We use the term "ideal" because real gases do not follow Eq. (10-21) precisely, particulary at high pressures or when the gas is near liquefaction point.

To determine the constant $\frac{p_o V_o}{T_o}$ we must incorporate the effect of the amount or mass of gas that is present. For gases it is useful to use instead of mass an amount of substance the unit of which is mole. One mole (abbr. mol) is defined as the amount of substance which contains as many atoms or molecules as there are in 0,012 kg of carbon 12. The number of atoms in one mole is known as Avogadro's number N_A and its accepted value is

$$N_A = 6,02214.10^{23} \text{ mol}^{-1}.$$

Following Avogadro's hypothesis one moles of gases at the same temperature and pressure occupy the same volumes. Thus for, so called standard conditions, that is $T_o = 273,15$ K and $p_o = 1,01325.10^5$ Pa one mol of gas occupies a volume $V_m = 22,4.10^{-3} \text{ m}^3$. We can therefore write

$$\frac{p_o V_o}{T_o} = \frac{p_o V_m}{T_o} \, n = R.n , \qquad (10-22)$$

where n represents the number of moles, and the constant

$$R = \frac{p_o V_m}{T_o}$$

is called the universal gas constant. This constant has the same value for all gases, namely

$$R = 8,314 \text{ J.K}^{-1}.\text{mol}^{-1}.$$

Substituting Eq. (10-22) into Eq. (10-21) we obtain equation of state of ideal gas as

$$pV = nRT . \qquad (10-23)$$

The ideal gas law is an extremely useful tool to calculate the relation between state variables.

11. KINETIC THEORY

The concept that matter is made up of atoms which are in continuous random motion is called the kinetic theory.

The earliest and most direct experimental evidence for the reality of atoms is provided by the quantitative studies of Brownian motion. This motion is named after the English botanist Robert Brown who discovered in 1827 that pollen suspended in water shows a continuous random motion, see Fig. 11-1, when viewed under a microscope.
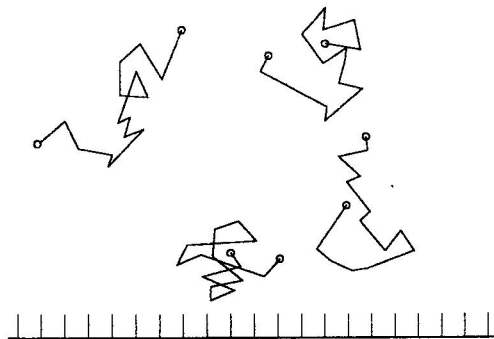
The suspended particles are extremely large compared to the molecules of the fluid and are being continually bombarded on all sides by them. If the particles are sufficiently large and the number of molecules great, equal numbers of molecules strike the

Figure 11 - 1

particles on all sides at each instant. For smaller particles and fewer molecules the number of molecules striking various sides of the particle at any instant, being merely a matter of chance, may not be equal; that is fluctuations occur.

Hence the particle at each instant suffers an unbalanced force causing it to move this or that way. The particles therefore act just like very large molecules in the fluid, and their motions should be qualitatively the same as the motions of the fluid molecules.

Kinetic theory can be also used to explain some properties of liquids and solids.

We now investigate the properties of a gas from the point of view of kinetic theory, which is based on the laws of classical mechanics. But to apply Newton's laws to each one of the vast number of molecules in a gas ($> 10^{25}$ m^3) is far beyond the capability of present computers. Instead we take a statistical approach and determine averages of certain quantities, and these averages correspond to microscopic variables.

We make the following assumptions about the molecules in a gas: ·
1. A gas consists of particles, called molecules.
2. The molecules are in random motion and obey Newton's laws of motion.
3. The total number of molecules is large.
4. The volume of the molecules is a negligibly small fraction of the volume occupied by the gas.
5. No appreciable forces act on the molecules except during a collision.
6. Collisions are elastic and are of negligible duration.

Under these assumptions gases follow the ideal gas law closely, and indeed we shall refer to such a gas as an ideal gas.

11 - 1 K i n e t i c   C a l c u l a t i o n   o f   P r e s s u r e

Let us now calculate the pressure of an ideal gas from kinetic theory. For purposes of argument, we imagine that the molecules are contained in a rectangular vessel whose ends have area A and whose length is ℓ as shown Fig. 11-2. The pressure exerted by the gas on the walls of its container is, according to our model, due to the collisions of the molecules with the walls. Let us focus our attention on the wall, of area A, at the left end of the container and examine what happens when one molecule strikes this wall, as shown in Fig. 11-3. This molecule exerts a force on the wall and the wall exerts an equal and opposite force back on the molecule. The magnitude of this force, according to Newton's second law, is equal to
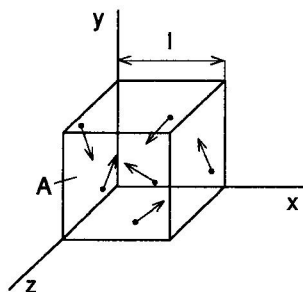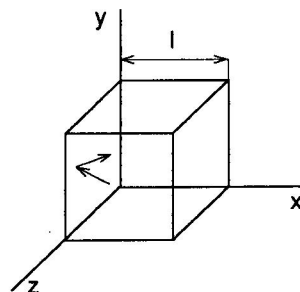

Figure 11 - 2

Figure 11 - 3

the molecule's rate of change of momentum, $F = dp/dt$. Assuming the collision is elastic, only the x component of the molecule's momentum changes, and it changes from $- mv_x$ (it is moving in the negative x direction) to $+ mv_x$. Thus the change in momentum, $\triangle(mv)$, which is the final momentum minus the initial momentum, is

$$\triangle(mv) = mv_x - (- mv_x) = 2mv_x$$

for one collision. This molecule will make many collisions with the wall, each separated by a time $\triangle t$, which is the time it takes the molecule to travel across the box and back again, a distance equal to 2ℓ. Thus $2\ell = v_x \triangle t$ or $\triangle t = 2\ell/v_x$. The time $\triangle t$ between collisions is very small so the number of collisions per second is very large. Thus the average force - averaged over many collisions - will be equal to the force exerted during one collision divided by the time between collisions (Newton's second law):

$$F = \frac{\triangle(mv)}{\triangle t} = \frac{2mv_x}{2\ell/v_x} = \frac{mv_x^2}{\ell} \qquad \text{due to one molecule}$$

During its passage back and forth across the container, the molecule may collide with the tops and sides of the container, but this does not alter its x component of momentum and thus does not alter our result. It may also collide with other molecules, which may change its v_x. However, any loss (or gain) of momentum is acquired by the other molecule, and because we will sum over all the molecules in the end, this effect will be included. So our result above is not altered.

Of course the actual force due to one molecule is intermittent, but because a huge number of molecules are striking the wall per second, the force is pretty steady. To calculate the force due to all the molecules in the box, we have to add the contributions of each. Thus the average net force on the wall is

$$F = \frac{m}{\ell} (v_{x1}^2 + v_{x2}^2 + \ldots + v_{xN}^2) ,$$

where v_{x1} means v_x for particle number 1 (and so on) and the sum extends over the total of N molecules. Now the average value of the square of the x component of velocity is

$$\overline{v_x^2} = \frac{v_{x1}^2 + v_{x2}^2 + \ldots + v_{xN}^2}{N} .$$

Thus we can write the average force as

$$F = \frac{m}{\ell} N\overline{v_x^2} .$$

We know that the square of any vector is equal to the sum of the squares of its components. Thus $v^2 = v_x^2 + v_y^2 + v_z^2$ for any velocity v. Taking averages we obtain

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} .$$

Since the velocities of the molecules in our gas are assumed to be random, there is no preference for one direction or another. Hence

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$$

and therefore

$$\overline{v^2} = 3\overline{v_x^2} .$$

We substitute this into the equation for the average force F :

$$F = \frac{m}{\ell} N \frac{\overline{v^2}}{3} .$$

The pressure on the wall is then

$$p = \frac{F}{A} = \frac{1}{3} \frac{N m \overline{v^2}}{A \ell}$$

or

$$p = \frac{1}{3} \frac{N m \overline{v^2}}{V} , \tag{11-1}$$

where $V = A\ell$ is the volume of the container. This is the result we were seeking, the pressure in a gas expressed in terms of molecular properties.

Equation (11-1) can be rewritten in a clearer form by multiplying both sides by V and slightly rearranging the right side:

$$pV = \frac{2}{3} N(\frac{1}{2} m \overline{v^2}) . \tag{11-2}$$

The quantity $\frac{1}{2} m \overline{v^2}$ is the average kinetic energy of the molecules in the gas.

11 - 2 Kinetic Interpretation of Temperature

If we compare Eq. (11-2) with the ideal gas law, Eq. (10-23), we obtain:

$$\frac{2}{3} N(\frac{1}{2} m \overline{v^2}) = nRT .$$

Taking into account that

$\frac{N}{n} = N_A$ is Avogadro´s number

and $\frac{R}{N_A} = k$ is Boltzmann´s constant we have:

$$\frac{1}{2} m \overline{v^2} = \frac{3}{2} kT . \tag{11-3}$$

This equation tells us that

> the average translational kinetic energy of molecules in a gas
> is directly proportional to the absolute temperature.

The higher the temperature, according to kinetic theory, the faster the molecules are moving on the average. This relation is one of the triumphs of the kinetic theory. Equation (11-3) implies that as the temperature approaches absolute zero the kinetic energy of molecules approaches zero. Modern quantum theory, however, tells us this is not quite so; instead, as absolute zero is approached, the kinetic energy approaches a very small nonzero minimum value. Even though all real gases become liquid or solid above 0 K, molecular motion does not cease, even at absolute zero.

We can use Eq. (11-3) to calculate how fast molecules are moving on the average. Notice that the average in Eqs (11-1) through (11-3) is over the square of the velocity. The square root of $\overline{v^2}$ is called the root-mean-square velocity, v_{rms} (since we are taking the square root of the mean of the square of the velocity):

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}} . \tag{11-4}$$

The mean speed, $\overline{v}$, is the average of the magnitudes of the speeds themselves; $\overline{v}$ is generally not equal to v_{rms}. The difference between the mean speed and the rms speed can be seen in the following sections.

11 - 3 Dalton´s Law

If the molecules of the gas in the container are of several different kinds with respective masses m_j and number of molecules N_j we can write Eq. (11-1) in the following way:

$$p = \frac{1}{3V} \sum_j N_j m_j \overline{v_j^2} . \qquad (11\text{-}5)$$

From Eq. (11-5) we have at once the important result that, according to our theory, the pressure of a mixture of two or more ideal gases is simply the sum of the pressures which they would exert if each occupied the same volume by itself, or

$$p = p_1 + p_2 + \ldots + p_j . \qquad (11\text{-}6)$$

Eq. (11-6) is called Dalton's Law. This law is known experimentally to be true at sufficiently low densities; the departures from this law are becoming noticeable in ordinary gases only when under considerable pressure.

11 - 4 Distribution of Molecular Speeds

The molecules in a gas are assumed to be in random motion, which means that many molecules have speeds less than the average speed and others have speeds greater than the average. In 1859, James Clerk Maxwell (1831 - 1879) worked out a formula for the most probable distribution of speeds in a gas containing N molecules

$$f(v) = 4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-\frac{1}{2}\frac{mv^2}{kT}} . \qquad (11\text{-}7)$$

$f(v)$ is called the Maxwell distribution of speeds, and is plotted in Fig. 11-4. The quantity $f(v)dv$ represents the number of molecules that have speed between v and $v + dv$. Notice that $f(v)$ does not give the number of molecules with speed v; $f(v)$ must be multiplied by dv to give the number of molecules (clearly the number of molecules must depend on the "width" or "range" of velocities, dv). In the formula for $f(v)$, m is the mass of a single molecule, T is the absolute temperature, and k is Boltzmann's constant. Since N is the total number of molecules in the gas, when we sum over all the molecules in the gas we must get N; thus we must have

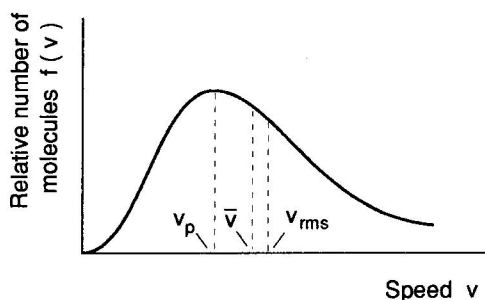$$\int_0^\infty f(v)\, dv = N . \qquad (11\text{-}8)$$
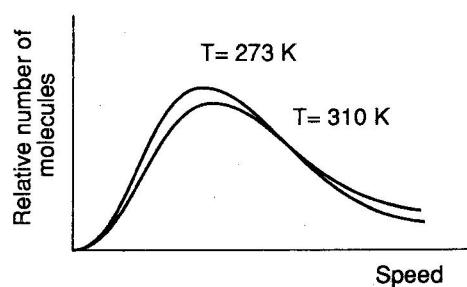

Figure 11 - 4

Figure 11 - 5

The Maxwell distribution for a given gas depends only on the absolute temperature. Fig. 11-5 shows the distributions for two different temperatures. Just as v_{rms} increases with temperature, so the whole distribution curve shifts to the right at higher temperatures.

The distribution of molecules in a liquid also resembles the curve of Fig. 11-4. This explains why some molecules in a liquid (the fast ones) can escape through the surface (evaporate) at temperatures well below the normal boiling point.

E x a m p l e : Determine formulas for (a) the average speed, $\bar{v}$, and (b) the most probable speed, v_p, of molecules in an ideal gas at temperature T.

Solution: (a) The average value of any quantity is found by multiplying each possible value of that quantity (say, speed) by the number of molecules that have that value, and then summing all these numbers and dividing by N (the total number). We are given a continuous distribution of speeds (Eq. 11-7) so the sum becomes an integral over the product of v and the number $f(v)\,dv$ that have speed v :

$$\bar{v} = \frac{\int_0^\infty vf(v)\,dv}{N} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty v^3 e^{-\frac{1}{2}\frac{mv^2}{kT}}\,dv \ .$$

We can look up the definite integral in the tables, or integrate by parts, and obtain

$$\bar{v} = 4\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\left(\frac{2k^2T^2}{m^2}\right) = \sqrt{\frac{8}{\pi}\frac{kT}{m}} \approx 1{,}60\sqrt{\frac{kT}{m}} \ .$$

(b) The most probable speed is that speed which occurs more than any others, and thus is that speed where $f(v)$ has its maximun value. Since $df(v)/dv = 0$ at this point, we have

$$\frac{df(v)}{dv} = 4\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\left(2v\,e^{-\frac{mv^2}{2kT}} - \frac{2mv^3}{2\,kT}e^{-\frac{mv^2}{2kT}}\right) = 0 \ .$$

Solving for v , we get

$$v_p = \sqrt{\frac{2kT}{m}} \doteq 1{,}41\sqrt{\frac{kT}{m}} \ .$$

(Another solution is $v = 0$, but this corresponds to a minimum, not a maximum.) In summary,

$$v_p = \sqrt{2\frac{kT}{m}} \doteq 1{,}41\sqrt{\frac{kT}{m}}$$

$$\bar{v} = \sqrt{\frac{8}{\pi}\frac{kT}{m}} \doteq 1{,}60\sqrt{\frac{kT}{m}}$$

$$v_{rms} = \sqrt{3\frac{kT}{m}} \doteq 1{,}73\sqrt{\frac{kT}{m}}$$

These are all indicated in Fig. 11-4.

11 - 5 M e a n   F r e e   P a t h

Between successive collisions a molecule in a gas moves with constant speed along a straight line. The average distance between such successive collisions is called the mean free path.

If we were to follow the path of a particular molecule, we would expect to see it follow a zigzag path as shown in Fig. 11-6.
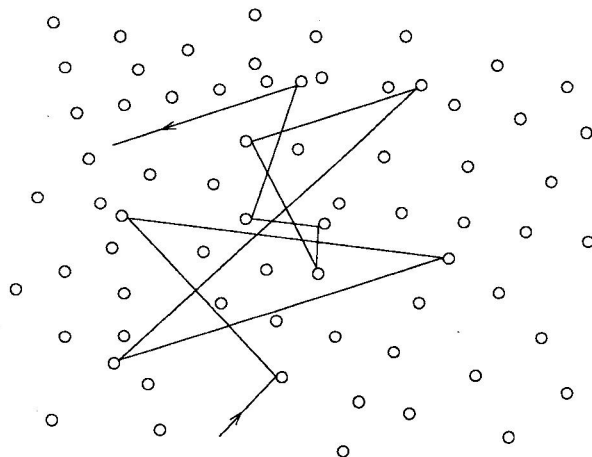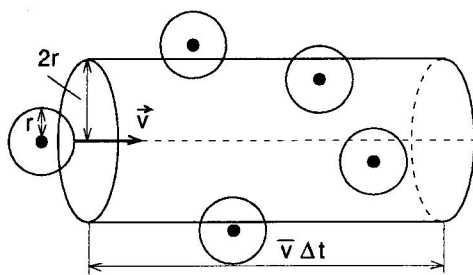
Let us determine the mean free path.

Figure 11 - 6

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Figure 11 - 7

Suppose our gas is made up of molecules which are hard spheres of radius r. A collision will occur whenever the centers of two molecules come within a distance 2r of one another. Let us follow a molecule as it traces a straight-line path. In Fig.11-7 the dashed line represents the path of our particle if it made no collisions. Also shown is a cylinder of radius 2r, if the center of another molecule lies within this cylinder, a collision will occur. (Of course, when a collision occurs the particle's path would change direction, as would our imagined cylinder, but our result won't be altered by unbending a zigzag cylinder into a straight one for purposes of calculation.) Assume our molecule is an average one, moving at the mean speed in the gas, $\bar{v}$. For the moment, let us assume that the other molecules are not moving, and that the concentration of molecules (number per unit volume) is N_0. Then the number of molecules whose center lies within the cylinder of Fig. 11-7 is N_0 times the volume of this cylinder, and this also represents the number of collisions that will occur. In a time Δt, our molecule travels a distance $\bar{v}\Delta t$, so the length of the cylinder is $\bar{v}\Delta t$ and its volume is $\pi(2r)^2\bar{v}\Delta t$. Hence the number of collisions that occur in a time Δt is

$$N_0 \, \pi(2r)^2 \, \bar{v}\Delta t \ .$$

We define the mean free path λ as the average distance between two successive collisions. This distance is equal to the distance traveled ($\bar{v}\Delta t$) in time Δt divided by the number of collisions made in time Δt :

$$\lambda = \frac{\bar{v}\Delta t}{N_0 \, \pi(2r)^2 \, \bar{v}\Delta t} = \frac{1}{4\pi r^2 N_0} \ . \tag{11-9}$$

Thus we see that λ is inversely proportional to the cross-sectional area ($= \pi r^2$) of the molecules and to their concentration N_0. However Eq. (11-9) is not fully correct since we assumed the other molecules are all at rest. In fact they are moving, and the number of collisions in time Δt must depend on the relative speed of the colliding molecules, rather than on $\bar{v}$. Hence the number of collisions per second is

$$N_0 \, \pi(2r)^2 v_{rel} \Delta t \ ,$$

where v_{rel} is the average relative speed of colliding molecules. A careful calculation shows that for Maxwellian distribution of speeds

$$v_{rel} = \sqrt{2}.\bar{v}$$

Hence the mean free path is

$$\lambda = \frac{1}{4\pi\sqrt{2}.r^2.N_0} \ . \tag{11-10}$$

11 - 6 Equipartition of Energy

Let us now find the total energy of a gas containing a large number of molecules. The energy of such a gas, regarded as the internal energy of its molecules, can be divided into a number of different parts, as follows:

  a) translational kinetic energy,
  b) rotational kinetic energy,

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c) energy of vibrations of the atoms in a molecule,

d) mutual potential energy of the molecules as a whole.

At low densities the mutual energy, type d, becomes negligible. The translational kinetic energy of the molecules moving as wholes is likewise quite distinct at low densities from the other forms. We can therefore express the kinetic energy of a gas containing N molecules of the same mass m as

$$E_k = \sum_{i=1}^{N} W_i = \frac{1}{2} m \sum_{i=1}^{N} v_i^2 = \frac{1}{2} N.m.v_{rms}^2 . \qquad (11\text{-}11)$$

For the root-mean-square velocity we can use Eq. (11-4) so that we have

$$E_k = \frac{1}{2} Nm \frac{3kT}{m} = \frac{3}{2} NkT = \frac{3}{2} nRT . \qquad (11\text{-}12)$$

We can see that internal energy of a gas depends only on the temperature and distributes itself in equal shares to each of the independent ways in which the molecules can absorb energy. This theorem is called the equipartition of energy and was deduced by Clerk Maxwell. Each such independent mode of energy absorption is called a degree of freedom.

From Eq. (11-12) we can see that the kinetic energy of translation per one mole of gaseous molecules is

$$E_k = \frac{3}{2} RT .$$

The kinetic energy of translation per mole is the sum of three terms, namely

$$\frac{1}{2} M \overline{v_x^2} ; \qquad \frac{1}{2} M \overline{v_y^2} ; \qquad \frac{1}{2} M \overline{v_z^2} .$$

The theorem of equipartition requires that each such term contribute the same amount to the total energy per mole, or $\frac{1}{2}$ RT per degree of freedom.

We can therefore say that the average kinetic energy per one degree of freedom is:

- for one mole of gas $\qquad \frac{1}{2}$ RT $\qquad\qquad\qquad\qquad$ (11-13)

- for one particle $\qquad \frac{1}{2}$ kT $\qquad\qquad\qquad\qquad$ (11-14)

For monoatomic gas with three degrees of freedom the average kinetic energy of one particle is

$$E_k = \frac{3}{2} kT \qquad\qquad\qquad (11\text{-}15)$$

or for one mole of gas

$$E_k = \frac{3}{2} RT \qquad\qquad\qquad (11\text{-}16)$$

For a diatomic gas we can think of each molecule as two spheres joined by a rigid rod. Such a molecule can rotate about any one of three mutually perpendicular axes. However the moment of inertia about an axis along the rigid rod should be negligible compared to that about axes perpendicular to the rod, so that the rotational energy should consist of only two terms. Each rotational degree of freedom is required by equipartition to contribute the same energy as each translational degree, so that a diatomic gas having both rotational and translational motion will have five degrees of freedom and therefore its average kinetic energy per one mole is

$$E_k = \frac{5}{2} RT \qquad\qquad\qquad (11\text{-}17)$$

For polyatomic gases, each molecule contains three or more spheres (atoms) joined together by rods in our model, so that the molecule is capable of rotating energetically about each of three mutually perpendicular axes. Hence, a polyatomic gas having both rotational and translational motion will have six degrees of freedom, therefore its average kinetic energy per one mole is

$$E_k = 3 RT \qquad\qquad\qquad (11\text{-}18)$$