

## Degrees of freedom:

If a particle moves along a straight line, say along X-axis, its position is completely specified by one coordinate only. The particle is said to possess one degree of freedom. If the particle moves on a plane, say XY-plane, its position is completely specified by two coordinates (x,y). Hence, the particle is said to have two degrees of freedom. If the particle moves in space, three coordinates (x,y,z) are required to specify its position completely. Hence, the particle has now three degrees of freedom. Thus, a material particle can have at most three degrees of freedom. For monoatomic gas molecules (like Ar, Xe etc.) which can be treated as particles, the number of degrees of freedom is three.

A rigid body can, however, not only translate but also can rotate about any axis passing through itself. The most general kind of rotational motion can be resolved analytically into rotation of the body about three mutually perpendicular axes passing through any point fixed in itself. Hence the position of a rigid body is completely known if we know the three coordinate of the centre of gravity and three angles to determine the orientation of the body. Thus, degrees of freedom contributed by rotation are three. Polyatomic gas molecules have finite size and should not be treated as particle. They can also rotate and hence should have degrees of freedom due to rotation.

Thus, the degrees of freedom is defined as the number of independent coordinates necessary to specify the position and configuration in space of a dynamical system.

If an atom is treated as a point, then the number of degrees of freedom is three and if it is treated as sphere, it can have six degrees of freedom, three corresponding to translation and the remaining three corresponding to rotation.

Degrees of freedom can be looked into from another angle. If a particle moves along a line (say X-direction), the kinetic energy of the particle is  $\frac{1}{2}m\dot{x}^2$ . If it moves in a plane (say XY-plane), its kinetic

energy is given by  $\frac{1}{2}m(\dot{x}^2 + \dot{y}^2)$ . If it moves in space, the kinetic energy is  $\frac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$ . For

rigid body, kinetic energy due to rotation is  $E = \frac{1}{2}(I_1\omega_1^2 + I_2\omega_2^2 + I_3\omega_3^2)$ , where  $\omega_1, \omega_2, \omega_3$  are

the components of the angular velocity in the directions of the three principal axes and  $I_1, I_2, I_3$  are the moments of inertia about those axes. Besides translation and rotation, a rigid body can also vibrate or oscillate. In case of diatomic molecules, atoms in the molecule can also oscillate along the line joining them. This contributes extra energy. Assuming simple harmonic vibrations along X-axis,

this extra energy is given by  $E_0 = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}kx^2$ , where  $m = \frac{m_1m_2}{m_1 + m_2}$  is the reduced mass,  $m_1$  and

$m_2$  being the masses of two atoms, and  $x$  is the increase in distance between two atoms over their equilibrium separation.

The number of degrees of freedom can be defined in slightly different way as: the number of independent quadratic variables (squared terms) by which the energy of the dynamical system is determined.

Degrees of freedom of a system is additive. For a complex system consisting of several individual particles, we know its configuration if we know the configuration of all the constituent particles and hence for such a system the number of degrees of freedom is equal to the sum of the number of degrees of freedom of the constituents. For a material system consisting of  $N$  particles  $(x_1, y_1, z_1), (x_2, y_2, z_2), \dots, (x_N, y_N, z_N)$  subjected to constraint represented analytically by  $m$  equations

$$F_j(x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_N, y_N, z_N) = 0$$

where  $j = 1, 2, 3, \dots, m$ , then if  $m < 3N$ , the number of degrees of freedom is given by

$$f = 3N - m$$

### Principle of equipartition of energy:

Maxwell showed that, if the molecules during their motion obey the laws of mechanics, the mean kinetic energy of a system of molecules in thermal equilibrium at the temperature  $T$ , is uniformly distributed among all the degrees of freedom, and for each degree of freedom of a molecule it is equal to  $\frac{1}{2}kT$ , where  $k$  is the Boltzmann constant. This theorem of uniform distribution of kinetic energy among the degrees of freedom is known as the principle of equipartition of energy. In classical physics such a theorem has been proved. The theorem is not universal, it is rather a limiting case under certain special conditions. Nevertheless, the theorem has been proved to be useful in developing molecular theories. It was applied successfully by Boltzmann to rotational and vibrational energies. Later on it was derived by Gibbs and Lorentz by using Statistical Mechanics.

The principle may be restated in slightly different way as follows:

If the energy of a system associated with any degree of freedom is a quadratic function of the variable specifying the degree of freedom (i.e., proportional to the square of the coordinate or component of velocity), then in a state of thermal equilibrium of the system at a temperature  $T$ , the mean value of the corresponding energy equals to  $\frac{1}{2}kT$ .

### Verification of the principle of equipartition of energy:

We consider one mole of a gas at temperature  $T$  and in a volume  $V$ . Let  $u, v, w$  be the components of velocity  $c$  of a molecule along three rectangular Cartesian axes, so that

$$c^2 = u^2 + v^2 + w^2 \dots\dots\dots(1)$$

$$\therefore \overline{c^2} = \overline{u^2} + \overline{v^2} + \overline{w^2} \dots\dots\dots(2)$$

Since no particular direction is preferred by the gas molecules,

$$\overline{u^2} = \overline{v^2} = \overline{w^2} \dots\dots\dots(3)$$

From equations (2) and (3), we have

$$\therefore \overline{u^2} = \overline{v^2} = \overline{w^2} = \frac{1}{3} \overline{c^2} \dots\dots\dots(4)$$

We have,

$$p = \frac{1}{3} mnC^2 = \frac{1}{3} \rho C^2$$

$$\text{Or, } p = \frac{1}{3} \frac{M}{V} nC^2$$

$$\therefore pV = \frac{1}{3} MC^2$$

$$\text{Or, } \frac{1}{3} MC^2 = RT$$

$$\therefore \frac{1}{2} MC^2 = \frac{3}{2} RT$$

Dividing both sides by the Avogadro number  $N_A$ , we have the kinetic energy per molecule

$$\frac{1}{2} mC^2 = \frac{3}{2} kT \dots\dots\dots(5)$$

Again, the average kinetic energy of translation of a gas molecule for each degree of freedom is

$$\varepsilon = \frac{1}{2} m\overline{u^2} = \frac{1}{2} m\overline{v^2} = \frac{1}{2} m\overline{w^2} = \frac{1}{2} m \cdot \frac{1}{3} \overline{c^2} = \frac{1}{3} \cdot \frac{1}{2} mC^2 = \frac{1}{3} \cdot \frac{3}{2} kT = \frac{1}{2} kT$$

**Degrees of freedom and specific heat:**

We consider a gm-mole of a gas at temperature T. Let  $f$  be the degrees of freedom of each molecule. By principle of equipartition of energy, average kinetic energy per degree of freedom is

$\frac{1}{2} kT$ . Therefore, the total energy of a gm-mole of the gas is given by

$$U = N_A \cdot f \cdot \frac{1}{2} kT = \frac{1}{2} fRT \dots\dots\dots(1)$$

where  $N_A$  is the Avogadro number.

$$\therefore \text{Molar heat capacity (specific heat) at constant volume, } C_v = \left(\frac{dU}{dT}\right)_v = \frac{1}{2} fR$$

But from thermodynamics we know,  $C_p - C_v = R$ , where  $R$  = the universal gas constant.

∴ Molar heat capacity at constant pressure,  $C_p = C_v + R = \frac{1}{2} fR + R = (1 + \frac{f}{2})R$ .

Hence, the ratio of the two molar heat capacities is given by

$$\gamma = \frac{C_p}{C_v} = \frac{(1 + \frac{f}{2})R}{\frac{1}{2} fR} = 1 + \frac{2}{f}$$

This is an important expression relating  $f$  and  $\gamma$ .

While, the principle of thermodynamics gives us only an expression for the difference of the two specific heats, molecular theory, with equipartition law, predicts their actual values and their ratio  $\gamma$  in terms of the degrees of freedom  $f$  and the universal gas constant  $R$ . It can also be noted that, according to the molecular theory  $C_p$ ,  $C_v$  and  $\gamma$  are all constants and independent of the temperature.

(i) Monoatomic gas:

For monoatomic gas having only kinetic energy of translation, the number of degrees of freedom is  $f = 3$ .

$$\therefore C_v = \frac{1}{2} fR = \frac{3}{2} R$$

$$\text{and } \gamma = 1 + \frac{2}{f} = 1 + \frac{2}{3} \approx 1.67$$

This is in good agreement with the values of  $C_v$  and  $\gamma$  for monoatomic gases and their specific heats are also found to be independent of temperature.

(ii) Diatomic gas:

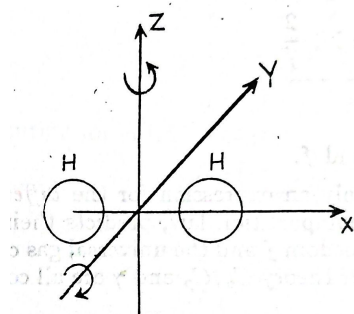


Fig.2.12 Degrees of freedom of a diatomic molecule

In diatomic gases, the molecule may be assumed to be made up of two atoms at a certain distance from each other, held rigidly together by attractive force (dumbbell shape). There is a constraint that the distance between two atoms is constant. Therefore, the number of degrees of freedom is

$$f = 3N - m = 3 \times 2 - 1 = 5$$

Three of them are for translation and two are for rotation. The molecule can have rotation about both Y- and Z-axis producing new orientations but it produces no new orientations for rotation about the line joining them (here X-axis). Hence, diatomic molecules will have two rotational degrees of freedom.

$$\therefore C_v = \frac{1}{2} fR = \frac{5}{2} R$$

$$\text{and } \gamma = 1 + \frac{2}{f} = 1 + \frac{2}{5} = 1.40$$

These values match exactly with the values for  $H_2, N_2, \dots$  etc., except for  $Cl_2$  near room temperature.

However, the atomic bond is not perfectly rigid and the atoms may also vibrate along the line joining them and thereby introduce two vibrational degrees of freedom, since the vibrational energy is partly kinetic and partly potential. Then  $f = 7$ .

$$\therefore C_v = \frac{1}{2} fR = \frac{7}{2} R$$

$$\text{and } \gamma = 1 + \frac{2}{f} = 1 + \frac{2}{7} \approx 1.28$$

These values, however, do not match with the observed values for diatomic gases. Thus it appears that near room temperature diatomic molecules behave as if vibrational degrees of freedom do not become effective. And vibrational energy for gases at ordinary temperatures is negligibly small.

(iii) Triatomic gas:

In a triatomic gas molecule, if the atoms arrange themselves at the vertices of a triangle, the number of degrees of freedom would be  $f = 3N - m = 3 \times 3 - 3 = 6$ , three for translation and three for rotation.

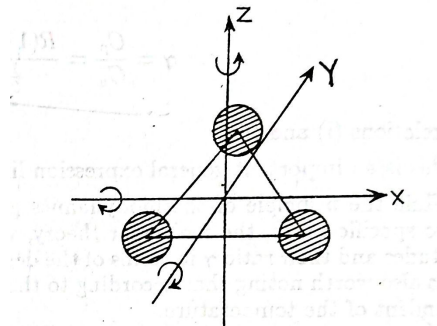


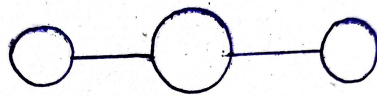
Fig.2.13 Degrees of freedom of a triatomic molecule arranged at the vertices of a triangle

Here the number of constraints is three, as their mutual interatomic distances are fixed.

$$\therefore C_v = \frac{1}{2} fR = 3R$$

$$\text{and } \gamma = 1 + \frac{2}{f} = 1 + \frac{2}{6} \approx 1.33$$

However, the molecules can arrange themselves linearly. Here the number of constraints would be two and the number of degrees of freedom would be  $f = 3N - m = 3 \times 3 - 2 = 7$ .



$$\therefore C_v = \frac{1}{2} fR = \frac{7}{2}R$$

$$\text{and } \gamma = 1 + \frac{2}{f} = 1 + \frac{2}{7} \approx 1.28$$

According to molecular theory, as the number of atoms in a molecule increases, the number of degrees of freedom also increases and hence, the ratio of specific heats decreases. This feature is also observed in experiments.

The theory also predicts that  $\gamma$  is never less than 1 and greater than 1.67, which is fact. But, divergence between the theory and experiment emerges when the temperature variation of specific heat is studied. Except monoatomic gas, specific heats of all gases increase with temperature and decreases when the temperature is decreased whereas the molecular theory predicts they are independent of temperature. This suggests that molecular theory and classical equipartition theory are not the complete story, there are something more. The quantum mechanics and statistical mechanics can provide us the insight.