6.5.5 Gas Laws

The observable properties of a gas such as its temperature and pressure can be related to the mass and velocity of its constituent molecules by the kinetic theory of gases. If we heat a solid, liquid or gas, what we are essentially doing is increasing the kinetic energy of the molecules. If we consider a system consisting of a closed vessel with gas inside, the motion of the molecules at any instant can be shown to be roughly equivalent to two equal and opposite streams moving in each of the three mutually perpendicular axis. The pressure (P) which a gas exerts on the surface of the vessel is a measure of the rate at which momentum is transferred to the surface from molecules which strike it and rebound. On the assumption that the kinetic energy of all the molecules in an enclosed space is constant and by making further assumptions about the nature of a perfect gas, a simple relation can be established between pressure and kinetic energy per unit volume.

If each molecule is assumed to have a mass (m), average velocity (v), and the length of each side of the vessel (Figure 3.10) is (L). If there are N molecules in the vessel, and thus N/6 in one stream, the number which strikes one end in a brief interval of time (t) will be the fraction of those contained within a length vt of the vessel; that is Nvt/6L. If we suppose that the molecules do not lose energy as they rebound and that the velocity (v) is simply reversed in direction during interaction, then the momentum will have changed from mv towards the wall to mv away from the wall; a change of 2mv for each molecule. The total change of momentum of all the molecules in time (t) is thus Nvt /6L × 2mv. According to Newton's second law of motion, the reaction at the end is equal to the rate of change of momentum of the molecules per unit time which is. Then the pressure (P) which the gas exerts per unit area is given by

$$P = \frac{2Nm \times v^2}{6AL} \tag{6.15}$$

but (AL) is the volume V of the vessel, so that

$$P = \frac{1}{3}\frac{N}{V}mv^2 \tag{6.16}$$

since N×m is the mass of the gas and Nm/V is the density we can also write equation 3.16 as

$$P = \frac{1}{3}\rho v^2 \text{ (where } \rho \text{ is the density)}$$

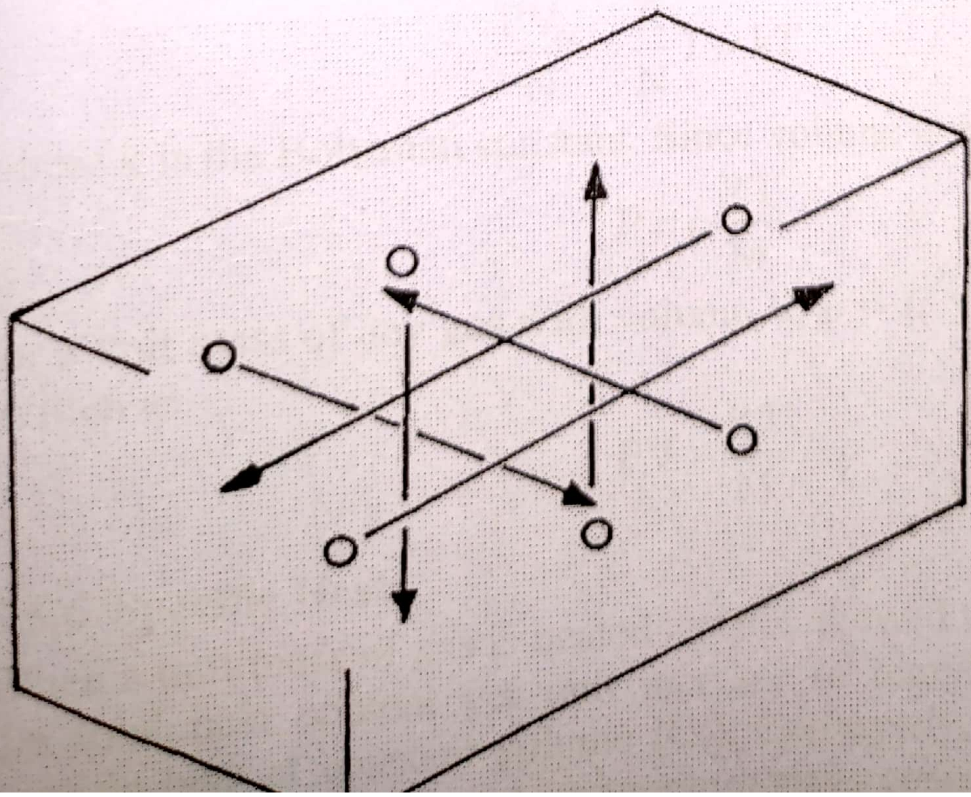

Figure 3.10 Representation of molecular motion in kinetic theory.

Again, since the mean kinetic energy E of a molecule is ½ mv^2, we have

$$P = \frac{2}{3}\frac{NE}{V} \quad (6.17)$$

or

$$PV = \frac{2}{3}NE \quad (6.18)$$

combining Boyle's and Charles gas Laws we have

$$PV \alpha T \quad (6.19)$$

where V is the volume of gas at an absolute T(K). To establish a constant of proportionality, a standard amount of gas may be defined by the volume occupied by a mole at standard pressure (101.3 k Pa = 1013 millibar and 273.2 k) which is (22.4 litres).

Then

$$PV_m = RT \quad (6.20)$$

where $R = 8.314\ J\ mol^{-1}\ K^{-1}$ and is called the molar gas constant or universal gas constant and has the dimensions of molecular specific heat.

Since the pressure exerted by a gas is a measure of its kinetic energy per unit volume, PV_m is proportional to the kinetic energy of a mole. A mole of any substance contains N molecules where $N = 6.023 \times 10^{23}$ and is known as the Avagadros constant. It follows that the mean energy per molecule is proportional to

$$\frac{PV_m}{N} = \frac{R}{N}T = kT \quad (6.21)$$

where k is the Boltzman constant. Since volume is equal to mass/density

$$P = \rho\frac{RT}{M} \quad (6.22)$$

for a unit mass of any gas with volume V, ρ = 1/ V so equation 3.22 can be written as

$$PV = \frac{RT}{M} \quad (6.23)$$