

## 6.17: Problems

- For an oxygen molecule at 25 C, calculate (a) the most probable velocity, (b) the average velocity, (c) the root-mean-square velocity.
- For a gas of oxygen molecules at 25 C and 1.00 bar, calculate (a) the collision frequency, (b) the mean time between collisions, (c) the mean free path. The diameter of an oxygen molecule, as estimated from gas-viscosity measurements, is  $3.55 \times 10^{-10}$  m.
- For oxygen molecules at 25 C, calculate (a) the fraction with speeds between 150 and 151  $\text{m s}^{-1}$ , (b) the fraction with speeds between 400 and 401  $\text{m s}^{-1}$ , (c) the fraction with speeds between 550 and 551  $\text{m s}^{-1}$ .
- For a hydrogen molecule at 100 C, calculate (a) the most probable velocity, (b) the average velocity, (c) the root-mean-square velocity.
- For a gas of hydrogen molecules at 100 C and 1.00 bar, calculate (a) the collision frequency, (b) the mean time between collisions, (c) the mean free path. The diameter of a hydrogen molecule, as estimated from gas-viscosity measurements, is  $2.71 \times 10^{-10}$  m.
- For a uranium hexafluoride ( $\text{UF}_6$ ) molecule at 100 C, calculate (a) the most probable velocity, (b) the average velocity, (c) the root-mean-square velocity.
- For a gas of uranium hexafluoride molecules at 100 C and 1.00 bar, calculate (a) the collision frequency, (b) the mean time between collisions, (c) the mean free path. Assume that the diameter of a uranium hexafluoride molecule is  $7.0 \times 10^{-10}$  m.
- What is the average kinetic energy of hydrogen molecules at 100 C? What is the average kinetic energy of uranium hexafluoride ( $\text{UF}_6$ ) molecules at 100 C?
- Assuming the temperature in interstellar space is 2.73 K, calculate, for a hydrogen atom, (a) the most probable velocity, (b) the average velocity, (c) the root-mean-square velocity.
- Assuming that interstellar space is occupied entirely by hydrogen atoms at a particle density of  $10^2$  molecules  $\text{m}^{-3}$ , calculate (a) the collision frequency, (b) the mean number of years between collisions, (c) the mean free path. Assume that the diameter of a hydrogen atom is  $2.40 \times 10^{-10}$  m.
- Ignoring any effects attributable to its charge and assuming that the temperature is 2.73 K, calculate, for an electron in interstellar space, (a) the most probable velocity, (b) the average velocity, (c) the root-mean-square velocity.
- If a wall of a gas-filled container contains a hole, gas molecules escape through the hole. If all of the molecules that hit the hole escape, but the hole is so small that the number escaping has no effect on the velocity distribution of the remaining gas molecules, we call the escaping process **effusion**. That is, we call the process effusion only if it satisfies three rather stringent criteria. First, the hole must be large enough (and the wall must be thin enough) so that most molecules passing through the hole do not hit the sides of the hole. Second, a molecule that passes through the hole must not collide with anything on the other side that can send it back through the hole into the original container. Third, the hole must be small enough so that the escaping molecules do not create a pressure gradient; the rate at which gas molecules hit the hole and escape must be determined entirely by the equilibrium distribution of gas velocities and, of course, the area of the hole. Show that the number of molecules effusing through a hole of area  $A$  in time  $t$  is

$$At \left( \frac{N}{V} \right) \left( \frac{kT}{2\pi m} \right)^{1/2}$$

where  $(N/V)$  is the number density of molecules in the container, and  $m$  is their molecular mass.

- A vessel contains hydrogen and oxygen at 350 K and partial pressures of 0.50 bar and 1.50 bar, respectively. These gases effuse into a vacuum. What is the ratio of hydrogen to oxygen in the escaping gas?
- How could we use effusion to estimate the molecular weight of an unknown substance?
- An equimolar mixture of  $^{235}\text{UF}_6$  and  $^{238}\text{UF}_6$  is subjected to effusion. What is the ratio of  $^{235}\text{U}$  to  $^{238}\text{U}$  in the escaping gas?
- Calculate the number of nitrogen molecules that collide with  $10^{-6}$   $\text{m}^2$  of wall in  $10^{-6}$  s, if the pressure is 1.00 bar and the temperature is 300 K.

17. Air is approximately 20% oxygen and 80% nitrogen by volume. Assume that oxygen and nitrogen molecules both have a radius of  $1.8 \times 10^{-8}$  m. For air at 1.0 bar and 298 K, calculate:

- The number of collisions that one oxygen molecule makes with nitrogen molecules every second.
  - The number of collisions that occur between oxygen and nitrogen molecules in one cubic meter of air every second.
  - The number of collisions that one oxygen molecule makes with other oxygen molecules every second.
  - The number of collisions that occur between oxygen molecules in one cubic meter of air every second.
  - The number of collisions that occur between oxygen and nitrogen molecules in one cubic meter each second in which the kinetic energy along the line of centers exceeds  $100 \text{ kJ mol}^{-1}$  or  $1.66 \times 10^{-19}$  J per collision.
  - The number of oxygen-nitrogen collisions that occur in which the kinetic energy along the line of centers exceeds  $50 \text{ kJ mol}^{-1}$ .
18. Show that  $\int_0^\infty \rho_v(v) dv \neq 1$ .

19. For what volume element,  $\mathfrak{v}$ , is

$$P(\mathfrak{v}) = f_{xyz}(v_x, v_y, v_z)?$$

20. Using the model we develop in [Section 2.10](#):

- Show that the pressure,  $P_1(v)$ , attributable to a single molecule of mass  $m$  and velocity  $v$  in a container of volume  $V$  is

$$P_1(v) = \frac{mv^2}{3V}$$

- In [Section 4.6](#), we find that this pressure is

$$\delta P_1(v) = \frac{2mv^2 \cos^2 \theta}{V}$$

for a molecule whose velocity vector lies between  $\theta$  and  $\theta + d\theta$  and between  $\varphi$  and  $\varphi + d\varphi$ . This angular region comprises a solid angle whose magnitude is  $d\Omega = \sin\theta d\theta d\varphi$ . Since the solid angle surrounding a given point is  $4\pi$ , the probability that a randomly oriented velocity vector lies between  $\theta$  and  $\theta + d\theta$  and between  $\varphi$  and  $\varphi + d\varphi$  is

$$\frac{d\Omega}{4\pi} = \frac{\sin\theta d\theta d\varphi}{4\pi}$$

Therefore, given that the scalar component of a molecule's velocity is  $v$ , its contribution to the pressure at  $A$  is

$$dP_1(v) = \left( \frac{mv^2}{2\pi V} \right) \cos^2 \theta \sin\theta d\theta d\varphi$$

To find the pressure contribution made by this molecule irrespective of the values of  $\theta$  and  $\varphi$ , we must integrate  $dP_1(v)$  over all values of  $\theta$  and  $\varphi$  that allow the molecule to impact the wall at  $A$ . Recalling that these ranges are  $0 \leq \theta < \pi/2$  and  $0 \leq \varphi < 2\pi$ , show that

$$P_1(v) = \frac{mv^2}{3V}$$

21. Taking  $P_1(v) = mv^2/3V$  as the contribution made to the pressure by one molecule whose velocity is  $v$ :

- Show that the expected value for the contribution made to the pressure by one molecule when the Maxwell-Boltzmann distribution function describes the distribution of molecular velocities is

$$\langle P_1(v) \rangle = \frac{kT}{V}$$

- Show that the variance of the contribution made to the pressure by one molecule is

$$\sigma_{P_1(v)}^2 = \frac{2k^2 T^2}{3V^2}$$

What is the standard deviation,  $\sigma_{P_1(v)}$ ?

(c) What is the value of the ratio

$$\frac{\sigma_{P_1(v)}}{\langle P_1(v) \rangle}$$

(d) Taking  $3 \times 10^{15}$  as the number of collisions of  $N_2$  molecules at 1 bar and 300 K with one one square millimeter per microsecond, what pressure,  $P_{avg}$ , would we find if we could measure the individual contribution made by each collision and compute their average? What would be the variance,  $\sigma_{avg}^2$ , of this average? The standard deviation,  $\sigma_{avg}$ ? The ratio  $\sigma_{avg}/P_{avg}$ ?

22. Let  $\epsilon = mv^2/2$  be the translational kinetic energy of a gas molecule whose mass is  $m$ . Show that the probability density function for  $\epsilon$  is

$$\frac{df}{d\epsilon} = 2\pi \left( \frac{1}{\pi kT} \right)^{3/2} \epsilon^{1/2} \exp \left( \frac{-\epsilon}{kT} \right)$$

Letting the translational kinetic energy per mole be  $E = \bar{N}\epsilon$ , show that

$$\frac{df}{dE} = 2\pi \left( \frac{1}{\pi RT} \right)^{3/2} E^{1/2} \exp \left( \frac{-E}{RT} \right)$$

### Notes

<sup>1</sup> Our collision model and quantitative treatment of the role of activation energy in chemical reaction rates follow those given by Arthur A. Frost and Ralph G. Pearson, ***Kinetics and Mechanism***, 2<sup>nd</sup> Ed., John Wiley and Sons, New York, 1961, pp 65-68. See also R. H. Fowler, ***Statistical Mechanics***, Cambridge University Press, New York, 1936.

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