

Degrees of Freedom

Degrees of freedom may be defined as the number of independent ways in which a system may possess translational, vibrational or rotational motion.

Or, it may also be defined as the minimum number of independent variables required to describe completely the state of a physical system.

Let us consider a diatomic molecule (A-B) to find the number of independent ways in which the molecule may possess translational, vibrational or rotational motions.

The movement of center of mass of the molecule may take place in three directions viz. x, y and z direction. So, it has 3 translational degrees of freedom (shown in **Figure 1.9**).

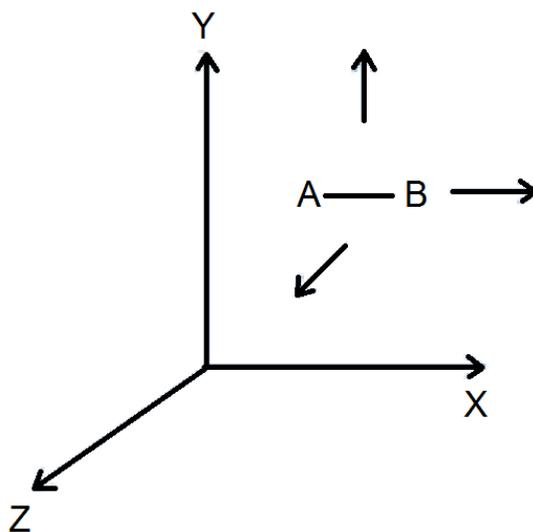


Fig. 1.9 Translational motion of the molecule A-B

There are two axes (here y and z) perpendicular to the line (here x axis) joining the two atoms about which the rotation of atoms (constituting the molecule) may take place. These two rotations contribute to two rotational degrees of freedom (shown in **Figure 1.10**).

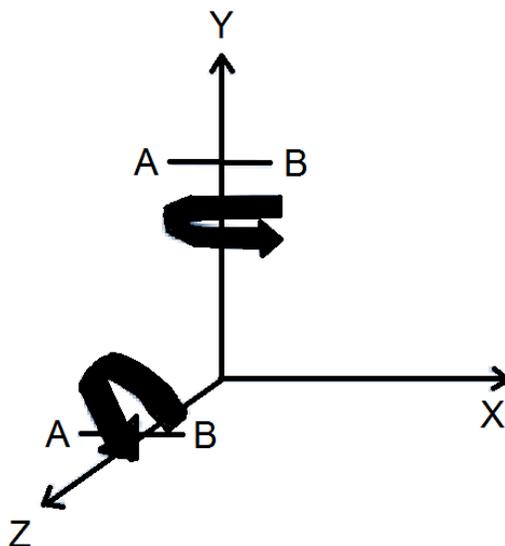


Fig. 1.10 Rotational motion of the molecule A-B

If we consider the vibrational motion along the line joining the atoms, we get only one degree of freedom, as only one vibration is possible along the line joining the two atoms. This vibrational motion is significant only at higher temperatures because to vibrate the atoms in a molecule higher energy is needed which is obtained at higher temperature. The vibrational degree of freedom is frozen out at room temperature.

So, for a diatomic molecule at higher temperatures, there are six independent modes of motion (3 translational + 2 rotational + 1 vibrational) known as six degrees of freedom. However, at low temperature, as no significant vibrational motion is observed, so, we get only five degrees of freedom.

In general, if there are N atoms present in a molecule, then there are $3N$ (3 for each atom) degrees of freedom that describe the motion of the molecule in relation to the coordinates (x, y and z). The movement of center of mass of the molecule may take place in three directions viz. x, y and z direction. So, it has 3 translational degrees of freedom out of $3N$ degrees of freedom leaving $(3N-3)$.

The rotation of a non-linear molecule can be resolved into 3 components about the 3 perpendicular axes (x, y and z) which will give 3 degrees of freedom. The molecule

is now left with $(3N-6)$ degrees of freedom. Since the only other motion that is allowed is internal vibration, so, we can say that a non-linear molecule has $(3N-6)$ internal vibrations.

Again, the rotation of a linear molecule can be resolved into 2 components about the 3 perpendicular axes (x, y and z) as there is no rotation about the bond axis, so, we have 2 degrees of freedom. The molecule is now left with $(3N-5)$ degrees of freedom. Since the only other motion that is allowed is internal vibration, so, we can say that a linear molecule has $(3N-5)$ internal vibrations. **Table 1.2** shows the various degrees of freedom for various systems.

Table 1.2 various degrees of freedom for various systems

System	Translation	Rotation	Vibration	Total Degrees of Freedom
Monatomic	3	0	0	3
Diatomic	3	2	1	6
Linear Polyatomic ($N > 2$)	3	2	$3N-5$	$3N$
Non-linear Polyatomic ($N > 2$)	3	3	$3N-6$	$3N$