## 2.2 KINETIC THEORY

The concept that matter is made up of atoms which are in continuous random motion is called **kinetic theory.** Since the molecules are in random motion many of them have speeds less than the average speed and others have speeds greater than the average. The formula for the most probable distribution of speeds in a gas containing $N$ molecules is

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

where $f(v)$ is called **Maxwell distribution function,** $k$ is Botzmann's constant, $T$ is the thermodynamic temperature and $m$ is the mass of the molecule. The quantity $f(v)dv$ represents the number of molecules that have speeds between $v$ and $v+dv$. Note 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. 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

$$\int_0^\infty f(v)dv=N$$

**The speeds** of individual molecules vary over a wide range of magnitude. To characterise these speeds we introduce:

- **average speed** which is defined as the average of the speeds of all the molecules;

$$\bar{v}=\frac{1}{N}\int_0^\infty v.f(v)dv \qquad\qquad \bar{v}\approx 1.60\sqrt{\frac{kT}{m}}$$

- **most probable speed,** which is the speed which occurs more than any others; it is found as the extremum of Maxwell's distribution function

$$\frac{df(v)}{dv}=0 \qquad\qquad v_p\approx 1.41\sqrt{\frac{kT}{m}}$$

- **root-mean-square speed** is defined as the average over the square of the speeds

$$v_{rms}^2=\frac{1}{N}\int_0^\infty v^2 f(v)dv. \quad v_{rms}\approx 1.73\sqrt{\frac{kT}{m}}$$

**The pressure** of the molecules on the walls of the container due to the collisions of the molecules with the walls is

$$P=\frac{1}{3}\frac{mN}{V}v_{rms}^2$$

where $V$ is the volume of the container and $N$ is the number of molecules enclosed in the container. The ratio

$$\frac{N}{V}=N_0 \quad \text{is called the concentration of molecules.}$$

If the molecules of the gas in the container are of several different kinds, then the pressure of this mixture of gases is equal to the sum of the pressures which they would exert if each occupied the same volume by itself. This fact is expressed by **Dalton's law**

$$P = \sum_i P_i$$

**The mean free path** is defined as the average distance between successive collisions of a molecule in a gas

$$\lambda = \frac{1}{4\pi\sqrt{2}\,r^2 N_0}$$

where $r$ is the radius of the molecule and $N_0$ is the concentration of the molecules.

**The internal energy** of the gas is equal to the sum of:
  - translational kinetic energy,
  - rotational kinetic energy,
  - energy of vibrations,
  - mutual potential energy of molecules.

At low densities and for the ideal gas the prevailing role is played by translational kinetic energy. Thus we have

$$E_k = \sum_1^n W_i$$

**The average value of the kinetic energy** of the gas which consists of the same molecules and each molecule has i-degrees of freedom is:

$$\frac{i}{2} k T \qquad \text{- per one molecule}$$

$$\frac{i}{2} R T \qquad \text{- per one mole.}$$

**The equipartition of energy theorem** tells us that each degree of freedom shares an equal amount of kinetic energy

$$\frac{1}{2} k T \qquad \text{- per one particle}$$

$$\frac{1}{2} R T \qquad \text{- per one mole}$$

A monatomic molecule has 3 degrees of freedom, a diatomic molecule has 5 degrees of freedom and a molecule consisting of 3 or more atoms has 6 degrees of freedom.

**Problem 2-16.** Eight particles have the following speeds, given in m/s: 1.0; 6.0; 4.0; 2.0; 6.0; 3.0; 2.0 and 5.0. Calculate the average and the root-mean-square speeds..

Solution: The average speed of the particles is:

$$\bar{v} = \frac{1.0 + 6.0 + 4.0 + 2.0 + 6.0 + 3.0 + 2.0 + 5.0}{8} = 3.6\,m.s^{-1}$$

The root-mean-square speed of the particles is:

$$v_{rms} = \sqrt{\frac{1.0^2 + 6.0^2 + 4.0^2 + 2.0^2 + 6.0^2 + 3.0^2 + 2.0^2 + 5.0^2}{8}} = 4.1\,m.s^{-1}$$

Notice that average and root-mean-square speeds are different.

**Problem 2-17.** Determine formulas for (a) the average speed, (b) the most probable speed and (c) the root-mean-square speed for Maxwell's distribution of speeds.

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 the total number of molecules $N$. We are given Maxwell's distribution, which is a continuous function of speeds, so the sum becomes an integral over the product of $v$ and the number $f(v)dv$ that have speed $v$:

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

The integral $\qquad I = \int_0^\infty v^3 e^{-\frac{mv^2}{2kT}}\,dv$

can be solved by substitution: $\quad \dfrac{m\,v^2}{2kT} = y^2 \qquad \dfrac{m}{kT}\,vdv = 2ydy$

After substitution, the integral I takes the following form:

$$I = \frac{4k^2T^2}{m^2}\int_0^\infty y^3 e^{-y^2}\,dy$$

We use integration by parts to solve the integral $\quad I_1 = \int_0^\infty y^3 e^{-y^2}\,dy$

$$u = y^2 \qquad \text{and} \quad v' = y.e^{-y^2}$$

so that for $I_1$ we obtain

$$I_1 = \int_0^\infty y^3 e^{-y^2}\,dy = \frac{1}{2}$$

Finally, after substitution for the average speed we obtain

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

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

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

Solving for $v$ we get three roots: $v_1 = 0$; $v_2 = \infty$ and $v_p = \sqrt{\dfrac{2kT}{m}}$. From the analysis of the second derivation it is obvious that $v_1$ and $v_2$ correspond to the minimum of the distribution function and the most probable speed is therefore

$$v_p = 1.41\sqrt{\frac{kT}{m}}.$$

(c) The root-mean-square speed is defined as the average value of the squares of the speeds of all the molecules or

$$v_{rms}^2 = \frac{1}{N}\int_0^\infty v^2 f(v)dv = 4\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\int_0^\infty v^4 e^{-\frac{mv^2}{2kT}}dv$$

The integral $I' = \displaystyle\int_0^\infty v^4 e^{-\frac{mv^2}{2kT}}dv$ can be solved using the following formula

$$I_{2n} = \int_{-\infty}^\infty e^{-ax^2}x^{2n}dx = 2\int_0^\infty e^{-ax^2}x^{2n}dx = \frac{(2n-1)(2n-3)...5.3.1}{2^n}\sqrt{\frac{\pi}{\alpha^{2n+1}}}$$

In the case of integral $I'$ we have $n=2$ and $\alpha = \dfrac{m}{2kT}$ so that we have

$$I' = \frac{1}{2}\frac{3.1}{2^2}\sqrt{\frac{\pi}{\left(\dfrac{m}{2kT}\right)^5}}$$

Substituting for $I'$ into the integral for $v_{rms}^2$ we finally obtain for the root-mean-square speed

$$v_{rms} = \sqrt{\frac{3kT}{m}} = 1.73\sqrt{\frac{kT}{m}}.$$

**Problem 2-18.** Calculate the mass of an oxygen molecule and its average, root-mean-square and the most probable speed at temperature $t=0\,^{\circ}C$. ($M_{O_2} = 32\ kg\cdot kmol^{-1}$).

Solution: The mass of the oxygen molecule is

$$m = \frac{M_{O_2}}{N_A} = \frac{32}{6.023 \times 10^{26}} = 5.31 \times 10^{-26}\ kg$$

where $N_A$ is Avogadro's number. The average speed of oxygen molecules is

$$\bar{v} = \sqrt{\frac{8kT}{\pi\,m}} \approx \sqrt{\frac{8 \times 1.38 \times 10^{-23} \times 273.15}{\pi\ 5.31 \times 10^{-26}}} = 425.1\ m.s^{-1}$$

Root-mean square-speed is

$$v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3 \times 1.38 \times 10^{-23} \times 273.15}{\pi\ 5.31 \times 10^{-26}}} = 461.5\ m.s^{-1}$$

The most probable speed is

$$v_p = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2 \times 1.38 \times 10^{-23} \times 273.15}{\pi\ 5.31 \times 10^{-26}}} = 376.8\ m.s^{-1}$$

**Problem 2-19.** Calculate the rms speed of the molecules in a gas with a density of $\rho = 3 \times 10^{-2}\ kg.m^{-3}$ and a pressure $P=3.6\ kPa$.

Solution: $\qquad v_{rms} = \sqrt{\frac{3kT}{m}}\quad$ where the mass of the molecule is $\quad m = \frac{M}{N_A}$.

Substituting for $m$ into the expression for rms speed we have

$$v_{rms} = \sqrt{\frac{3kTN_A}{M}}$$

The product $N_A k = R$; where $R$ is a universal gas constant. Thus we have

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

From the ideal gas law $PV=nRT$ we can substitute for $RT$:

$$v_{rms} = \sqrt{\frac{3PV}{nM}} = \sqrt{\frac{3P}{\rho}} \qquad \text{because} \quad \frac{nM}{V} = \rho$$

Substituting numerical values we finally obtain

$$v_{rms} = \sqrt{\frac{3 \times 3.6 \times 10^3}{3 \times 10^{-2}}} = 600\ m.s^{-1}.$$

**Problem 2-20.** Calculate the pressure of an ideal gas on the walls of the container if the Maxwell distribution function for the $x$-component of velocity is given:

$$\psi(v_x) = \frac{1}{w\sqrt{\pi}} e^{-\frac{v_x^2}{w^2}}$$

where $w = \sqrt{\frac{2kT}{m}}$.

Solution: The pressure exerted by the gas on the walls of its container is due to the collisions of the molecules with the walls. When one molecule strikes the wall it exerts a force on it. The force due to all the molecules per unit area is equal to the pressure.
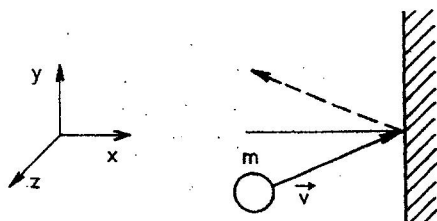
Assuming that the collision of the molecule with the wall is elastic, the normal component of linear momentum $(m\,v_x)$ changes to $(-m\,v_x)$. The $y$ and $z$ components of the linear momentum remain unchanged. Thus the total change of the linear momentum of the molecule due to its collision with the wall is:

$$m\,v_x - (-m\,v_x) = 2m\,v_x.$$

We denote the number of molecules within the volume $V$ as $N$. Thus the density of molecules $N_0$ expresses the number of molecules per unit of volume or

$$N_0 = \frac{N}{V}.$$

To calculate the pressure $dP(v_x)$ we have to determine the number of molecules with components of velocity from $v_x$ to $(v_x + dv_x)$ which per unit of time collide with a unit area of the container. We denote this number of molecules as $dn(v_x)$.

The number of molecules per unit volume with velocities within the interval from $v_x$ to $(v_x + dv_x)$ is $dn_0(v_x) = N_0\psi(v_x)dv_x$.
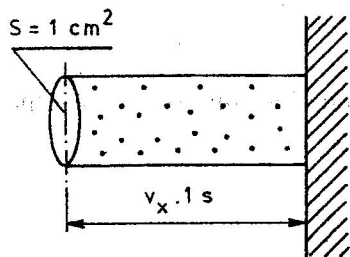
The number of molecules with velocities $v_x$ colliding per one second with an area of $1\ cm^2$ is equal to the number of molecules enclosed within a cylinder of base $1\ cm^2$ and height $v_x$ or

$$dn(v_x) = v_x . 1. \, dn_0(v_x) = v_x N_0 \psi(v_x)dv_x$$

The pressure exerted by these molecules on the wall is therefore

$$dP(v_x) = 2mv_x.dn(v_x)\frac{1}{1}.$$

The total pressure of all the molecules on the walls of the container is

$$P = \int dP(v_x) = \int_0^\infty 2mv_x.dn(v_x)$$

Since the velocities change from zero to infinity we have to integrate within these limits. After substitution into the previous integral we have

$$P = \int_0^\infty 2mv_x . N_0 \, v_x \, \frac{1}{w\sqrt{\pi}} \, e^{-\frac{v_x^2}{w^2}} dv_x$$

After a little rearrangement we have

$$P = 2mN_0 \frac{1}{w\sqrt{\pi}} \int_0^\infty v_x^2 e^{-\frac{v_x^2}{w^2}} dv_x$$

To solve the integral $I = \int_0^\infty v_x^2 e^{-\frac{v_x^2}{w^2}} dv_x$ we can use the formula from part c of problem 2-17. In this case we therefore have $n=1$ and $\alpha = \frac{1}{w^2}$.

Thus we have

$$I = \int_0^\infty v_x^2 e^{-\frac{v_x^2}{w^2}} dv_x = \frac{1}{2} \cdot \frac{1}{2} \sqrt{\frac{\pi}{\alpha^3}} = \frac{1}{4} \sqrt{\frac{\pi}{\left(\frac{1}{w^2}\right)^3}} = \frac{1}{4} w^3 \sqrt{\pi} .$$

Substituting onto the expression for pressure and bearing in mind the fact that $w = \sqrt{\frac{2kT}{m}}$ we obtain

$$P = 2m.N_0 \frac{1}{w\sqrt{\pi}} \frac{1}{4} w^3 \sqrt{\pi} = N_0 \, kT .$$

Thus we reach the final formula $\qquad P = N_0 \, kT$.

We see that the pressure of the gas on the wall of the container depends on the density of the gas and its temperature.

We can also rewrite this equation for one mole of gas. In this case we have

$$N_0 = \frac{N_A}{V_m}$$

where $N_A$ is the Avogadro's number and $V_m$ is the volume of one mole. Substituting into the expression for pressure we obtain

$$P.V_m = N_A . k.T$$

.Taking into account that $N_A . k = R$ we finally obtain the ideal gas law for one mole of gas

$$P.V_m = R.T .$$

**Problem 2-21.** Calculate the partial pressures of nitrogen and oxygen in dry air, assuming that the ratio of the amount of substance of nitrogen $n_1$ to the amount of substance of oxygen $n_2$ in dry air is

$$\frac{n_1}{n_2} = \frac{78.1}{21} .$$

Solution: According Dalton's law the pressure of a mixture of two or more ideal gases is equal to the sum of the pressures which they would exert if each occupied the same volume. In our case the total pressure of air will be the sum of pressures of nitrogen $P_1$ and oxygen $P_2$ or

$$P = P_1 + P_2. \tag{1}$$

Each of the components of the mixture will have such a pressure as if it occupied the whole volume $V$ alone. Thus we can write the ideal gas law for each of the components of the mixture

$$P_1 V = \frac{m_1}{M_1} RT \qquad \text{and} \qquad P_2 V = \frac{m_2}{M_2} RT . \tag{2}$$

Summing these two equations we obtain

$$PV = \left( \frac{m_1}{M_1} + \frac{m_2}{M_2} \right) RT . \tag{3}$$

From equations 2 and 3 we determine pressure of each component of the mixture, assuming that the mass and molar mass is known:

$$P_1 = \frac{\dfrac{m_1}{M_1}}{\dfrac{m_1}{M_1} + \dfrac{m_2}{M_2}} P \qquad \text{and} \qquad P_2 = \frac{\dfrac{m_2}{M_2}}{\dfrac{m_1}{M_1} + \dfrac{m_2}{M_2}} P .$$

We denote the amount of substance of nitrogen and oxygen as

$$n_1 = \frac{m_1}{M_1} \qquad \text{(for nitrogen)}$$

$$n_2 = \frac{m_2}{M_2} \qquad \text{(for oxygen)}$$

We can therefore rewrite the ideal gas law as

$$PV = (n_1 + n_2) RT .$$

For the partial pressures of nitrogen and oxygen we obtain

$$P_1 = \frac{n_1}{n_1 + n_2} P \qquad \text{and} \qquad P_2 = \frac{n_2}{n_1 + n_2} P .$$

Substituting numerical values we have for partial pressure of nitrogen

$$P_1 = \frac{n_1}{n_1 + n_2} P = \frac{\dfrac{n_1}{n_2}}{\dfrac{n_1}{n_2} + 1} P = \frac{78.1}{78.1 + 21} P = 0.78 P .$$

Similarly, for partial pressure of oxygen we have

$$P_2 = \frac{21}{78.1 + 21} = 0.21 P .$$

Finally for the atmospheric pressure $P=101kPa$ the partial pressure of nitrogen in the air is *79 kPa* and the partial pressure of oxygen is *21 kPa.*

**Problem 2-22.** Calculate the collision frequency of a neon molecule at temperature $t=327\,°C$ and pressure $P=133\,Pa$. The diameter $d$ of the neon molecule is $2.04 \times 10^{-10}\,m$ and its molar weight is $M_{Ne} = 20.2\,kg.kmol^{-1}$.

Solution: The collision frequency of the molecule moving among molecules of the same sort is given by the expression

$$Z_m = \sqrt{2}\, N_0\, \pi\, d^2\, \overline{v}$$

The expression for the average speed of the molecule was found in part (a) of problem 2-17:

$$\overline{v} = \sqrt{\frac{8kT}{\pi m}}$$

We can express the density of neon for a given temperature and pressure on the basis of the results obtained in problem 2-20 as

$$N_0 = \frac{P}{kT}.$$

Substituting for average speed and density of neon into the expression for the collision frequency we have

$$Z_m = Pd^2 \sqrt{\frac{16\pi}{mkT}}.$$

The mass of the neon molecule can be found from

$$m = \frac{M_{Ne}}{N_A}.$$

Finally, for the given temperature and pressure, for the collision frequency we obtain

$$Z_m = Pd^2 \sqrt{\frac{16\pi\, N_A}{M_{Ne}\, kT}} = 133 \times \left(2.04 \times 10^{-10}\right)^2 \sqrt{\frac{16\pi \times 6.02 \times 10^{26}}{20.2 \times 1.38 \times 10^{-23} \times 600}} =$$

$$= 2.35 \times 10^6\ s^{-1}.$$

**Problem 2-23.** Calculate for molecules of oxygen, nitrogen and for a helium atom:
   (a) the average speed $\overline{v}$,
   (b) the mean free path $\lambda$ for pressures $0.133\,Pa;\ 133\,Pa$ and $101\,kPa$;
   (c) the collision frequency $Z_m$ for pressures $0.133\,Pa;\ 133\,Pa$ and $101\,kPa$.
The temperature is $0\,°C$.
The diameters and molar masses of the molecules are respectively:
$d_{O_2} = 2.96 \times 10^{-10}\,m$      $d_{N_2} = 3.16 \times 10^{-10}\,m$      $d_{He} = 2.2 \times 10^{-10}\,m$
$M_{O_2} = 32\,kg.kmol^{-1}$      $M_{N_2} = 28\,kg.kmol^{-1}$      $M_{He} = 4\,kg.kmol^{-1}$.

Solution:
(a) The average speed is given by the expression

$$\overline{v} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8kTN_A}{\pi M}} = \sqrt{\frac{8RT}{\pi M}}$$

Substituting numerical values we have

$$\bar{v}_{O_2} = \sqrt{\frac{8 \times 8.314 \times 10^3 \times 273.15}{32\,\pi}} = 425.1\,m.s^{-1}$$

$$\bar{v}_{N_2} = 454.3\,m.s^{-1}$$

$$\bar{v}_{He} = 1201.8\,m.s^{-1}$$

Note that the speeds of the particles do not depend on the pressure but on the temperature and on the sort of particles only.

(b) The mean free path $\lambda$ is given by the expression:

$$\lambda = \frac{\bar{v}}{Z_m} = \frac{\bar{v}}{\sqrt{2}\,N_0\,\pi\,d^2\,\bar{v}} = \frac{1}{\sqrt{2}\,N_0\,\pi\,d^2}$$

where $N_0 = \dfrac{N_A}{V_m}$ is the density of the particles. Using the ideal gas law for one mole of gas $P.V_m = R.T$ and bearing in mind the fact that $kN_A = R$ we can express density as

$$N_0 = \frac{N_A}{V_m} = \frac{N_A}{V_m}\frac{P}{P} = \frac{N_A P}{RT} = \frac{P}{kT}$$

Substituting into the expression for the mean free path we obtain

$$\lambda = \frac{1}{\sqrt{2}\,\pi\,d^2}\frac{kT}{P}$$

From this expression we see that the mean free path is inversely proportional to the pressure. As an example we calculate the mean free path of helium for pressure $0.133\,Pa$:

$$\lambda_{He} = \frac{1}{\sqrt{2}\pi\left(2.2 \times 10^{-10}\right)^2}\frac{1.38 \times 10^{-23} \times 273.15}{0.133} = 13.1 \times 10^{-2}\,m$$

The numerical values of the mean free path (expressed in meters) for different gases and pressures are arranged in the following table:

| Gas | 0.133 Pa | 133 Pa | 101 kPa |
|---|---|---|---|
| oxygen | $7.26 \times 10^{-2}$ | $7.26 \times 10^{-5}$ | $9.56 \times 10^{-8}$ |
| nitrogen | $6.37 \times 10^{-2}$ | $6.37 \times 10^{-5}$ | $8.38 \times 10^{-8}$ |
| helium | $13.1 \times 10^{-2}$ | $13.1 \times 10^{-5}$ | $17.3 \times 10^{-8}$ |

(c) For collision frequency of particles we have already obtained (see problem 2-22):

$$Z_m = Pd^2\sqrt{\frac{16\pi\,N_A}{M_{Ne}\,kT}}.$$

As a numerical example we calculate the collision frequency for a molecule of oxygen for pressure $P = 0.133\,Pa$:

$$Z_m = 0.133\left(2.96 \times 10^{-10}\right)^2 \sqrt{\frac{16\pi 6.02 \times 10^{26}}{32 \times 1.38 \times 10^{-23} \times 273.15}} = 5.8 \times 10^3 \ s^{-1}.$$

The numerical values of the collision frequency (in $s^{-1}$) for different gases and pressures are shown in the following table:

| Gas | 0.133 Pa | 133 Pa | 101 kPa |
|---|---|---|---|
| oxygen | $5.8 \times 10^3$ | $5.8 \times 10^6$ | $4.45 \times 10^9$ |
| nitrogen | $7.13 \times 10^3$ | $7.13 \times 10^6$ | $5.42 \times 10^9$ |
| helium | $9.17 \times 10^3$ | $9.17 \times 10^6$ | $6.95 \times 10^9$ |

From the obtained results it is seen that collision frequencies are very high, even for low pressures.

**Problem 2-24.** What is the translational kinetic energy of monatomic molecules in a gas:
  (a) at temperature $t=27\,°C$?
  (b) at the temperature inside the Sun, supposing that this temperature is
    $2 \times 10^7\ K$? (This part of the problem has only an illustrative value).
Does this energy depend on the chemical composition of the molecule?

Solution:
(a) Following equipartition of the energy theorem each degree of freedom shares an equal amount of energy $\frac{1}{2}kT$. Since the monatomic molecule has three degrees of freedom its

translational kinetic energy is $\frac{3}{2}kT$ or

$$W_k = \frac{3}{2}1.38 \times 10^{-23}(27+273.15) = 6.21 \times 10^{-21}\,J$$

(b) The kinetic energy of atoms inside the Sun is

$$W_k = \frac{3}{2}1.38 \times 10^{-23} \times 2 \times 10^7 = 4.15 \times 10^{16}\,J.$$

From the presented expressions it is obvious that kinetic energy does not depend on the chemical composition of the molecules. That is to say that at the same temperature monatomic molecules of different gases will have the same kinetic energy.

**Problem 2-25.** Calculate the angular velocity of a rotating hydrogen molecule at temperature *300 K*. The moment of inertia of a hydrogen molecule is about $5 \times 10^{-47}\,kg.m^2$.

Solution: A hydrogen molecule is a typical example of a diatomic molecule. At ordinary temperatures a diatomic molecule can be viewed as a rigid body, replaced by a rigid rod - a dumbbell molecule. The moment of inertia along the axis of the rod is negligible compared to its moments of inertia about axes normal to the rod. Hence we assign energies only to the rotational degrees of freedom about the two axes perpendicular to the rod and to each other. Since the molecule undergoes translational
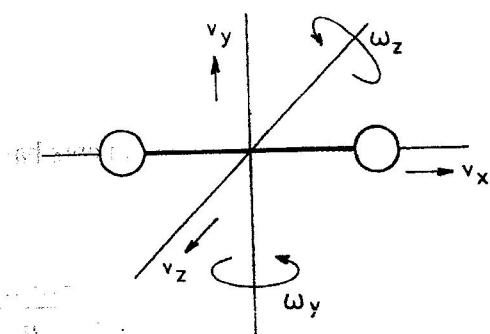
motion only and it has only two degrees of freedom, then following equipartition of the energy theorem, its rotational kinetic energy is $\frac{2}{2}kT$.

However the kinetic energy of rotational motion can be also expressed as $\frac{1}{2}J\omega^2$.

From a comparison of these two expressions we obtain for angular frequency:

$$\omega = \sqrt{\frac{2kT}{J}} = \sqrt{\frac{2 \times 1.38 \times 10^{-23} \times 300}{5 \times 10^{-47}}} = 1.3 \times 10^{13} \, s^{-1}.$$

**Problem 2-26.** Following the principles of kinetic theory calculate the specific heat at constant volume $c_v$ for (a) argon and (b) nitrogen. ($M_{Ar} = 40 \, kg.kmol^{-1}$ ; $M_{N_2} = 28 \, kg.kmol^{-1}$).

Solution: Each gas is composed of molecules of the same sort. If each of the molecules has $i$-degrees of freedom, the kinetic energy of the molecule is $\frac{i}{2}kT$.

The total internal energy of one mole of gas is therefore

$$U_k = N_A \frac{i}{2}kT$$

where $N_A$ is the Avogadro number. Any arbitrary amount of gas contains $n$ moles of molecules. This amount of substance is $n = \frac{m}{M}$. Thus the total internal energy of this amount of gas is

$$U_k = \frac{m}{M}N_A \frac{i}{2}kT = \frac{m}{M}\frac{i}{2}RT.$$

When a gas is heated at constant volume all the heat added is used to increase its internal energy and the temperature of the gas increases by $\Delta T$. Thus we have

$$(Q)_V = \Delta U = \frac{m}{M}\frac{i}{2}R(T + \Delta T) - \frac{m}{M}\frac{i}{2}RT = \frac{m}{M}\frac{i}{2}R\Delta T.$$

Specific heat is defined as $\qquad c_V = \frac{(Q)_V}{m\Delta T}$

so that after substitution we obtain $\qquad c_V = \frac{i}{2}\frac{R}{M}.$

(a) Since argon is a monatomic gas it has three degrees of freedom; $i=3$. Thus we have

$$c_V = \frac{3}{2}\frac{R}{M_{Ar}} = \frac{3}{2}\frac{8314}{40} = 311 J.kg^{-1}.K^{-1}.$$

(b) Since nitrogen is a diatomic gas $i=5$. Thus we have

$$c_V = \frac{5}{2}\frac{R}{M_{N_2}} = \frac{5}{2}\frac{8314}{28} = 742\,J.kg^{-1}.K^{-1}.$$

**Problem 2-27.** Calculate the molar weight of a mixture of gases with components having masses $m_1, m_2 ... m_k$ and molar weights $M_1, M_2 ... M_k$.

$$\left[ M = \frac{m}{n} = \frac{n_1 M_1 + n_2 M_2 + ... + n_k M_k}{n_1 + n_2 + ... + n_k} \right]$$

**Problem 2-28.** Calculate the molar weight of dry air, assuming that the ratio of the amount of substance of nitrogen $n_1$ to the amount of substance of oxygen $n_2$ is $\frac{n_1}{n_2} = \frac{78.1}{21}$.

$(M_{O_2} = 32kg.kmol^{-1}; M_{N_2} = 28\,kg.kmol^{-1})$.

$$\left[ M = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2} = 28.8kg.kmol^{-1} \right]$$

**Problem 2-29.** Calculate the density of the molecules of an ideal gas if the pressure acting on the walls of the container at temperature $t=27\,°C$ is $P=0,1\,Pa$.

$$\left[ N_0 = \frac{P.N_A}{R.T} = 2.4\times10^{19}\,m^{-3} \right]$$

**Problem 2-30.** The speed of sound in air at temperature $t=27\,°C$ is $348\,m/s$. Compare this speed with the root-mean-square speed of nitrogen molecules at the same temperature. $(M_{N_2} = 28\,kg.kmol^{-1})$.

$$\left[ \frac{v_{rms}}{v_s} = 1.485 \right]$$

**Problem 2-31.** Calculate the pressure for which the mean free path of a hydrogen molecule at temperature $68\,°C$ is equal to $\lambda=2\,cm$. The diameter of a hydrogen molecule is $d = 2.3\times10^{-10}\,m$.

$$\left[ P = \frac{kT}{\pi\lambda d^2\sqrt{2}} = 1Pa \right]$$

**Problem 2-32.** Compute the change in average kinetic energy of argon molecules if at constant volume the gas is added the amount of heat $Q_V = 3516\,J$. The mass of argon is $m=200\,g$ and $M_{Ar} = 40\,kg.kmol^{-1}$.

$$\left[ \Delta U = \frac{M_{Ar}Q_V}{mN_A} = 116.8\times10^{-23}\,J \right]$$