Thus, we have

$$\left(\frac{M}{2\pi RT}\right)^{3/2} = \left\{\frac{(0.028\ \text{kg mol}^{-1})}{2\times 3.14\times(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(300\ \text{K})}\right\}^{3/2}$$

$$= 2.390\times 10^{-9}\ \text{kg}^{3/2}\ \text{J}^{-3/2} = 2.390\times 10^{-9}\ \text{m}^{-3}\ \text{s}^{3}$$

$$\exp\left(-\frac{Mu^2}{2RT}\right) = \exp\left\{-\frac{(0.028\ \text{kg mol}^{-1})(422.09\ \text{m s}^{-1})^2}{2(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(300\ \text{K})}\right\}$$

$$= \exp(-1.000) = 0.367\,9$$

Hence $$\frac{dN}{N} = 4\times 3.14\times(2.390\times 10^{-9}\ \text{m}^{-3}\ \text{s}^{3})(422.09\ \text{m s}^{-1})^2(0.367\,9)(4.22\ \text{m s}^{-1})$$

$$= 8.303\times 10^{-3}$$

Example 1.16.2 What is the ratio of the number of molecules having speeds in the range of $2u_{mp}$ and $2u_{mp} + du$ to the number of molecules having speeds in the range of u_{mp} and $u_{mp} + du$?

Solution If dN_1 is the number of molecules in the speed range u_{mp} to $u_{mp} + du$ and dN_2 is the corresponding number in the speed range $2u_{mp}$ to $2u_{mp} + du$, then according to the Maxwell distribution, we have

$$\frac{dN_1}{N} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} u_{mp}^2 \exp(-Mu_{mp}^2/2RT)\,du$$

and $$\frac{dN_2}{N} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} (2u_{mp})^2 \exp(-4Mu_{mp}^2/2RT)\,du$$

Therefore $$\frac{dN_2}{dN_1} = 4\frac{\exp(-4Mu_{mp}^2/2RT)}{\exp(-Mu_{mp}^2/2RT)} = 4\exp(-3Mu_{mp}^2/2RT)$$

Now, since $u_{mp}^2 = \dfrac{2RT}{M}$, therefore $\dfrac{dN_2}{dN_1} = 4\,e^{-3} = 0.199$

1.17 DERIVATION OF SOME EXPRESSIONS FROM THE MAXWELL DISTRIBUTION

Maxwell distribution expression (Eq. 1.16.1) can be used to derive expressions for average speed, root mean square speed, average kinetic energy and the fraction of molecules possessing kinetic energies greater than some specified energy.

Average Speed

The average value of speeds is given by the relation

$$\bar{u} = \frac{u_1 + u_2 + \cdots + u_N}{N} = \frac{1}{N}\sum_i u_i \tag{1.17.1}$$

Equation (1.17.1) can be written in the form

$$\bar{u} = \frac{1}{N}\int_0^\infty u\,dN_u = \int_0^\infty u\frac{dN_u}{N} \tag{1.17.2}$$

where dN_u is the number of molecules having speed u. The summation of different speeds is replaced by integration since all types of speed ranging from zero to infinity are involved.

Substituting dN_u/N from Eq. (1.16.1) in Eq. (1.17.2), we get

$$\bar{u} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_0^\infty u^3 \exp(-Mu^2/2RT)\,du$$

which on integration yields

$$\bar{u} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\left\{2\left(\frac{RT}{M}\right)^2\right\} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8kT}{\pi m}} \tag{1.17.3}$$

Root Mean Square Speed

The mean square speed is given by

$$\overline{u^2} = \frac{u_1^2 + u_2^2 + \cdots + u_N^2}{N} = \frac{1}{N}\sum_i u_i^2 = \frac{1}{N}\int_0^\infty u^2\,dN_u \tag{1.17.4}$$

Using Eq. (1.16.1), we get

$$\overline{u^2} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_0^\infty u^4 \exp(-Mu^2/2RT)\,du$$

which on integration yields

$$\overline{u^2} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\left\{\left(\frac{RT}{M}\right)^{5/2}\frac{3}{\sqrt{2}}\sqrt{\pi}\right\} = 3\frac{RT}{M}$$

Thus,
$$u_{rms} = \sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3kT}{m}} \tag{1.17.5}$$

Example 1.17.1

Arrange root mean square, most probable and average speeds in the order of decreasing value. Discuss the effects of temperature and pressure on these speeds.

Solution

From Eqs (1.16.4), (1.17.3) and (1.17.5), we find that

$$u_{mp} = \sqrt{\frac{2RT}{M}};\quad \bar{u} = \sqrt{\frac{8RT}{\pi M}};\quad \sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{M}}$$

Therefore

$$\frac{\sqrt{\overline{u^2}}}{\bar{u}} = \frac{\sqrt{3RT/M}}{\sqrt{8RT/\pi M}} = \sqrt{\frac{3\pi}{8}} = \sqrt{\frac{3}{8/\pi}} = \frac{1.732}{1.596}$$

$$\frac{\sqrt{\overline{u^2}}}{u_{mp}} = \frac{\sqrt{3RT/M}}{\sqrt{2RT/M}} = \sqrt{\frac{3}{2}} = \frac{1.732}{1.414}$$

Hence $\sqrt{\overline{u^2}} : \bar{u} : u_{mp} :: 1.732 : 1.596 : 1.414$

From this, it follows that

$$\sqrt{\overline{u^2}} > \bar{u} > u_{mp}$$

It may be concluded that all the three speeds are directly proportional to the square root of absolute temperature and are independent of pressure of gas.

Example 1.17.2 For O_2 gas molecules, the root means square speed at T_1, the average speed at T_2 and most probable speed at T_3 are all equal to 1.5×10^3 m s^{-1}. Calculate T_1, T_2 and T_3.

Solution We can calculate T_1, T_2 and T_3 as follows.

$$\sqrt{\overline{u_1^2}} = \sqrt{\frac{3RT_1}{M}} = 1.5 \times 10^3 \text{ m s}^{-1}$$

which gives $T_1 = (1.5\times10^3 \text{ m s}^{-1})^2 \dfrac{M}{3R} = \dfrac{(1.5\times10^3 \text{ m s}^{-1})^2(0.032 \text{ kg mol}^{-1})}{3(8.314 \text{ J K}^{-1} \text{ mol}^{-1})}$

$= 2\,887$ K

$$u_{av} = \sqrt{\frac{8RT_2}{\pi M}} = 1.5\times10^3 \text{ m s}^{-1}$$

which gives $T_2 = (1.5\times10^3 \text{ m s}^{-1})^2\left(\dfrac{\pi M}{8R}\right) = \dfrac{(1.5\times10^3 \text{ m s}^{-1})^2(3.14\times0.032 \text{ kg mol}^{-1})}{8(8.314 \text{ J K}^{-1} \text{ mol}^{-1})}$

$= 3\,399$ K

$$u_{mp} = \sqrt{\frac{2RT_3}{M}} = 1.5\times10^3 \text{ m s}^{-1}$$

which gives $T_3 = \dfrac{(1.5\times10^3 \text{ m s}^{-1})^2(M)}{2R} = \dfrac{(1.5\times10^3 \text{ m s}^{-1})^2(0.032 \text{ kg mol}^{-1})}{2(8.314 \text{ J K}^{-1} \text{ mol}^{-1})}$

$= 4\,330$ K

Example 1.17.3 Calculate the temperature at which the average speed of H_2 equals that of O_2 at 320 K.

Solution We have $\bar{u}(O_2) = \sqrt{\dfrac{8RT}{\pi M}} = \left\{\dfrac{8R(320 \text{ K})}{\pi(0.032 \text{ kg mol}^{-1})}\right\}^{1/2}$

$$\bar{u}(H_2) = \sqrt{\frac{8RT}{\pi M}} = \left\{\frac{8RT}{\pi(0.002 \text{ kg mol}^{-1})}\right\}^{1/2}$$

Since $\bar{u}(O_2) = \bar{u}(H_2)$

therefore $\dfrac{8R(320 \text{ K})}{\pi(0.032 \text{ kg mol}^{-1})} = \dfrac{8RT}{\pi(0.002 \text{ kg mol}^{-1})}$

which gives $T = 20$ K

Example 1.17.4 Calculate the root mean square, average and most probable speeds of H_2 molecules. The density of the gas at 101.325 kPa is 0.09 g dm^{-3} ($\equiv$ 0.09 kg m^{-3}). Assume ideal behaviour.

Solution The three speeds can be calculated as follows:

$$\sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3pV_{\mathrm{m}}}{M}} = \sqrt{\frac{3p}{\rho}} = \left\{\frac{3(101.325 \times 10^3 \text{ Pa})}{(0.09 \text{ kg m}^{-3})}\right\}^{1/2} = 1838 \text{ m s}^{-1}$$

$$\bar{u} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8pV_{\mathrm{m}}}{\pi M}} = \sqrt{\frac{8p}{\pi\rho}} = \left\{\frac{8(101.325 \times 10^3 \text{ Pa})}{3.14(0.09 \text{ kg m}^{-3})}\right\}^{1/2} = 1694 \text{ m s}^{-1}$$

$$u_{\mathrm{mp}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2pV_{\mathrm{m}}}{M}} = \sqrt{\frac{2p}{\rho}} = \left\{\frac{2(101.325 \times 10^3 \text{ Pa})}{(0.09 \text{ kg m}^{-3})}\right\}^{1/2} = 1501 \text{ m s}^{-1}$$

Average Kinetic Energy

The average kinetic energy is given by

$$\bar{\varepsilon} = \frac{1}{N}\left(\frac{1}{2}m\,u_1^2 + \frac{1}{2}m\,u_2^2 + \cdots + \frac{1}{2}m\,u_N^2\right)$$

$$= \frac{1}{N}\frac{m}{2}\sum_i u_i^2 = \frac{1}{N}\frac{m}{2}\int_0^\infty u^2 \, \mathrm{d}N_u$$

Substituting $\mathrm{d}N_u/N$ from Eq. (1.16.1) and intergrating the resultant expression, we have

$$\bar{\varepsilon} = \frac{1}{2}m\left(\frac{3kT}{m}\right) = \frac{3}{2}kT \qquad (1.17.6)$$

Expression of Energy Distribution

The Maxwell distribution of speeds (Eq. 1.16.1) can be converted into energy distribution by substituting

$$\varepsilon = \frac{1}{2}mu^2$$

which gives

$$u = \left(\frac{2}{m}\right)^{1/2} \varepsilon^{1/2}$$

Differentiating, we have

$$\mathrm{d}u = \left(\frac{1}{2m}\right)^{1/2} \varepsilon^{-1/2} \, \mathrm{d}\varepsilon$$

The energy range $d\varepsilon$ corresponds to the speed range du, and so the number of particles dN_u having speeds between u and $u + du$ corresponds to the number of particles dN_ε having energies between ε and $\varepsilon + d\varepsilon$. Replacing u and du in Eq. (1.16.1) in terms of ε and $d\varepsilon$, we have

$$dN_\varepsilon = 2\pi N\left(\frac{1}{\pi kT}\right)^{3/2} \varepsilon^{1/2} \exp(-\varepsilon/kT)\, d\varepsilon \tag{1.17.7}$$

Figure 1.17.1 shows the plot of $(1/N)\,(dN_\varepsilon/d\varepsilon)$ versus ε. Shape of this curve is different from that of the speed distribution curve. The energy distribution has a vertical tangent at the origin and thus it rises much more rapidly than the speed distribution curve which starts with a horizontal tangent. After passing the maximum, the energy distribution falls off more gently than does the speed distribution. As usual, the distribution is broadened at higher temperatures. Thus, a greater proportion of the molecules possess higher energies.

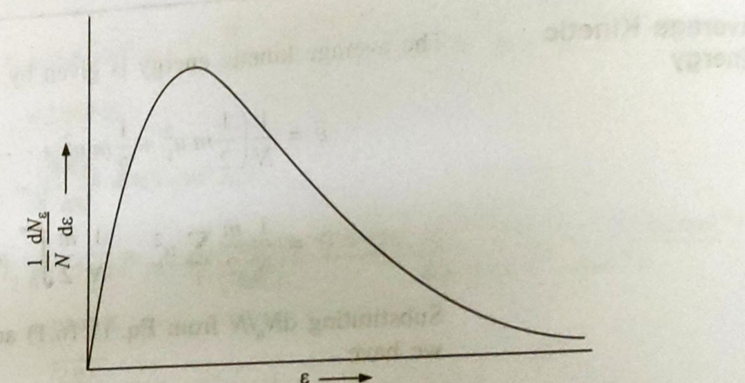

Fig. 1.17.1 Plot of $(1/N)\,(dN_\varepsilon/d\varepsilon)$ versus ε

Fraction of Molecules Possessing Kinetic Energies Greater than some Specified Energy

The fraction of molecules having energies greater than ε' is given by

$$\frac{N(\varepsilon')}{N} = \int_{\varepsilon'}^{\infty} \frac{dN_\varepsilon}{N} \tag{1.17.8}$$

Substituting dN_ε/N from Eq. (1.17.7) in the above expression, we have

$$\frac{N(\varepsilon')}{N} = 2\pi\left(\frac{1}{\pi kT}\right)^{3/2} \int_{\varepsilon'}^{\infty} \varepsilon^{1/2} \exp(-\varepsilon/kT)\, d\varepsilon$$

which on integration yields

$$\frac{N(\varepsilon')}{N} = 2\left(\frac{\varepsilon'}{\pi kT}\right)^{3/2} \exp(-\varepsilon'/kT), \qquad (\varepsilon' >> kT) \tag{1.17.9}$$

Equation (1.17.9) describes how the fraction of molecules having kinetic energies greater than ε' varies with temperature. Due to the exponential dependence, this fraction varies quite rapidly with temperature, particularly at low temperatures. This equation is often required in describing many concepts of physical chemistry. For example, in the study of effect of temperature on reaction rates, we require the fraction of molecules having energies equal to or greater than some minimum energy (known as threshold energy). It is known that only those molecules which have energies equal to or greater than the threshold energy can react chemically. Since this fraction increases with temperature, the rate of a chemical reaction also increases with temperature.

Example 1.17.5 Calculate the fraction of N_2 molecules at 101.325 kPa and 300 K whose kinetic energies are in the range of $\bar{\varepsilon} - 0.005\,\bar{\varepsilon}$ and $\bar{\varepsilon} + 0.005\,\bar{\varepsilon}$.

Solution The average kinetic energy at 300 K is

$$\bar{\varepsilon} = \frac{3}{2}kT = \frac{3}{2}(1.380\,6 \times 10^{-23}\ \mathrm{J\ K^{-1}})(300\ \mathrm{K}) = 6.213 \times 10^{-21}\ \mathrm{J}$$

Now $\quad \mathrm{d}\varepsilon = (\bar{\varepsilon} + 0.005\,\bar{\varepsilon}) - (\bar{\varepsilon} - 0.005\,\bar{\varepsilon}) = 0.01\,\bar{\varepsilon} = 6.213 \times 10^{-23}\ \mathrm{J}$

Equation for energy distribution is

$$\frac{\mathrm{d}N_\varepsilon}{N} = 2\pi\left(\frac{1}{\pi kT}\right)^{3/2} \varepsilon^{1/2} \exp(-\varepsilon/kT)\,\mathrm{d}\varepsilon$$

Therefore, we have

$$\left(\frac{1}{\pi kT}\right)^{3/2} = \left(\frac{1}{3.14 \times (1.380\,6 \times 10^{-23}\ \mathrm{J\ K^{-1}})(300\ \mathrm{K})}\right)^{3/2}$$

$$= 6.742 \times 10^{29}\ \mathrm{J^{-3/2}}$$

$$\exp(-\varepsilon/kT) = \exp\left(-\frac{6.213 \times 10^{-21}\ \mathrm{J}}{(1.380\,6 \times 10^{-23}\ \mathrm{J\ K^{-1}})(300\ \mathrm{K})}\right) = 0.223$$

Thus $\quad \frac{\mathrm{d}N_\varepsilon}{N} = 2 \times 3.14 \times (6.742 \times 10^{29}\ \mathrm{J^{-3/2}})(6.213 \times 10^{-21}\mathrm{J})^{1/2}$

$$\times (0.223)(6.213 \times 10^{-23}\ \mathrm{J}) = 4.624 \times 10^{-3}$$

Example 1.17.6 Calculate the number of molecules in one mole of an ideal gas that have energies greater than four times the average thermal energy at 25 °C and 50 °C.

Solution The average thermal energy $\bar{\varepsilon}$ is given as

$$\bar{\varepsilon} = \frac{3}{2}kT$$

The expression which gives the fraction of molecules having energies greater than ε is given as

$$\frac{N(\varepsilon)}{N_A} = 2\left(\frac{\varepsilon}{\pi kT}\right)^{1/2} \exp(-\varepsilon/kT)$$

Now, $\quad \varepsilon = 4\bar{\varepsilon} = 4\left(\frac{3}{2}kT\right) = 6\,kT$

Substituting this in the above expression, we have