule of the gas (which looks like a dumbbell) has three translational degrees of freedom (it can move along x, y or z direction), 2 rotational degrees of freedom (It can rotate around any two of the axes which are perpendicular to the bond joining two atoms. However, the rotation around the axis along the bond between two atoms does not much contribute to energy, which results in it having only 2 rotational degrees of freedom.). At low temperatures, the atoms of a diatomic molecule do not vibrate much along the bond direction, i.e., the vibration mode is not excited. Hence, D = 5.

For a monoatomic gas, D=3, because there are three translational degrees of freedom (there can be movement in x, y and z direction). The rotational degrees of freedom are zero because rotation about any axis does not much contribute to the energy of the atom.

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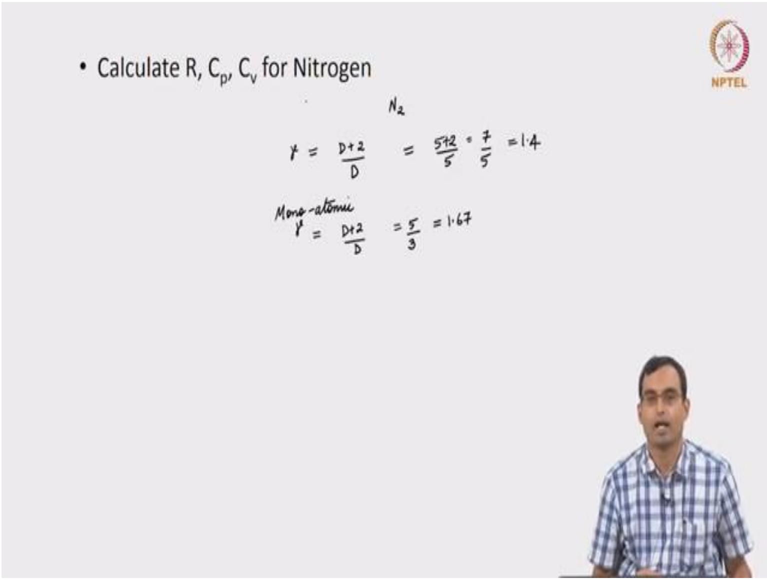

Nitrogen is a diatomic gas. Here, $\gamma = \frac{D+2}{D} = \frac{5+2}{5} = 1.4$ at low temperatures. For a monoatomic gas, $\gamma = \frac{3+2}{3} = 1.67$.

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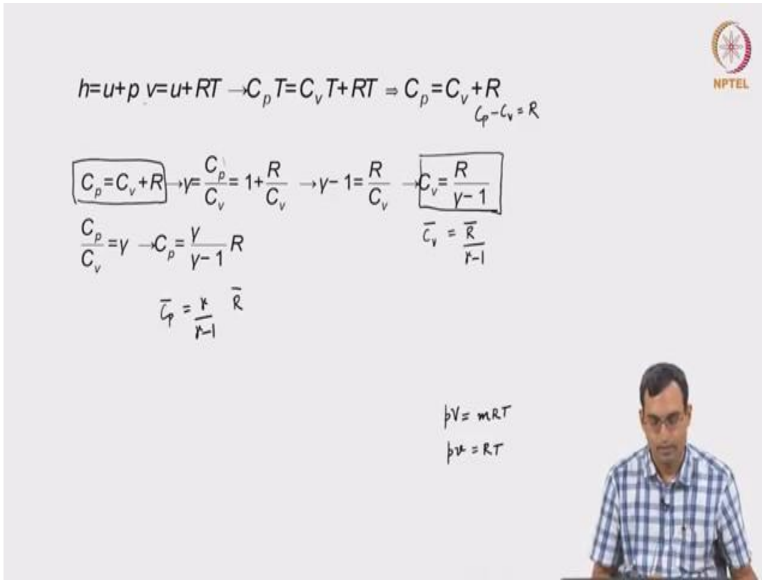

Let’s find the relation between C_p, C_v and R.

We know that, h = u + pv = u + RT (pv = RT is the ideal gas equation). Writing h and u in terms of C_p and C_v, $C_pT = C_vT+RT$. Hence, $C_p = C_v + R$ or $C_p - C_v = R$. If the unit of C_p and C_v is J/kg·K, then R will also have unit J/ kg·K. If we are using molar specific heats, the unit of C_p and C_v is J/ kmol·K. In that case, $\bar{C}_p - \bar{C}_v = \bar{R}$ and $\bar{R}$ is the universal gas constant. Now, $\gamma = \frac{C_p}{C_v} = \frac{C_v+R}{C_v} = 1 + \frac{R}{C_v}$. Hence, $\gamma - 1 = \frac{R}{C_v}$. Thus, $C_v = \frac{R}{\gamma-1}$. Also, $\bar{C}_v = \frac{\bar{R}}{\gamma-1}$. Since, $C_p = C_v\gamma = \frac{\gamma}{\gamma-1}R$. Also, $\bar{C}_p = \frac{\gamma}{\gamma-1}\bar{R}$.

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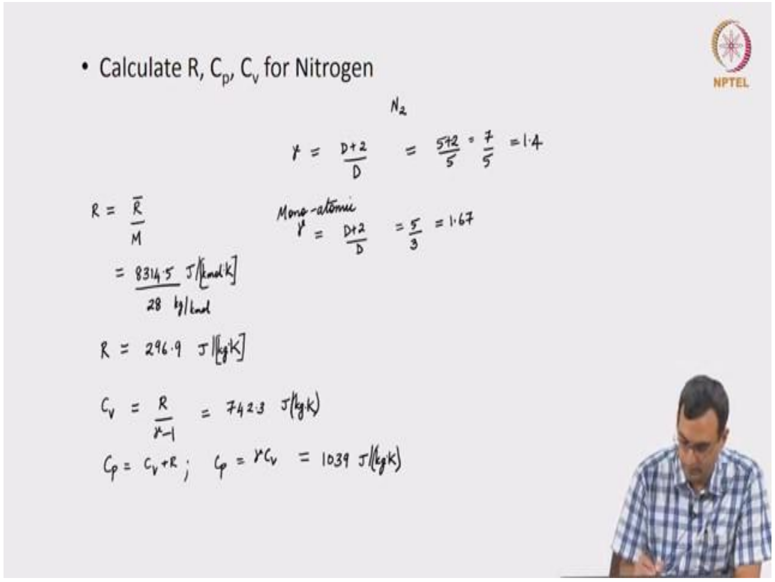

Let’s calculate R, C_p, C_v for nitrogen using all the relations we developed.

$$R = \frac{\bar{R}}{M} = \frac{8314.5}{28} = 296.9\, J/kg \cdot K.$$

$$C_v = \frac{R}{\gamma - 1} = 742.3\, J/kg \cdot K$$

$$C_p = C_v + R = \gamma C_v = 1039\, J/kg \cdot K$$

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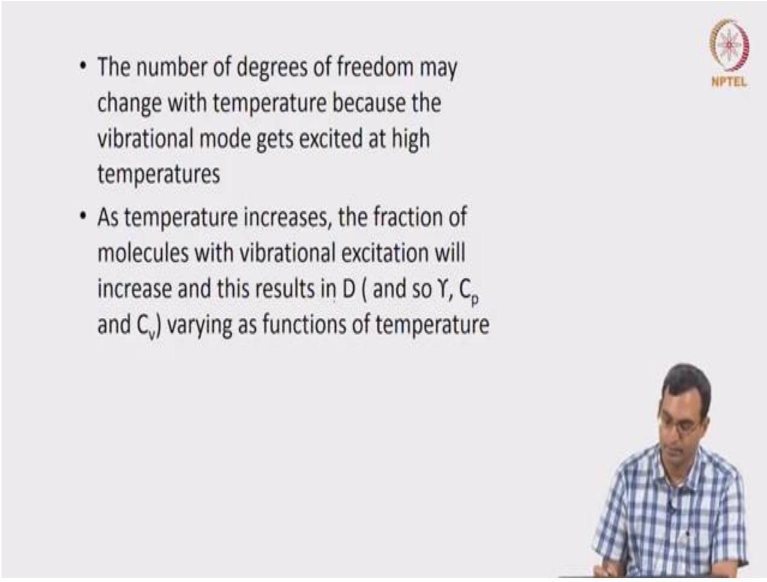

The number of degrees of freedom of a gas may change with temperature because the vibrational mode gets excited at high temperatures, i.e. contribution of vibrational energy to the total energy becomes significant. Hence, as temperature increases, the fraction of molecules with vibrational excitation will increase and this results in D (and so γ, C_p and C_v) varying as function of temperature.