5.5 Deductions from the Kinetic Theory

We will now examine some of the laws for ideal gases that we had looked at previously to see whether or not they are consistent with the kinetic theory.

5.5.1 Boyle's Law

$PV = f(T) =$ Constant at constant temperature.

From the simple kinetic theory, we showed that $P = \dfrac{mN\overline{C}^2}{3V}$.

Therefore, $PV = \dfrac{mN\overline{C}^2}{3}$, according to the kinetic theory. The kinetic theory would be consistent with Boyle's law provided the right had side term can be shown to be a function of temperature only for a fixed mass of the gas.

Maxwell (1860) showed that molecules of all gases at a given temperature posses the same average kinetic energy.

$\overline{E}_k = \dfrac{1}{2} m\overline{C}^2 =$ constant at constant temperature. This gives $\mathrm{m}\overline{\mathrm{C}}^2 = 2\overline{\mathrm{E}}_\mathrm{k}$. When this is substituted in the above expression for PV, we get

$$\mathrm{PV} = \frac{2}{3}\mathrm{N}\overline{\mathrm{E}}_\mathrm{k}$$

For a given N, i.e. at fixed number of moles, N is constant and $\overline{E}_k$ is a function of temperature only. Therefore,

$PV = f(T) =$ Constant at constant temperature. <--- Boyle's Law

5.5.2 Avogadro's Law

"Two gases of equal volumes at the same pressure and temperature contain equal number of molecules."

For Gas #1: $P_1V_1 = \dfrac{1}{3} n_1 m_1 \overline{C}_1^2$

For Gas #2: $P_2V_2 = \frac{1}{3}n_2m_2\overline{C}_2^2$

If we have equal volumes at same pressure, $P_1 = P_2$ and $V_1 = V_2$.

Therefore,

$$\frac{1}{3}\mathrm{n}_1\mathrm{m}_1\overline{\mathrm{C}}_1^2 = \frac{1}{3}\mathrm{n}_2\mathrm{m}_2\overline{\mathrm{C}}_2^2 \text{ or } \mathrm{n}_1\mathrm{m}_1\overline{\mathrm{C}}_1^2 = \mathrm{n}_2\mathrm{m}_2\overline{\mathrm{C}}_2^2$$

Now, if the two gases are at the same temperature, then the mean kinetic energy of their molecules would be the same.

$$\frac{1}{2}m_1\overline{C}_1^2 = \frac{1}{2}m_2\overline{C}_2^2 \text{ or } \mathrm{m}_1\overline{\mathrm{C}}_1^2 = \mathrm{m}_2\overline{\mathrm{C}}_2^2$$

Combining these two equations (divide the first by the second), we get

$n_1 = n_2$ <----- no of molecules are the same. Which is Avogadro's Law.

5.5.3 Temperature and motion of molecules

According to the kinetic theory:

- The motion of molecules is reflected in the temperature and pressure of the gas.
- Temperature is the measure of the average kinetic energy of the molecules.
- Pressure is a direct result of the net force that results from the repeated impacts of molecules with the container walls.

As the temperature increases, the kinetic energy increases. Therefore, temperature is a function of the kinetic energy, but we have not said anything about the nature of this functional relationship.

The simplest functional form would be a direct proportionality. i.e.

$(\overline{E}_k)$ *or* $\frac{1}{2}m\overline{C}^2 \propto T$. Let us see if this is valid.

We know that $PV = \frac{mn\overline{C}^2}{3}$.

If $\frac{1}{2}m\overline{C}^2 \propto T$, we can write

$$m\frac{\overline{C}^2}{2} = (Cont.)(T) = k^{'}T .$$

Which gives $m\overline{C}^2 = 2k'T$

When this is substituted into the Kinetic Theory Equation for PV,
$PV = \frac{mn\overline{C}^2}{3}$, we get
$$PV = \frac{2}{3}k'nT = knT$$
Note that we have substituted k for (2/3) k' and, n is the number of molecules in a given volume of gas.

For one mole of gas n = Avogadro's number and
V = v_m, the molar volume (volume of one mole of gas).

Therefore,

$Pv_m = kN_A\, T$

Let $kN_A = R$, then we get

$PV_m = RT$

This is the ideal gas law. So we have shown that the assuming the temperature to be directly proportional to kinetic energy is totally consistent with the ideal gas law.

Also, $k = R/N_A$ is the gas constant per molecule. Its experimentally determined value is

(k) = 1.380662 x 10^{-23}J/K. It is called the **<u>Boltzmann's constant</u>**.

Also note that
$$PV_m = \frac{2}{3}\left(\frac{1}{2}N_A m\overline{C}^2\right) = \frac{2}{3}E_{k,m}$$
or
$$E_{k,m} = {}^3\!/_2\, PV = \frac{3}{2}RT$$
Thus the total kinetic energy of all molecules in one mole of an ideal gas is equal to (3/2)RT.

At T = 0, the kinetic energy becomes zero.

One final result is the average speed of the molecules.

Knowing that $mN_A = M$, the molar mass, the total mass of one mole of gas or N_A molecules, we can say

$$E_{k,m} = N_A\left(\frac{1}{2}m\overline{C}^2\right) = mN_A\left(\frac{1}{2}\overline{C}^2\right)$$

or

$$\overline{C}^2 = \frac{2E_{k,m}}{mN_A} = \frac{3RT}{M}$$

$$\sqrt{\overline{C}^2} = \sqrt{\frac{3RT}{M}}$$

This relates the root mean square speed to the temperature and molar mass of the gas. Note that at any given temperature the average speed is inversely proportional to the molar mass. <u>This result was used in the first laboratory experiment for measuring the density of gases</u>.

Values of r.m.s speeds for some gases at 0 ^{o}C are listed in Table 5-1, (P. 141)

Example Problem 5-3

Evaluate the r.m.s. velocity for N_2 at 25°C.

Solution

The appropriate equation is 5.44. For nitrogen N_2, the molar mass is 0.02802 kg/mol. The temperature is 25°C or 298.15 K and R is 8.314 J/mol K. Hence,

$$\sqrt{\overline{c^2}} = \sqrt{3RT/M} = \sqrt{\frac{(3)(8.314)(298.15)}{0.02802}\ \frac{m^2}{s^2}} = 515\,m/s$$

5.5.4 Distribution of Molecular Velocities

All molecules of a gas, even an ideal gas, do not move at the same velocity, except at absolute zero of temperature where they do not move at all. There is a distribution of molecular velocities, some molecules travelling slowly and some faster.

If you plot the fraction of molecules having a particular speed against value of the speed, you will get a curve somewhat similar to the normal bell-shaped curve.

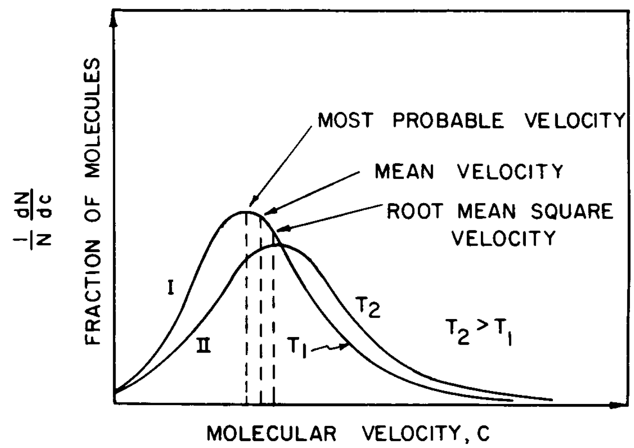

Figure 5-6 Distribution of Molecular Velocities

The fraction of molecules having a particular speed reaches a maximum at certain speed. If you pick a molecule at random, it would be more likely to have this speed than any other, because the fraction of molecules having this speed is the maximum. This speed is called the most probable speed. Its value is given by

$C_{mp} = \sqrt{\dfrac{2RT}{M}}$, the most probable speed.

Another useful speed is the mean velocity, $\overline{C}$, which is the arithmatic mean of all speeds.

$$\overline{C} = \frac{C_1 + C_2 + C_3 + - - - + C_N}{N}$$

Its value is given by

$$\overline{C} = \frac{1}{N}\int_0^\infty C dN = \sqrt{\frac{8RT}{\pi M}}$$

Recall that the root mean square speed (R.M.S. speed) is given by

$$\sqrt{\overline{C^2}} = \sqrt{\frac{3RT}{M}}$$

Example Problem

A 1 litre tank contains one mol of hydrogen gas at room temperature of 25°C.

(a) Determine the pressure in the tank using the ideal gas law.

(b) Determine the total kinetic energy possessed by the molecules of hydrogen in the tank.

(c) Determine the R.M.S. speed of the molecules in the tank.

(a) $P = \frac{nRT}{V} = \frac{1\ \text{mol} \times 8.314\,(\text{J/mol.K}) \times (273.15 + 25)\text{K}}{0.001\text{m}^3} = 2{,}479{,}000\,\text{Pa}$

(b) Kinetic energy per mole is

$$E_{k,m} = \frac{3}{2}RT = 1.5 \times 8.314\text{J}/(\text{molK}) \times 298.15\,\text{K} = 3{,}718\,\text{J/mol}$$

(c) R.M.S. speed is given by

$$\sqrt{\overline{C^2}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314\text{J}/(\text{molK}) \times 298.15\text{K}}{0.002\,\text{kg/mol}}} = 1928\,\text{m/s}$$

The hydrogen molecule travels more than a mile in one second.