Principle of Equipartition of Energy

From the kinetic theory of gases we know that the average translational kinetic energy of a molecule of an Ideal gas is given by

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

According to the law of equipartition of energy,

The total energy of a molecule is divided equally amongest the various degrees of freedom of the molecule.

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

$$\varepsilon = \varepsilon_x + \varepsilon_y + \varepsilon_z \quad \text{—— (2)}$$

Since the motion of gas molecule is random and the motion along the three Cartesian axes is equally probable. Hence from equation (1) and (2)

$$\varepsilon_x = \varepsilon_y = \varepsilon_z = \tfrac{1}{3}\text{rd of } \varepsilon = \frac{1}{2} kT \quad \text{—— (3)}$$

Equation (3) shows that each component of kinetic motion contributes equally to the total kinetic energy and that the kinetic energy for each degree of freedom is $\frac{1}{2} kT$ per molecule OR $\frac{1}{2} RT$ per mole.

It is shown that each rotational degree of freedom also contributes $\frac{1}{2}$ KT per molecule or $\frac{1}{2}$ RT per mole to the total energy.

The vibrational motion, the two atoms oscillate against each other. The molecule, therefore, possesses both potential and kinetic energy. This means that the energy of vibration involves two degrees of freedom.

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

Thus, if a gaseous species has n_1 translational degrees of freedom, n_2 ~~rotational~~ rotational degrees of freedom and n_3 vibrational degrees of freedom, then the total energy of the species $= n_1(KT/2) + n_2(KT/2) + n_3(KT/2)$