3.4. *The specific heats of gases*

Because of the equipartition of energy, if a given molecule has f degrees of freedom then, in a classical gas at temperature T, it will have an average energy of $(f \times \frac{1}{2}kT)$. The energy of a gramme molecule of the gas at temperature T will thus be

$$E = N_A \times f \times \tfrac{1}{2}kT \qquad \textbf{3.21}$$

The corresponding specific heat of the gas at constant volume is then

$$\begin{aligned} C_v &= \left\{\frac{\partial E}{\partial T}\right\}_v = \tfrac{1}{2}N_A kf \qquad \textbf{3.22} \\ &= \tfrac{1}{2}Rf \end{aligned}$$

per gramme molecule.

If the gas molecules are monatomic, only the three components of the kinetic energy of translation will contribute to the energy of the gas. There will then be three degrees of freedom, i.e. $f = 3$. (As will be discussed later, any change in the rotational motion of the atom about an axis through its center will require an energy so large compared with the normal thermal energy kT that such rotation is said to be 'hindered'.) The specific heat of the gas is obtained from equation 3.22, with $f = 3$, as

$$C_v \text{ (monatomic)} = \frac{3}{2}R$$

If the molecules of the gas are diatomic there will be five degrees of freedom. Besides the three degrees of freedom of translation which were present for the monatomic molecules there will be two degrees of freedom of rotation as illustrated in Fig. 2. If the axis joining the two atoms of the molecule is taken as the z-axis the rotational energy is given by two quadratic terms as

$$E_{rot} = \tfrac{1}{2}I_x\omega_x^2 + \tfrac{1}{2}I_y\omega_y^2$$

where I_x and I_y are the moments of inertia about the x- and y-axes and ω_x, ω_y are the appropriate angular velocities. The rotation of the molecule about its own axis is again hindered at normal temperatures and this is also the case, in general, with the vibration of the atoms along their axis. The specific heat is obtained by substituting for $f = 5$ in equation 3.22 to give

$$C_v \text{ (diatomic)} = \frac{5}{2}R \qquad \textbf{3.23}$$

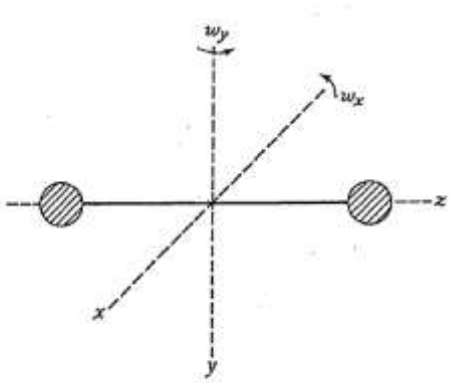

Fig. 2. Possible rotations of a diatomic molecule.

For a triatomic, or more complex, molecule there are generally six degrees of freedom. Of these there are three degrees of freedom of translation together with three degrees of freedom of rotation corresponding to three independent axes about which the rotation is not hindered at normal temperatures. Substituting for $f = 6$ in equation 3.22 gives the specific heat for such gases as

$$C_v \text{ (triatomic)} = 3R \tag{3.24}$$

While this value may hold for some types of molecules with more than two atoms, in many cases there are contributions from vibrational energy and the value of f will be greater than six.

If use is made of the relationship between the principal specific heats of a perfect gas, namely that

$$C_p - C_v = R$$

then the ratio $\gamma = C_p / C_v$ may be determined for each of the three cases considered here. If the value of C_v is taken from equation 3.22 as $\frac{1}{2} R f$ then $C_p = R(1 + \frac{1}{2} f)$ and

$$\gamma = 1 + \frac{2}{f}$$

Then, taking the respective values of f, this ratio becomes

$$\gamma \text{ (monatomic)} = 5/3$$

$$\gamma \text{ (diatomic)} = 7/5$$

And $$\gamma \text{ (triatomic)} = 4/3$$

For more complex molecules with $f > 6$, will be less than 4/3 and may, in some cases, be nearer 1.1