

1. (a) True or False? The kinetic energy corresponding to the most probable molecular speed in the Maxwell–Boltzmann speed distribution is equal to the most probable kinetic energy.

False, the transformation shifts the probability distribution

- (b) Perform a change of variables and express the Maxwell–Boltzmann speed distribution, $F(u)$, in terms of the kinetic energy, $\varepsilon = \frac{1}{2}mu^2$ by using conservation of probability $F(u)du = F(\varepsilon)d\varepsilon$. Then use the new distribution $F(\varepsilon)$ to find the most probable kinetic energy $\varepsilon_{\text{prob}}$ and compare it to $KE(u_{\text{prob}}) = \frac{1}{2}m(u_{\text{prob}})^2$.

Express u in terms of ε :

$$\varepsilon = \frac{1}{2}mu^2 \implies u = \sqrt{\frac{2\varepsilon}{m}}$$

$$du = \frac{d\varepsilon}{mu} = \frac{d\varepsilon}{m\sqrt{\frac{2\varepsilon}{m}}} = \frac{d\varepsilon}{\sqrt{2\varepsilon m}}$$

Substitute in to eliminate u from $F(u)du$:

$$F(\varepsilon)d\varepsilon = F(u)du = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} u^2 e^{-mu^2/2k_B T} du$$

$$F(\varepsilon)d\varepsilon = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \left(\frac{2\varepsilon}{m}\right) e^{-\varepsilon/k_B T} \frac{d\varepsilon}{\sqrt{2\varepsilon m}}$$

$$F(\varepsilon) = \frac{2\pi}{(\pi k_B T)^{3/2}} \varepsilon^{1/2} e^{-\varepsilon/k_B T}$$

Take derivative and set equal to 0 for $\varepsilon_{\text{prob}}$:

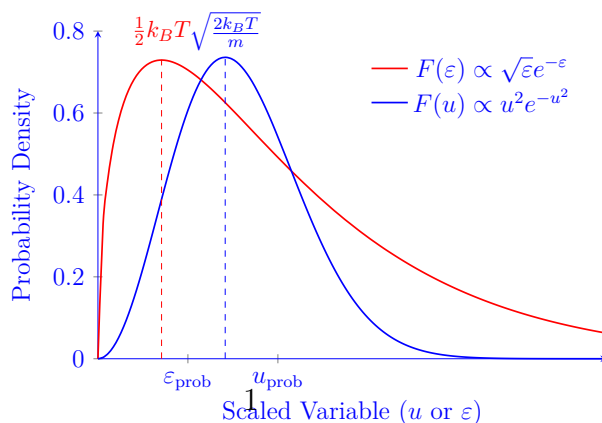
$$\frac{d}{d\varepsilon} F(\varepsilon) = \frac{d}{d\varepsilon} [\varepsilon^{1/2} e^{-\varepsilon/k_B T}] = 0$$

$$0 = \varepsilon^{1/2} e^{-\varepsilon/k_B T} \left(-\frac{1}{k_B T}\right) + e^{-\varepsilon/k_B T} \left(\frac{1}{2}\varepsilon^{-1/2}\right)$$

$$\frac{1}{2\varepsilon^{1/2}} = \frac{\varepsilon^{1/2}}{k_B T} \implies \boxed{\varepsilon_{\text{prob}} = \frac{k_B T}{2}}$$

$$u_{\text{prob}} = \sqrt{\frac{2k_B T}{m}} \implies KE(u_{\text{prob}}) = \frac{1}{2}m \left(\sqrt{\frac{2k_B T}{m}}\right)^2$$

$$\boxed{KE(u_{\text{prob}}) = k_B T}$$



2. At an altitude of 150 km, the pressure is 2.63×10^{-9} atm and the temperature is 500 K. Assuming air is pure nitrogen, calculate the mean free path and the average collision frequency.

$$l = \frac{RT}{\sqrt{2} N_A \sigma P}$$

$$l = \frac{(0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(500 \text{ K})}{\sqrt{2} \cdot (6.022 \times 10^{23} \frac{1}{\text{mol}}) \cdot (0.430 \times 10^{-18} \text{ m}^2) \cdot (2.63 \times 10^{-9} \text{ atm})}$$

$$l = \frac{41.03 \text{ L}}{963.7 \text{ m}^2} = \boxed{42.6 \text{ m}}$$

$$Z_A = \frac{\langle v \rangle}{l} = \frac{\sqrt{\frac{8RT}{\pi M}}}{l} = \sqrt{\frac{8(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}})(500 \text{ K})}{\pi \cdot 0.02802 \frac{\text{kg}}{\text{mol}}}}$$

$$Z_A = \frac{615 \frac{\text{m}}{\text{s}}}{42.6 \text{ m}} = \boxed{14.4 \frac{1}{\text{s}}}$$

3. Wellin Hall has 20 rows of seats. Yuting releases hydrogen cyanide (HCN, toxic) from the front while our lovely TA Grace simultaneously releases laughing gas (N_2O) from the back. If you aren't already laughing and dying in pchem, which row of students will die while laughing? Consider a ratio of u_{rms} and think about how it relates to distance traveled.

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} \implies \frac{v_{\text{HCN}}}{v_{\text{N}_2\text{O}}} = \sqrt{\frac{M_{\text{N}_2\text{O}}}{M_{\text{HCN}}}}$$

$$\frac{v_{\text{HCN}}}{v_{\text{N}_2\text{O}}} = \sqrt{\frac{44 \frac{\text{g}}{\text{mol}}}{27 \frac{\text{g}}{\text{mol}}}} = 1.277$$

$$d_{\text{HCN}} + d_{\text{N}_2\text{O}} = 20$$

$$1.277 d_{\text{N}_2\text{O}} + d_{\text{N}_2\text{O}} = 20$$

$$d_{\text{N}_2\text{O}} = \frac{20}{2.277} = 8.78$$

Distance traveled proportional to velocity

$$\implies d_{\text{HCN}} = 20 - 8.78 = 11.22$$

$$\frac{d_{\text{HCN}}}{d_{\text{N}_2\text{O}}} = 1.277 \implies d_{\text{HCN}} = 1.277 d_{\text{N}_2\text{O}} \quad \text{Row 11 dies before laughing, so rows 12–20.}$$

4. Compare 1 mol of $\text{O}_2(\text{g})$ (MW=32 $\frac{\text{g}}{\text{mol}}$) to 0.5 mol of $\text{S}_2(\text{g})$ (MW=64 $\frac{\text{g}}{\text{mol}}$) at standard conditions by filling in the blanks with $<$, $>$, $=$, or X for cannot be determined. Assume equal cross-sectional area.

(a) average kinetic energy O_2 = average kinetic energy S_2

(b) u_{rms} O_2 > u_{rms} S_2

(c) collision frequency O_2 > collision frequency S_2

The temperature of S_2 is doubled under constant pressure but the O_2 temperature remains constant. Compare the following under these new conditions.

(d) average kinetic energy O_2 < average kinetic energy S_2

(e) u_{rms} O_2 = u_{rms} S_2

(f) collision frequency O_2 > collision frequency S_2

5. An unknown gas at standard conditions has total collision frequency $Z_{AA} = 1.63 \times 10^{35} \frac{1}{\text{s}\cdot\text{m}^3}$ and cross-sectional area $\sigma = 5.30 \times 10^{-19} \text{ m}^2$. Identify the gas.

$$\rho = \frac{N_A P}{RT} = \frac{(6.022 \times 10^{23} \frac{1}{\text{mol}})(1.00 \text{ atm})}{(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(273 \text{ K})} = 2.69 \times 10^{25} \frac{1}{\text{m}^3}$$

$$Z_{AA} = \frac{1}{\sqrt{2}} \rho^2 \sigma \langle u \rangle \implies \langle u \rangle = \frac{\sqrt{2} Z_{AA}}{\rho^2 \sigma}$$

$$\langle u \rangle = \frac{\sqrt{2} (1.63 \times 10^{35} \frac{1}{\text{s}\cdot\text{m}^3})}{(2.69 \times 10^{25} \frac{1}{\text{m}^3})^2 (5.30 \times 10^{-19} \text{ m}^2)} = 601 \frac{\text{m}}{\text{s}}$$

$$\langle u \rangle = \sqrt{\frac{8RT}{\pi M}} \implies M = \frac{8RT}{\pi \langle u \rangle^2}$$

$$M = \frac{8(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}})(273 \text{ K})}{\pi (601 \frac{\text{m}}{\text{s}})^2} = 0.016 \frac{\text{kg}}{\text{mol}} = 16 \frac{\text{g}}{\text{mol}} \implies \boxed{\text{CH}_4}$$

Homework Problem 32

1. What is the average time between collisions of a xenon atoms at standard conditions?