Kinetic Molecular Theory: A Closer Look

Pressure and Boyle's Law

The idea that the molecules of a gas are in constant chaotic motion can be expressed quantitatively in terms of the **kinetic molecular theory of gases**.

The kinetic theory is based on the following four assumptions:

1. **Particle motion:** The gas consists of molecules of mass m and diameter d in ceaseless random motion.

2. **Particle volume:** The size of the molecules is negligible (that means that their diameters are much smaller than the average distance travelled between collision.

3. **Particle collisions:** The molecules do not interact with each other, no attractive or repulsive forces are present. The molecules collide in perfectly elastic collisions in which the distance between their centers is d.

Let's define the **momentum** of a particle as the product of its mass times its velocity

$$p = mv$$

The greater the momentum of a particle, the greater the force it will exert on the walls upon collision. According to Newton's laws of motion, the force in a collision equals the rate of change of momentum.

Consider the arrangement in Figure 1. The momentum before the collision is mv_x and after the collision is $-mv_x$, therefore the change in momentum is $2mv_x$. There will be many molecules colliding with the wall in a time interval Δt, therefore the total change in momentum is the product of the change in momentum of each molecule multiplied by the number of molecules that reach the wall during the interval.
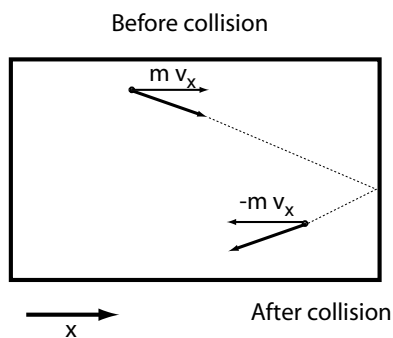
Figure 1: The pressure of a gas arises from the impact of its molecules on the walls. In an elastic collision of a molecule with a wall perpendicular to the x-axis the x-component of the velocity is reversed but the y- and z-components are unchanged.
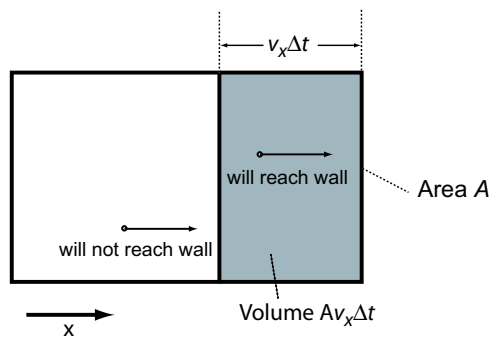

Figure 2: A molecule will reach the wall on the right during the time interval Δt if it is contained within in the volume $Av_x\Delta t$

If the molecules travel with a velocity v_x, all the molecules that are at a distance $v_x \Delta t$ from the wall will reach the wall in the time interval Δt, as illustrated in Figure 2. If the area of the wall is A, then all the molecules in the volume $A v_x \Delta t$ will collide with the wall in the interval Δt if they are travelling towards it. The number of particle per unit volume is

$$\frac{n N_A}{V}$$

where n is the number of moles of gas particles and N_A is Avogadro's constant, then the number of molecules in volume $A v_x \Delta t$ will be

$$\frac{n N_A}{V} A v_x \Delta t$$

On the average, half of the particles will be moving towards the wall, half of them will be moving away from it. Therefore, the average number of collisions in the interval Δt will be

$$\frac{1}{2} \frac{n N_A A v_x \Delta t}{V}$$

The total momentum change Δp will be the product of this quantity and the change per molecule $2 m v_x$

$$\frac{1}{2} \frac{n N_A A v_x \Delta t}{V} 2 m v_x = \frac{n m N_A A v_x^2 \Delta t}{V}$$

The product of the molecular mass m and Avogadro's constant N_A is the molecular mass of the gas M,

$$\Delta p = \frac{n M A v_x^2 \Delta t}{V}$$

Now we find the force on the wall, equal to the rate of momentum change, by dividing the total change by Δt

$$F = \frac{\Delta p}{\Delta t} = \frac{n M A v_x^2}{V}$$

And the dividing force by area we obtain the pressure on the wall

$$P = \frac{n M v_x^2}{V}$$

All the molecules are not moving at the same velocity, therefore we must substitute in the expression above the squared velocity for its average value, denoted $\langle v_x^2 \rangle$

$$P = \frac{nM\langle v_x^2 \rangle}{V} \ \text{ or } \ PV = nM\langle v_x^2 \rangle$$

which seems already very similar to the ideal gas equation of state.

Since the gas is at rest, there is no flow in any particular direction, then the average velocities v_x, v_y and v_z are equal. If we define the root mean square velocity u as

$$u = \sqrt{\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle}$$

then we can write $u = \sqrt{3\langle v_x^2 \rangle}$ and therefore

$$\langle v_x^2 \rangle = \frac{1}{3}\, u^2$$

and then

$$PV = \frac{1}{3}\, nMu^2 \tag{1}$$

If the root mean square velocity depends only on the temperature of the gas (we will treat this issue in detail in the next section), then at constant temperature for a given gas sample

$$PV = \text{constant}$$

as expressed by Boyle's law.

Temperature and kinetic energy

It has been established by experiment that the average speed of a sample of gas molecules depends only on the temperature and is not dependent on the type of gas (in other words, on its molecular mass). Some authors will write this fact as a fourth postulate for the kinetic molecular theory.

The average kinetic energy for one molecule can be written by definition as

$$\bar{E}_k = \frac{1}{2}\, mu^2$$

The average kinetic energy for a mol of gas will be given by

$$\bar{E}_{k,mol} = \frac{1}{2}\, N_A mu^2 \tag{2}$$

Given the equation of state for an ideal gas $PV = nRT$, we can substitute for PV the results from Equation 1, and we get

$$u = \sqrt{\frac{3RT}{M}} \tag{3}$$

that is, that the root mean square velocity of the molecules u is directly proportional to the square root of the absolute temperature and inversely proportional to the square root of the molar mass.

By substituting Equation 3 in 2 and applying the definition of molar mass as the product of the mass of the molecules m by Avogadro's constant N_A, we get

$$\bar{E}_{k,mol} = \frac{3}{2} RT$$

This equation shows that the absolute temperature is an index of the energy of the random motion of the molecules, the higher the energy, the higher the kinetic energy of the gas molecules. It also shows that the average kinetic energy of a gas does not depend on the molar mass. The average velocity does depend on the inverse of the square root of the molar mass, but in deriving the an expression for the kinetic energy, the masses cancel out.

References

[1] Atkins, Peter. *Physical Chemistry, 5th. ed.*, W. Freeman and Co., 1994, pp. 33-36