In the last lecture I talked about two basic concepts.

1. ***The ideal gas law, i.e. $PV = nRT$***
2. ***The statement that a mixture of ideal gases also behaves like an ideal gas with the total number of moles being equal to the sum of moles of individual components.***

$$\mathbf{n = n_1 + n_2 + ...n_c}$$

Today we are going to start on the kinetic theory of gases, but first we will look at an application of the basic concepts that we learned in the last lecture.

(Fall 2001Midterm)
An ideal gas mixture was put together by mixing the contents of three vessels, each containing a single component ideal gas at the specified temperature and pressure listed below.

Vessel number	Component in the vessel	Molar Mass, (kg/kmol)	Volume of the vessel, (m^3)	Temperature, (^oC)	Pressure, (kPa)
1	CH_4	16	0.85	0	800
2	CO_2	44	0.30	25	400
3	N_2	28	0.35	35	600

The mixed gas was transferred to a fourth container whose volume was known to be 1.0 m^3. The mixture was then heated to a temperature of 400 K. Calculate the following for this mixture:

a. Number of moles of each component in the mixture.(4.5 points)

$$n = \frac{PV}{RT}$$

$$= \frac{800 \, x \, 1000 \;\; x \, 0.85}{8.314 \, x \, (273.15 + 0.0)} = 299.4 \; for \; CH_4$$

$$= \frac{400 \, x \, 1000 \;\; x \, 0.30}{8.314 \, x \, (273.15 + 25)} = 48.4 \; for \; CO_2$$

$$= \frac{600 \, x \, 1000 \;\; x \, 0.35}{8.314 \, x \, (273.15 + 35)} = 82.0 \; for \; N_2$$

Total number of moles = 429.8 moles

b. Mass of each component in the mixture.(4.5 points)

For CH_4, Mass = 299.4 moles x 16 g/mole = *4790 g*.
For CO_2, Mass = 48.4 moles x 44 g/mole = *2130 g*
For N_2, Mass = 82.0 moles x 28 g/mol = *2295 g*
Total mass = *9215 g*

c. Mass fraction of CO_2 in the mixture.(2 points)

Mass fraction of CO_2 = 2130/(9215) = *0.231*

d. Mole fraction of CH_4 in the mixture. (2 points)

Mole fraction of CH_4 = 299.4/(429.8) = *0.697*

e. Pressure of the mixture after heating to 400 K. (4 points)

Pressure of mixture = nRT/V

$$= 429.8 \text{ moles} \times 8.314 \text{ J/(mol K)} \times 400 \text{ K} /(1.0 \text{ m}^3)$$
$$= \underline{1.429 \times 10^6 \text{ Pa}}$$

f. Partial pressure of CH_4 after heating to 400 K (3 points)

Partial pressure of CH4 = (mole fraction of CH4) x Total pressure

$$= 0.697 \times 1.429 \times 10^6 \text{ Pa}$$
$$= \underline{0.996 \times 10^6 \text{ Pa.}}$$

Kinetic Theory of Gases

There are two ways of studying the behaviour of ideal gases.

1. Ideal gas law – based on the experimental measurements of pressure, volume and temperature.

2. The kinetic theory – based on the basic properties of molecules.

In the kinetic theory considers

- How molecules interact with each other and with the walls of the container in which they reside

- How these interactions can be translated to pressure

To simplify the mathematics, some simplifying assumptions are made.

a) The actual volume of molecules is negligible compared to the total volume.

b) Molecules are rigid spheres with no interactive forces

c) Molecules move freely in all directions and collisions of the molecules with each other and with the walls of the container are perfectly elastic. That is, both momentum and kinetic energy are conserved in collisions.

Example Problem 5-2

One mole of a gas at normal temperature and pressure (O°C and 1 atm) occupies 0.0224 m^3. The diameter of the molecules constituting the gas is approximately 10^{-10}m. What fraction of the volume occupied by the gas is physically taken up by the molecules?

Solution

One mole of a gas contains 6.023×10^{23} molecules. The volume of a molecule, assumed spherical, is $4/3\pi R^3$ or $\pi D^3/6$. Hence, the volume actually taken up by the molecules is

$$\frac{\pi \times 10^{-30} \times 6.023 \times 10^{23}}{6}\ m^3$$

or

$$3.16 \times 10^{-7}\ m^3.$$

The volume ratio,

$$\frac{\text{volume of molecules}}{\text{volume occupied by gas}} = 1.41 \times 10^{-5}.$$

This is a small number which justifies assumption 1 of the kinetic theory.

Relationship between pressure and velocity of molecules

We will relate pressure (P) to the number, mass and velocity of the molecules.
$P = f(N, m, C)$.
First consider only one molecule in a cubical container length = width = height = a.

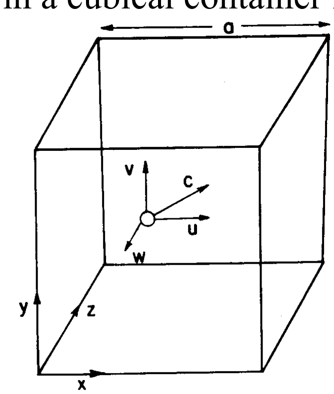

Figure 5-4 A Simple Model of Molecular Motion

Let us say that the molecule moves only up and down, with a velocity of v_z. It travels upward with velocity $+v_z$ and after colliding with the wall travels downward with a velocity $-v_z$. Since the collisions are perfectly elastic, speed remains constant, only direction changes.

The distance travelled between two successive collisions with the walls is a, the velocity is v_z. The number of collisions per unit time is given by

$n_c = v_z/(a)$

Since after each collision, the velocity becomes -ve of the pre-collision velocity, the change in momentum in each collision is $mv_z - (-mv_z) = 2mv_z$.

The rate of change of momentum = (Number of collisions per unit time) x (Change in momentum in each collision) = $(v_z/a) \times (2mv_z) = 2m(v_z)^2/a$

So far we considered only one dimensional motion, in vertical direction. Let us now consider 3-dimensional motion of the molecule.

The velocity vector for the molecule is

$\vec{C} = u\vec{i} + v\vec{j} + w\vec{k}$

Such that the speed of the molecules is given by,

$$C^2 = u^2 + v^2 + w^2$$

When the particle hits one side of the cube, only the component of velocity normal to this side changes direction. Let us say this direction is the x-direction. The speed in the x-direction is |u|.

The change in momentum due to collision in the x-direction would be -2m|u|.

The number of collisions per unit time in x direction would be $\frac{|u|}{a}$.

Change in momentum per unit time due to collisions in the x direction = $2m|u|\frac{|u|}{a} = 2m\frac{u^2}{a}$

Similarly the rates of change in momentum in y and z directions are $2m\frac{v^2}{a}$ and $2m\frac{w^2}{a}$.

The combined change of momentum per unit time for one molecule is

$$2m\frac{u^2}{a} + 2m\frac{v^2}{a} + 2m\frac{w^2}{a} = \frac{2m}{a}(u^2 + v^2 + w^2) = \frac{2mC^2}{a}$$

Now imagine that the cube contains a large number of molecules, (N), each travelling with a different speed. The combined change of momentum for all the molecules per unit time

$$=\frac{2m}{a}[c_1^2+c_2^2+c_3^2+----+c_n^2]$$

where, C_1, C_2, C_3, --- are speeds of individual molecules.

Let us now define a mean square velocity as

$\overline{C}^2=\dfrac{C_1^2+C_2^2+C_3^2+----+C_n^2}{n}$, then the rate of change of momentum for all molecules is

$$=\frac{2mn\overline{C}^2}{a}.$$

Now we recall the relationship between force and the rate of change of momentum, i.e **F = rate of change of momentum**. Therefore,

$$F=\frac{2mn\overline{C}^2}{a}.$$

This is the total force exerted on all sides of the cube.

We know that pressure is force per unit area. Therefore we can determine the pressure by dividing the force by the internal area of the cube.

The cube has six faces, each with an area of a^2. Therefore, the total area is $6a^2$. Dividing the force by this area gives the pressure.

$$P=\frac{\frac{2mn\overline{C}^2}{a}}{6a^2}=\frac{mn\overline{C}^2}{3a^3}=\frac{mn\overline{C}^2}{3V}$$

m = mass of one molecule --> easy to determine
n = No. of molecules in V volume --> easy
V = Volume of container --> easy
$\sqrt{\overline{C}^2}$ = root mean square velocity (r.m.s. velocity) unknown.

The above relationship can be written as: $\mathrm{PV}=\mathrm{n}\left(\dfrac{\mathrm{N_A m}\overline{\mathrm{C}}^2}{3}\right)$. Compare it with the ideal gas law, PV = nRT and you will see that there are noticeable similarities. The two relationships would be identical if we can show that $\mathrm{RT}=\dfrac{\mathrm{N_A m}\overline{\mathrm{C}}^2}{3}$.