Solutions to extra problems 1, 2, 4, 6

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Problem 1: computing average speeds, rms speeds, and most probable speeds of atoms in a gas

> A gas consists of a mixture of hydrogen molecules and helium atoms. Compute their average speeds, their rms speeds and their most probable speeds, for temperature T = 300K.

Solution

A gas consists of hydrogen molecules H_2 and helium atoms He at temperature

$$T = 300\,\mathrm{K}.$$

For a gas particle of molar mass M, the Maxwell–Boltzmann speeds are

$$v_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}}, \qquad v_{\text{rms}} = \sqrt{\frac{3RT}{M}}, \qquad v_{\text{mp}} = \sqrt{\frac{2RT}{M}},$$

where

$$R = 8.314\,\mathrm{J/(mol \cdot K)}.$$

Hydrogen molecules

For hydrogen

$$M_{\mathrm{H_2}} = 2.0\,\mathrm{g/mol} = 2.0 \times 10^{-3}\,\mathrm{kg/mol}.$$

$$v_{\text{avg}}(\mathrm{H_2}) = \sqrt{\frac{8(8.314)(300)}{\pi(2.0 \times 10^{-3})}}.$$

$$v_{\text{avg}}(\mathrm{H_2}) \approx 1.78 \times 10^3\,\mathrm{m/s}.$$

rms speed

$$v_{\text{rms}}(\mathrm{H_2}) = \sqrt{\frac{3(8.314)(300)}{2.0 \times 10^{-3}}}.$$

$$v_{\text{rms}}(\mathrm{H_2}) \approx 1.94 \times 10^3\,\mathrm{m/s}.$$

The most probable speed is

$$v_{\text{mp}}(\text{H}_2) = \sqrt{\frac{2(8.314)(300)}{2.0 \times 10^{-3}}}.$$

$$v_{\text{mp}}(\text{H}_2) \approx 1.58 \times 10^3\,\text{m/s}.$$

Helium atoms

Now the same calculations for helium atoms,

$$M_{\text{He}} = 4.0\,\text{g/mol} = 4.0 \times 10^{-3}\,\text{kg/mol}.$$

average speed

$$v_{\text{avg}}(\text{He}) = \sqrt{\frac{8(8.314)(300)}{\pi(4.0 \times 10^{-3})}}.$$

$$v_{\text{avg}}(\text{He}) \approx 1.26 \times 10^3\,\text{m/s}.$$

rms speed

$$v_{\text{rms}}(\text{He}) = \sqrt{\frac{3(8.314)(300)}{4.0 \times 10^{-3}}}.$$

$$v_{\text{rms}}(\text{He}) \approx 1.37 \times 10^3\,\text{m/s}.$$

most probable speed

$$v_{\text{mp}}(\text{He}) = \sqrt{\frac{2(8.314)(300)}{4.0 \times 10^{-3}}}.$$

$$v_{\text{mp}}(\text{He}) \approx 1.12 \times 10^3\,\text{m/s}.$$

Answer

$$\boxed{v_{\text{avg}}(\text{H}_2) \approx 1.78 \times 10^3\,\text{m/s}}$$

$$\boxed{v_{\text{rms}}(\text{H}_2) \approx 1.94 \times 10^3\,\text{m/s}}$$

$$\boxed{v_{\text{mp}}(\text{H}_2) \approx 1.58 \times 10^3\,\text{m/s}}$$

and

$$\boxed{v_{\text{avg}}(\text{He}) \approx 1.26 \times 10^3\,\text{m/s}}$$

$$\boxed{v_{\text{rms}}(\text{He}) \approx 1.37 \times 10^3\,\text{m/s}}$$

$$\boxed{v_{\text{mp}}(\text{He}) \approx 1.12 \times 10^3\,\text{m/s}.}$$

we can see that hydrogen has a smaller molar mass than helium, its characteristic molecular speeds are greater.

1 Problem 2

Derive the formula for the most probable speed of a molecule in a gas.

Solution:

To find the most probable speed, we must refer to the Maxwell-Boltzmann speed distribution directly. An important part of this derivation is to really think about the distribution and internalize its meaning. Loosely speaking, a distribution is something that "distributes" the values of a certain variable according to its probability. Near the vicinity of each speed v of a randomly chosen particle in a gas $f(v)$ tells us how probable v is. Now, if we want the most probable speed we are asking which v gives us the greatest probability i.e. maximum $f(v)$.

The Maxwell–Boltzmann speed distribution (for self consistency) is

$$f(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-mv^2/(2k_B T)}.$$

The most probable speed is the value of v where $f(v)$ is maximized. Since the constant factor does not affect the maximum, we can equally maximize

$$g(v) = v^2 e^{-mv^2/(2k_B T)}.$$

$$\frac{dg}{dv} = 2ve^{-mv^2/(2k_B T)} + v^2 e^{-mv^2/(2k_B T)} \left(-\frac{mv}{k_B T}\right).$$

$$\frac{dg}{dv} = e^{-mv^2/(2k_B T)} \left[2v - \frac{mv^3}{k_B T}\right].$$

$$e^{-mv^2/(2k_B T)} \left[2v - \frac{mv^3}{k_B T}\right] = 0.$$

Since the exponential is nonnegative

$$e^{-mv^2/(2k_B T)} \neq 0,$$

to maximize we need

$$2v - \frac{mv^3}{k_B T} = 0.$$

$$v\left(2 - \frac{mv^2}{k_B T}\right) = 0.$$

The solution $v = 0$ is not the maximum of the speed distribution, so

$$2 - \frac{mv^2}{k_B T} = 0.$$

$$\frac{mv^2}{k_B T} = 2,$$

$$v^2 = \frac{2k_B T}{m}.$$

$$\boxed{v_{\mathrm{mp}} = \sqrt{\frac{2k_B T}{m}}}$$

Using the molar mass M, this may also be written as

$$\boxed{v_{\mathrm{mp}} = \sqrt{\frac{2RT}{M}}}$$

where M carries units kg/mol.

2 Problem 4

At what temperature is the average speed of a nitrogen molecule $M = 28\,\text{g/mol}$ equal to $600\,\text{m/s}$?

Solution:
The average speed of a molecule in an ideal gas is

$$v_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}}.$$

Given the values

$$v_{\text{avg}} = 600\,\text{m/s}, \qquad M = 28\,\text{g/mol}.$$

In SI units:

$$M = 28\,\text{g/mol} = 0.028\,\text{kg/mol}.$$

Now the goal is to solve for T:

$$v_{\text{avg}}^2 = \frac{8RT}{\pi M}.$$

$$T = \frac{\pi M v_{\text{avg}}^2}{8R}.$$

using our previous values:

$$T = \frac{\pi(0.028)(600)^2}{8(8.314)}.$$

$$T = \frac{\pi(0.028)(360000)}{66.512}.$$

$$T \approx 476\,\text{K}.$$

Average speed derivation

To derive the average speed we can start with the Maxwell-Boltzmann distribution:

$$f(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-mv^2/(2k_B T)}.$$

Here $f(v)\,dv$ is the probability that a molecule has speed between v and $v+dv$. Again, here the interpretation is that $f(v)dv$ is the probability of finding particles with speeds in a range between v and $v+dv$. The average speed is defined by

$$\langle v \rangle = \int_0^\infty v f(v)\,dv.$$

Substituting the Maxwell-Boltzmann distribution gives

$$\langle v \rangle = \int_0^\infty v \left[4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/(2k_B T)} \right] dv.$$

$$\langle v \rangle = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_0^\infty v^3 e^{-mv^2/(2k_B T)} \, dv.$$

Let

$$a = \frac{m}{2k_B T}.$$

Then the integral takes on this form:

$$\int_0^\infty v^3 e^{-av^2} \, dv.$$

using the standard integral result:

$$\int_0^\infty x^{2n+1} e^{-ax^2} \, dx = \frac{n!}{2a^{n+1}}, \qquad a > 0.$$

For $n = 1$, this gives

$$\int_0^\infty v^3 e^{-av^2} \, dv = \frac{1}{2a^2}.$$

resuing the formula for (a)

$$\frac{1}{2a^2} = \frac{1}{2} \left(\frac{2k_B T}{m} \right)^2 = \frac{2(k_B T)^2}{m^2}.$$

$$\langle v \rangle = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \frac{2(k_B T)^2}{m^2}.$$

$$\langle v \rangle = 8\pi \frac{m^{3/2}}{(2\pi k_B T)^{3/2}} \frac{(k_B T)^2}{m^2}.$$

Collecting powers of m and $k_B T$,

$$\langle v \rangle = 8\pi \frac{(k_B T)^{1/2}}{m^{1/2}} \frac{1}{(2\pi)^{3/2}}.$$

$$\frac{8\pi}{(2\pi)^{3/2}} = \sqrt{\frac{8}{\pi}},$$

$$\boxed{\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}}}.$$

Therefore, the average speed of particles in a Maxwell-Boltzmann gas is

$$\boxed{v_{\text{avg}} = \sqrt{\frac{8k_B T}{\pi m}}}$$

3 Problem 6

At what temperature do oxygen molecules have the same rms speed as helium atoms have at 300 K?

Solution:

The rms speed is

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

We want the rms speed of oxygen molecules to equal the rms speed of helium atoms at 300 K. In equations,

$$v_{\text{rms},\text{O}_2} = v_{\text{rms},\text{He}}.$$

Using the rms speed formula,

$$\sqrt{\frac{3RT_{\text{O}_2}}{M_{\text{O}_2}}} = \sqrt{\frac{3RT_{\text{He}}}{M_{\text{He}}}}.$$

$$\frac{3RT_{\text{O}_2}}{M_{\text{O}_2}} = \frac{3RT_{\text{He}}}{M_{\text{He}}}.$$

$$\frac{T_{\text{O}_2}}{M_{\text{O}_2}} = \frac{T_{\text{He}}}{M_{\text{He}}}.$$

$$T_{\text{O}_2} = T_{\text{He}}\frac{M_{\text{O}_2}}{M_{\text{He}}}.$$

Using the values:

$$T_{\text{He}} = 300\,\text{K}, \qquad M_{\text{He}} = 4\,\text{g/mol}, \qquad M_{\text{O}_2} = 32\,\text{g/mol}.$$

$$T_{\text{O}_2} = 300\left(\frac{32}{4}\right).$$

$$T_{\text{O}_2} = 300(8).$$

Therefore,

$$\boxed{T_{\text{O}_2} = 2400\,\text{K}.}$$

Derivation of RMS

To derive the rms speeds we can use:

$$f(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/(2k_B T)}.$$

The root-mean-square speed is defined by

$$v_{\text{rms}} = \sqrt{\langle v^2 \rangle}.$$

So first we must compute—which is a similar process to what we did previously in Question 4 except now we have a swuare root of the velocity v in the integral.

$$\langle v^2 \rangle = \int_0^\infty v^2 f(v)\, dv.$$

Substituting the Maxwell-Boltzmann distribution

$$\langle v^2 \rangle = \int_0^\infty v^2 \left[4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/(2k_B T)} \right] dv.$$

$$\langle v^2 \rangle = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_0^\infty v^4 e^{-mv^2/(2k_B T)}\, dv.$$

Letting again

$$a = \frac{m}{2k_B T}.$$

We can isolte the integral (just to see the main mathematical structure without the constants in front); using a we get

$$\int_0^\infty v^4 e^{-av^2}\, dv.$$

the standard Gaussian integral gives us

$$\int_0^\infty x^{2n} e^{-ax^2}\, dx = \frac{(2n-1)!!}{2^{n+1}} \frac{\sqrt{\pi}}{a^{n+1/2}}, \qquad a > 0.$$

For $n = 2$

$$\int_0^\infty v^4 e^{-av^2}\, dv = \frac{3\sqrt{\pi}}{8a^{5/2}}.$$

so the result is:

$$\langle v^2 \rangle = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \frac{3\sqrt{\pi}}{8a^{5/2}}.$$

The remaining parts are just using the proper constants.

$$a = \frac{m}{2k_B T},$$

so

$$a^{5/2} = \left(\frac{m}{2k_B T}\right)^{5/2}.$$

putting everything together:

$$\langle v^2 \rangle = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \frac{3\sqrt{\pi}}{8} \left(\frac{2k_B T}{m}\right)^{5/2}.$$

$$\langle v^2 \rangle = \frac{3}{2}\pi^{1/2} \left(\frac{m}{2\pi k_B T}\right)^{3/2} \left(\frac{2k_B T}{m}\right)^{5/2}.$$

$$\langle v^2 \rangle = \frac{3}{2}\sqrt{\pi} \frac{m^{3/2}}{(2\pi k_B T)^{3/2}} \frac{(2k_B T)^{5/2}}{m^{5/2}}.$$

$$\langle v^2 \rangle = \frac{3}{2}\sqrt{\pi} \frac{(2k_B T)}{m} \frac{1}{\pi^{3/2}}.$$

$$\frac{\sqrt{\pi}}{\pi^{3/2}} = \frac{1}{\pi},$$

$$v_{\rm rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_B T}{m}}.$$

Thus the root-mean-square speed of particles in a Maxwell-Boltzmann gas is

$$\boxed{v_{\rm rms} = \sqrt{\frac{3k_B T}{m}}}.$$