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***Degrees of Freedom, Equipartition of Energy***

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# Degrees of Freedom and Law of Equipartition of Energy:

- **Molecular degrees of freedom refer to the number of ways a molecule in the gas phase may move, rotate, or vibrate in space. Three types of degrees of freedom exist, those being translational, rotational, and vibrational.**
- **Equipartition of energy, law of statistical mechanics stating that, in a system in thermal equilibrium, on the average, an equal amount of energy will be associated with each independent energy state.**



Based on the work of physicists James Clerk Maxwell of Scotland and Ludwig Boltzmann of Germany, this law states specifically that a system of particles in equilibrium at absolute temperature  $T$  will have an average energy of  $\frac{1}{2}kT$  associated with each degree of freedom, in which  $k$  is the Boltzmann constant. In addition, any degree of freedom contributing potential energy will have another  $\frac{1}{2}kT$  associated with it. For a system of  $s$  degrees of freedom, of which  $t$  have associated potential energies, the total average energy of the system is  $\frac{1}{2}(s + t)kT$ .

## Theorem of Equipartition of energy

Each degree of freedom contributes  $\frac{1}{2}k_B T$  to the energy of a system, where possible degrees of freedom are those associated with translation, rotation, and vibration of molecules.

$$\text{Total energy of a gas} = \frac{1}{2} f N k_B T$$

$$\text{Monatomic gas: } E_{int} = \frac{3}{2} N k_B T$$

Type of molecule	$N$	Degrees of freedom	Modes
Monatomic, e.g. Ne 	1	3	3 translational 0 rotational 0 vibrational
Diatomic, e.g. HCl 	2	6	3 translational 2 rotational 1 vibrational



## Degrees of freedom of a dynamical system

If a free material particle moves along a straight line, say along the  $x$ -axis, its position is completely specified by *one coordinate* only. The particle is said to possess *one degree of freedom*. If, however, the free particle moves over a plane, say the  $xy$ -plane, then to specify its position completely, *two coordinates* ( $x, y$ ) are needed. The particle is now said to have *two degrees of freedom*. Similarly, in order to completely specify the position of a particle in space, *three coordinates* ( $x, y, z$ ) are required. The particle has now *three degrees of freedom*.

Molecules, however, are not geometric points but are of finite size. They possess not only mass but also moment of inertia and therefore have kinetic energy of rotation, apart from that of translation. So molecules are expected to have rotational degrees of freedom as well. If not perfectly rigid structures, the molecules could also vibrate, giving rise to still more degrees of freedom. Spectroscopic analysis of light emitted or absorbed by molecules in the infrared demonstrates convincingly the rotations and vibrations of molecules.

It should be remembered, therefore, that by the number of degrees of freedom is meant *the number of independent coordinates necessary for specifying the position and configuration in space of a dynamical system*.

Let us look at it from another angle. The kinetic energy of the free particle in the first case is given by  $\frac{1}{2}m\dot{x}^2$ , that in the second by  $\frac{1}{2}m(\dot{x}^2 + \dot{y}^2)$  and in the third by  $\frac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$ . Similarly, for a complex molecule having rotational degrees of freedom, the kinetic energy is  $\frac{1}{2}I\omega^2$  where  $I$  is the moment of inertia and  $\omega$  the angular velocity. The angular velocity vector of a rotating molecule can have a component along all the three coordinate axes. An oscillator

however possesses not only kinetic energy but also potential energy, the latter being due to the force that restores the atom to its equilibrium position. The potential energy expression is  $\frac{1}{2}kx^2$  where  $k$  is the force constant and  $x$  the displacement relative to the position of equilibrium. As we shall see later that to be in accord with the principle of equipartition of energy in which potential energy is also to be included, we give a somewhat different definition of the number of degrees of freedom as : *the number of independent quadratic variables (squared terms) by which the energy of a system is determined*.

We may now generalise. If there is a material system consisting of  $N$  particles ( $x_1, y_1, z_1$ ), ( $x_2, y_2, z_2$ ), ..., ( $x_N, y_N, z_N$ ) subjected to smooth constraints represented analytically by  $m$ -equations

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

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

$$f = 3N - m$$

because this gives the number of independent quadratic variables determining the energy of the system.

### Principle of equipartition of energy (classical)

Maxwell showed that, if the molecules in 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 equals  $\frac{1}{2}kT$ , 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 statistical physics (classical means not quantum) such a theorem has been proved. We however know now that the theorem is not an universal law of nature. It is rather a limiting case under certain special conditions. Nevertheless, it has been proved extremely fruitful in the development of molecular theories. It was applied successfully by Boltzmann for the rotational and vibrational energies and was derived by Gibbs and Lorentz in the light of statistical mechanics.

The principle may also be reworded in a slightly different way : *if the energy of a system associated with any degree of freedom is a quadratic function of the variable specifying the degree of freedom (that is, proportional to the square of a coordinate or component of a velocity), then in a state of thermal equilibrium of the system at a temperature  $T$ , the mean value of the corresponding energy equals  $\frac{1}{2}kT$ .*

We shall now make a derivation of the equipartition theorem by two different methods.

**Derivation :** In deriving the principle of equipartition, the following *assumptions* are made: (i) the system consists of free particles (no constraints) only, (ii) the energy of the system is expressible as sum of the squares of positional or momentum coordinates whose number is equal to the number of the degrees of freedom, and (iii) the energy, unlike quantum concept, is not discrete but continuous in nature.

If a particle possesses  $F$  degrees of freedom, its energy  $E$  is given by

$$E = a_1\alpha_1^2 + a_2\alpha_2^2 + a_3\alpha_3^2 + \dots + a_F\alpha_F^2$$

where  $a$ 's are constants and  $\alpha$ 's are either positional or momentum coordinates.

Now, from Boltzmann's law, the number of particles between  $\alpha_1$  and  $\alpha_1 + d\alpha_1$ ,  $\alpha_2$  and  $\alpha_2 + d\alpha_2$  etc. having  $E$  as energy is

$$dN = ANe^{-E/kT} d\alpha_1 d\alpha_2 \dots d\alpha_F$$



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

$$\gamma = 1 + \frac{2}{f} = 1 + \frac{2}{3} = \frac{5}{3} = 1.67$$

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

**Diatomic gas :** In diatomic gases, the molecules may be pictured as made up of two atoms at a certain distance from each other but joined rigidly like a dumbbell. So here there is a constraint that the interatomic distance is fixed.

$$\therefore \text{Number of degrees of freedom, } f = 3N - m = 3 \times 2 - 1 = 5$$

Of these, 3 are of translation and 2 of rotation (Fig.2.12).

The moment of inertia about  $Y$  and  $Z$ -axis is much greater than that about  $X$ -axis and the latter can be neglected, so that the molecule has two rotational degrees of freedom.

$$\therefore C_v = \frac{1}{2}fR = \frac{5}{2}R = 2.5R$$

$$\gamma = 1 + \frac{2}{5} = \frac{7}{5} = 1.40$$

These are almost exactly the values for  $H_2$ ,  $N_2$ , etc.,  $Cl_2$  being an interesting exception, at near room-temperature.

However, since the atomic bond is not perfectly rigid, 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  $f = 7$  and the theory predicts

$$C_v = \frac{7}{2}R = 3.5R; \gamma = \frac{9}{7} = 1.30$$

These values, however, do not agree with those observed for diatomic gases, as already indicated.

It thus appears that near room-temperature diatomic molecules behave as if vibrational degrees of freedom do not become effective, the vibrational energy for gases at ordinary temperatures being negligibly small.

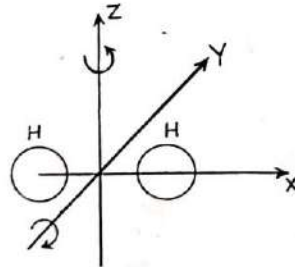


Fig.2.12 Degrees of freedom of a diatomic molecule

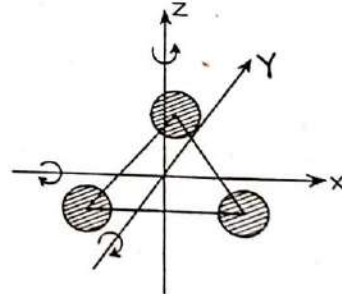
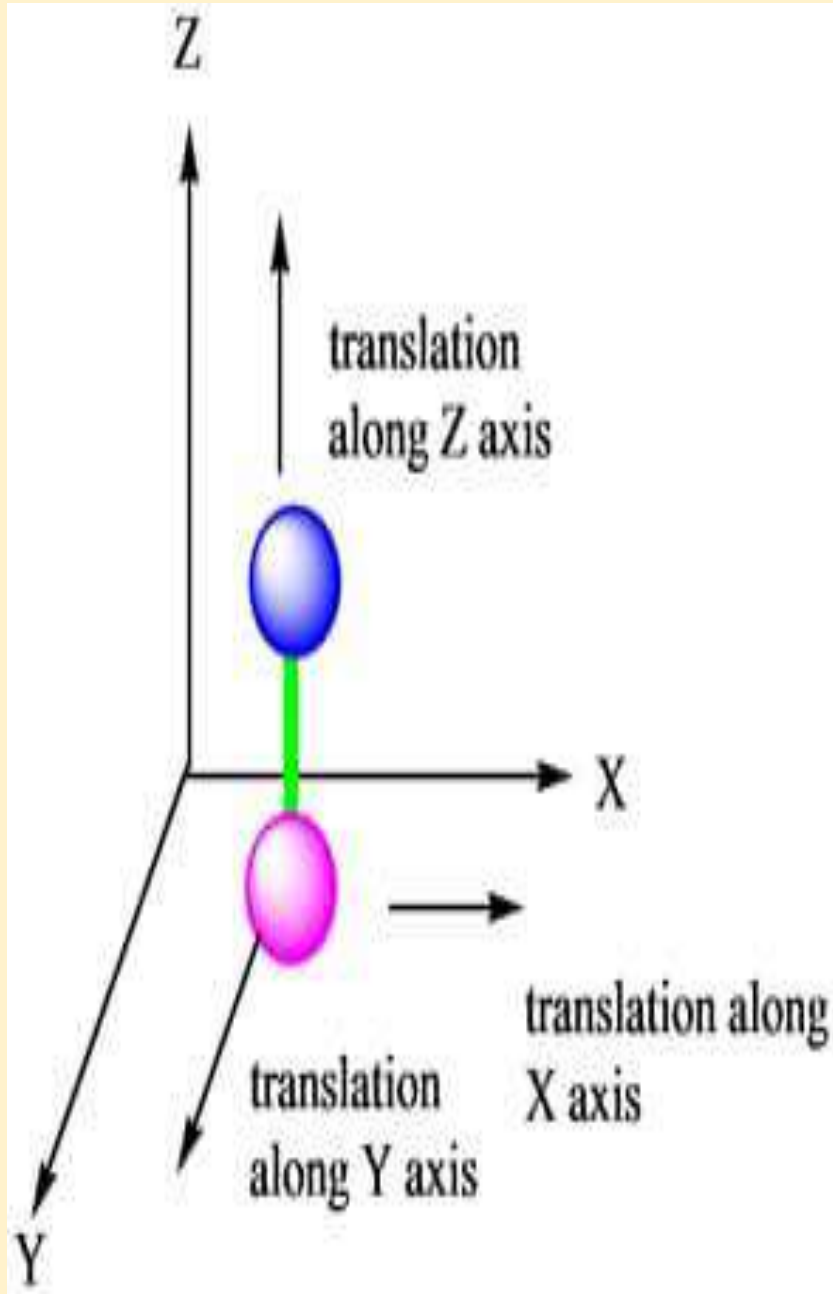
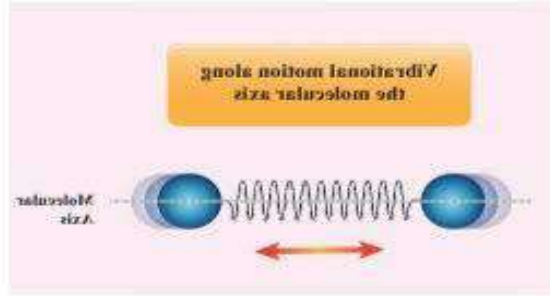


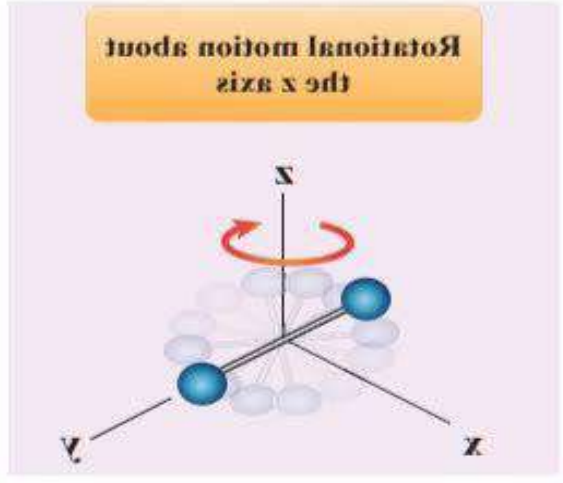
Fig.2.13 Degrees of freedom of a triatomic molecule arranged at the vertices of a triangle



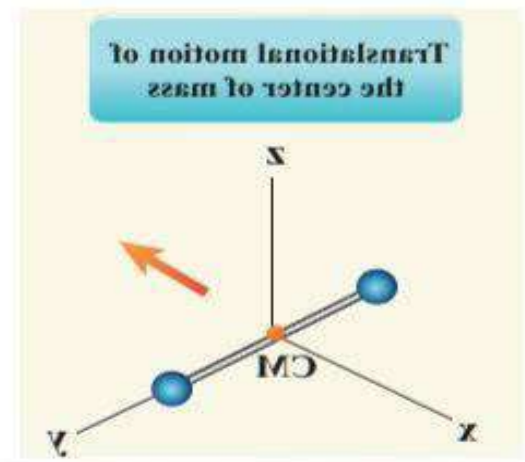
Degree of freedom of diatomic molecule



c



b



a

## *Few important Links:*

- 1. <https://youtu.be/zsTCoDiHtlw>
- 2. <https://youtu.be/jkeQA08xAng>
- 3. <https://youtu.be/B9ukqBYxIDs>