Degree of Freedom of a Gaseous Molecule:-

The degree of freedom of a molecule are defined as the independent number of parameters required to describe the state of the molecule completely.

On heating a gaseous molecule, there are three types of motion due to the energy provided. These are rotational, vibrational and translational motion. They can also be labelled as translational, rotational and vibrational degree of freedom.

Translational degree of freedom:-

Atoms can only have translational degrees of freedom. Let us consider an atom at mass point, and as a mass point with cartesian coordinates x, y, z as coordinates.

Thus velocity of translational motion with velocity c in three directions.

$$c^2 = c_x^2 + c_y^2 + c_z^2 \quad — ①$$

where c_x, c_y and c_z are the components of velocity c in three directions. On multiplying eq ① with $m/2$ where m is the mass of the atom equation becomes

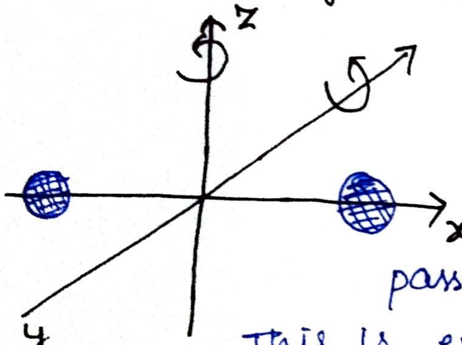
$$\frac{1}{2}mc^2 = \frac{1}{2}mc_x^2 + \frac{1}{2}mc_y^2 + \frac{1}{2}mc_z^2 \quad — ②$$

or Kinetic energy, $K.E. = E_K = E_{k,x} + E_{k,y} + E_{k,z}$ — ③

The rotational motion of an atom about an axis perpendicular to it and passing through its centre contributes negligible energy compared with its translational motion.

In case of atoms, three coordinates are needed to specify the centre of gravity of molecules. The centre of gravity has three translational degree of freedom.

Rotational degree of freedom:-

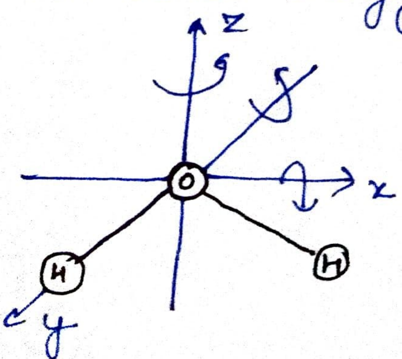


A diatomic molecule lying along x-axis can undergo rotation about mutually perpendicular Y-axis and Z-axis passing through the centre of gravity. This is expressed as by saying that the diatomic molecule has two rotational degree of freedom.

For I being moment of inertia of the molecule and ω as the angular velocity, then rotational energy is given by

$$E_{rot} = I\omega^2$$

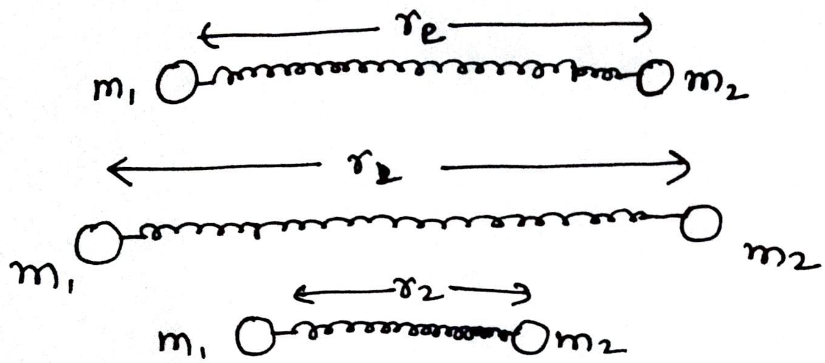
It may be noted that moment of inertia of the molecule and hence its rotational energy, along the x-axis is negligible.



All the linear molecules such as CO_2, C_2H_2 have rotational degrees of freedom because their rotational motion is similar to diatomic molecule.

Non linear molecules such as H_2O, H_2S, CH_4, C_6H_6 etc. can undergo rotation about the three cartesian axes so that they have three rotational degrees of freedom.

Vibrational degrees of freedom:-



For diatomic molecules with mass m_1 and m_2 vibrate back and forth relative to their centre of mass in opposite directions.

The two masses reach their extremes in opposite directions at the same time.
The diatomic molecule has one vibrational degree degree of freedom and only one frequency of vibration called fundamental frequency of vibration.

The bond of molecules behave as a spring during the vibrational motion and the motion of molecule is a S.H.M (simple Harmonic motion) provided that the displacement from the nucleus is not that much. At two extremes of motions which corresponds to extension and compression of the chemical bond between the two atoms.

In such situation the potential energy is maximum. when the atoms are in their equilibrium position, the kinetic energy is maximum. Thus there is an exchange between kinetic energy and potential energy constantly during the vibration.

For a polyatomic molecule containing n atoms or nuclei, has 3n degrees of freedom since each atom requires 3 degrees of freedom in the x, y and z directions to specify its position.

On reducing rotational and translational degrees of freedom it can be deduced that

1. for linear molecule vibrational degrees of freedom is 3N-5.
2. For non-linear molecule vibrational degrees of freedom is 3N-6.

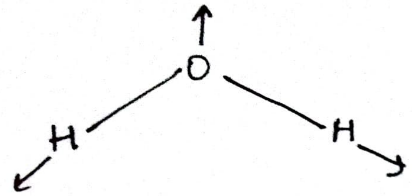
→ Normal modes of vibration :-

It is defined as the molecular motion in which all the atoms in the molecules in the molecule vibrate with same frequency and all the atoms pass through their equilibrium positions simultaneously.

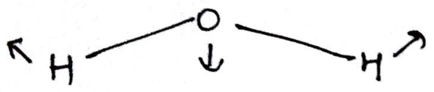
The relative vibrational amplitudes of the indivisual atoms may be different in magnitude and direction but the centre of gravity of molecule does not changes.

There may be streching or bending vibrations of the molecular bonds. There is symmetric or assymmetric streching and in plane or out of the plane. These modes are observed in the infra-red region (6500-4000 cm^{-1})

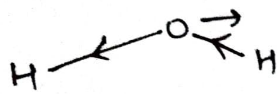
Various modes of vibraltion H_2O and CO_2 molecules:-

① 

Symmetric Streching

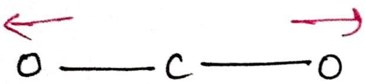
② 

Asymmetric ~~stre~~ bending

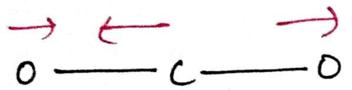
③ 

Asymmetric streching.

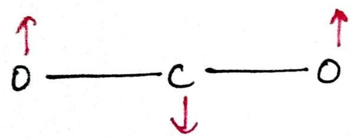
For non linear triatomic molecule

① 

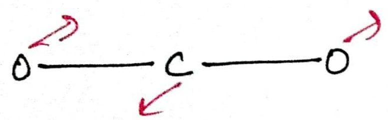
Symmetric streching

② 

Asymmetric streching

③ 

Bending (in plane)

④ 

Bending (out of plane)

Q: Calculate the various degrees of freedom (rotational, translation and vibrational degrees) of following molecules:-

a) He

b) HCl

c) CO_2

d) C_6H_6

e) C_2H_2

f) H_2

Principle of equipartition of energy:-

Average translational kinetic energy of a molecule of an ideal gas is given by

$$\epsilon = \frac{3}{2} kT \quad \text{—— (1)}$$

According to the law of equipartition of energy, the total energy of a molecule is divided equally amongst various degrees of the freedom of the molecule.

The kinetic energy along x, y and z directions is given by

$$\epsilon = \epsilon_x + \epsilon_y + \epsilon_z \quad \text{—— (2)}$$

Since the motion of gas molecules is random and the motion along the three cartesian axes is equally probable. Thus from eqn (1) and (2)

$$\epsilon_x = \epsilon_y = \epsilon_z = \frac{1}{3}\epsilon = \frac{1}{2} kT \quad \text{—— (3)}$$

Each component of kinetic energy motion contributes equally to the total kinetic energy and that the kinetic energy and that kinetic energy for ~~the~~ each degree of freedom is $\frac{1}{2} kT$ per molecule or $\frac{1}{2} RT$ per mole.

Each rotational degree of freedom also contributes $\frac{1}{2} kT$ per molecule or $\frac{1}{2} RT$ per mole of the total energy.

As regards the vibrational motion, the atoms oscillate against each other. The molecules possess both kinetic and potential energy.

The energy of vibration has two degrees of freedom.

The vibrational motion in a molecule is associated with energy $= 2 \times \frac{1}{2} kT = kT$ per molecule or RT per mole.

If a gaseous species has n_1 translational degrees of freedom, n_2 rotational degrees of freedom and n_3 vibrational degrees of freedom.

The total energy of species is given by

$$E = n_1\left(\frac{kT}{2}\right) + n_2\left(\frac{kT}{2}\right) + n_3(kT)$$

CHAPTER OVER