CHAPTER 27

The Kinetic Theory of Gases

PROBLEMS AND SOLUTIONS

27–1. Calculate the average translational energy of one mole of ethane at 400 K, assuming ideal behavior. Compare your result to $\overline{U}^{\text{id}}$ for ethane at 400 K given in Figure 22.3.

From Section 18–1, for an ideal molecule

$$E_{\text{trans}} = \frac{3}{2}RT = 4.99\ \text{kJ}\cdot\text{mol}^{-1}$$

At $P = 0$ bar (ideal conditions), $\overline{U} \approx 14.6\ \text{kJ}\cdot\text{mol}^{-1}$ from Figure 22.3. Therefore, E_{trans} accounts for a third of the total energy.

27–2. Calculate the root-mean-square speed of a nitrogen molecule at 200 K, 300 K, 500 K, and 1000 K.

Using Equation 27.14, we find that

$$u_{\text{rms}} = \left(\frac{3RT}{M}\right)^{1/2} = \left[\frac{3(8.3145\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})T}{0.02802\ \text{kg}\cdot\text{mol}^{-1}}\right]^{1/2}$$

Substituting for T, we find the values below.

T/K	$u_{\text{rms}}/\text{m}\cdot\text{s}^{-1}$
200	421.9
300	516.8
500	667.2
1000	943.5

27–3. If the temperature of a gas is doubled, by how much is the root-mean-square speed of the molecules increased?

Let the original temperature of the gas be T and the original root-mean-square speed be $u_{\text{rms}}(T)$. Then (Equation 27.14)

$$u_{\text{rms}}(2T) = \left[\frac{3R(2T)}{M}\right]^{1/2} = 2^{1/2}u_{\text{rms}}(T)$$

The root-mean-square speed is increased by a factor of $\sqrt{2}$.

27–4. The speed of sound in air at sea level at 20°C is about 770 mph. Compare this value with the root-mean-square speed of nitrogen and oxygen molecules at 20°C.

Using Equation 27.14, we write

$$u_{\text{rms},\text{N}_2} = \left[\frac{3(8.31451\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(293\ \text{K})}{0.02802\ \text{kg}\cdot\text{mol}^{-1}}\right]^{1/2} = 511\ \text{m}\cdot\text{s}^{-1}$$

$$u_{\text{rms},\text{O}_2} = \left[\frac{3(8.31451\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(293\ \text{K})}{0.03200\ \text{kg}\cdot\text{mol}^{-1}}\right]^{1/2} = 478\ \text{m}\cdot\text{s}^{-1}$$

The speed of sound is

$$770\ \text{mph} = 1239\ \text{km}\cdot\text{h}^{-1} = 344\ \text{m}\cdot\text{s}^{-1}$$

Nitrogen and oxygen molecules travel significantly faster (33% and 28% faster, respectively) than sound in air at 20°C.

27–5. Arrange the following gases in order of increasing root-mean-square speed at the same temperature: O_2, N_2, H_2O, CO_2, NO_2, $^{235}UF_6$, and $^{238}UF_6$.

The heavier the gas, the slower it will travel. (In Equation 27.14, the denominator of the root-mean-square speed increases with increasing mass.) Thus, the arrangement of gases requested is

$$^{238}\text{UF}_6 < {}^{235}\text{UF}_6 < \text{NO}_2 < \text{CO}_2 < \text{O}_2 < \text{N}_2 < \text{H}_2\text{O}$$

27–6. Consider a mixture of $H_2(g)$ and $I_2(g)$. Calculate the ratio of the root-mean-square speed of $H_2(g)$ and $I_2(g)$ molecules in the reaction mixture.

In the mixture, the two components have the same temperature, so (using Equation 27.14)

$$\frac{u_{\text{rms},\text{H}_2}}{u_{\text{rms},\text{I}_2}} = \left(\frac{3RT/M_{\text{H}_2}}{3RT/M_{\text{I}_2}}\right)^{1/2} = \left(\frac{M_{\text{I}_2}}{M_{\text{H}_2}}\right)^{1/2} = \left(\frac{253.8}{2.016}\right)^{1/2} = 11.2$$

27–7. The speed of sound in an ideal monatomic gas is given by

$$u_{\text{sound}} = \left(\frac{5RT}{3M}\right)^{1/2}$$

Derive an equation for the ratio $u_{\text{rms}}/u_{\text{sound}}$. Calculate the root-mean-square speed for an argon atom at 20°C and compare your answer to the speed of sound in argon.

Using Equation 27.14 and the definition of u_{sound} above, we find

$$\frac{u_{\text{rms}}}{u_{\text{sound}}} = \left(\frac{3RT/M}{5RT/3M}\right)^{1/2} = \left(\frac{9}{5}\right)^{1/2} = \frac{3}{\sqrt{5}}$$

The root-mean square speed of an argon atom at 20°C is

$$u_{\text{rms}} = \left(\frac{3RT}{M}\right)^{1/2} = 428\ \text{m}\cdot\text{s}^{-1}$$

and, using the relation between u_{rms} and u_{sound} given above, the speed of sound in argon is 319 $\text{m}\cdot\text{s}^{-1}$.

27–8. Calculate the speed of sound in argon at 25°C.

The speed of sound in argon at 25°C is (using the equivalence given in Problem 27–7)

$$u_{\text{rms}} = \left(\frac{5RT}{3M}\right)^{1/2} = 321\ \text{m}\cdot\text{s}^{-1}$$

27–9. The speed of sound in an ideal polyatomic gas is given by

$$u_{\text{sound}} = \left(\frac{\gamma RT}{M}\right)^{1/2}$$

where $\gamma = C_P/C_V$. Calculate the speed of sound in nitrogen at 25°C.

Recall from Chapter 17 that $\overline{C}_V = 5R/2$ for a diatomic ideal gas (neglecting the vibrational contribution), and that $\overline{C}_P - \overline{C}_V = R$ (Equation 19.43). Then

$$u_{\text{sound}} = \left(\frac{C_P RT}{C_V M}\right)^{1/2} = \left[\frac{7(8.3145\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(298.15\ \text{K})}{5(0.02802\ \text{kg}\cdot\text{mol}^{-1})}\right]^{1/2} = 352\ \text{m}\cdot\text{s}^{-1}$$

27–10. Use Equation 27.17 to prove that $\partial u/\partial u_x = u_x/u$.

Begin with Equation 27.17:

$$\begin{aligned} u^2 &= u_x^2 + u_y^2 + u_z^2 \\ \frac{\partial}{\partial u_x} u^2 &= \frac{\partial}{\partial u_x}(u_x^2 + u_y^2 + u_z^2) \\ 2u\frac{\partial u}{\partial u_x} &= 2u_x \\ \frac{\partial u}{\partial u_x} &= \frac{u_x}{u} \end{aligned}$$

27–11. Give a physical argument why γ in Equation 27.24 must be a positive quantity.

Recall that $f(u_j)$ represents the probability distribution of the jth component of the velocity. As u_j increases, the probability of finding any molecule moving with speed u_j decreases, so that as $u_j \to \infty$, $f(u_j) \to 0$. If γ were negative $f(u_j)$ in Equation 27.24 would diverge as $u_j \to \infty$, so γ must be positive.

27–12. We can use Equation 27.33 to calculate the probability that the x-component of the velocity of a molecule lies within some range. For example, show that the probability that $-u_{x0} \le u_x \le u_{x0}$ is given by

$$\begin{aligned}\text{Prob}\{-u_{x0} \le u_x \le u_{x0}\} &= \left(\frac{m}{2\pi k_B T}\right)^{1/2} \int_{-u_{x0}}^{u_{x0}} e^{-mu_x^2/2k_BT} du_x \\ &= 2\left(\frac{m}{2\pi k_B T}\right)^{1/2} \int_0^{u_{x0}} e^{-mu_x^2/2k_BT} du_x\end{aligned}$$

Now let $mu_x^2/2k_BT = w^2$ to get the cleaner-looking expression

$$\text{Prob}\{-u_{x0} \le u_x \le u_{x0}\} = \frac{2}{\pi^{1/2}} \int_0^{w_0} e^{-w^2} dw$$

where $w_0 = (m/2k_BT)^{1/2} u_{x0}$.

It so happens that the above integral cannot be evaluated in terms of any function that we have encountered up to now. It is customary to express the integral in terms of a new function called the *error function*, which is defined by

$$\text{erf}(z) = \frac{2}{\pi^{1/2}} \int_0^z e^{-x^2} dx \qquad (1)$$

The error function can be evaluated as a function of z by evaluating its defining integral numerically. Some values of erf(z) are

z	erf(z)	z	erf(z)
0.20	0.22270	1.20	0.91031
0.40	0.42839	1.40	0.95229
0.60	0.60386	1.60	0.97635
0.80	0.74210	1.80	0.98909
1.00	0.84270	2.00	0.99532

Now show that

$$\text{Prob}\{-u_{x0} \le u_x \le u_{x0}\} = \text{erf}(w_0)$$

Calculate the probability that $-(2k_BT/m)^{1/2} \le u_x \le (2k_BT/m)^{1/2}$.

$$f(u_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-mu_x^2/2k_BT} \qquad (27.33)$$

Since $f(u_x)$ is the probability that a molecule has velocity u_x,

$$\begin{aligned}\text{Prob}\{-u_{x0} \le u_x \le u_{x0}\} &= \left(\frac{m}{2\pi k_B T}\right)^{1/2} \int_{-u_{x0}}^{u_{x0}} e^{-mu_x^2/2k_BT} du_x \\ &= 2\left(\frac{m}{2\pi k_B T}\right)^{1/2} \int_0^{u_{x0}} e^{-mu_x^2/2k_BT} du_x\end{aligned}$$

Now let $mu_x^2/2k_BT = w^2$. Then

$$\frac{mu_x du_x}{k_BT} = 2w dw$$

$$du_x = \frac{2k_BT}{m}\frac{w dw}{u_x} = \left(\frac{2k_BT}{m}\right)^{1/2} dw$$

Letting $w_0 = (m/2k_BT)^{1/2} u_{x0}$ and substituting into the probability expression above,

$$\text{Prob}\{-u_{x0} \le u_x \le u_{x0}\} = \frac{2}{\pi^{1/2}} \int_0^{w_0} e^{-w^2} dw$$

From the definition of an error function, it is easy to see that

$$\text{Prob}\{-u_{x0} \le u_x \le u_{x0}\} = \frac{2}{\pi^{1/2}} \int_0^{w_0} e^{-x^2} dx = \text{erf}(w_0)$$

To find the probability that $-(2k_BT/m)^{1/2} \le u_x \le (2k_BT/m)^{1/2}$, we first find w_0:

$$w_0 = \left(\frac{mu_{x0}^2}{2k_BT}\right)^{1/2} = \left[\frac{m(2k_BT)}{m(2k_BT)}\right]^{1/2} = 1$$

Since $\text{Prob}\{-u_{x0} \le u_x \le u_{x0}\} = \text{erf}(w_0)$, from the table of values of erf(z) we find that

$$\text{Prob}\{-(2k_BT/m)^{1/2} \le u_x \le (2k_BT/m)^{1/2}\} = \text{erf}(1) = 0.84270$$

27–13. Use the result of Problem 27–12 to show that

$$\text{Prob}\{|u_x| \ge u_{x0}\} = 1 - \text{erf}(w_0)$$

$$\begin{aligned}\text{Prob}\{|u_x| \ge u_{x0}\} &= 1 - \text{Prob}\{|u_x| \le u_{x0}\} \\ &= 1 - \text{Prob}\{-u_{x0} \le u_x \le u_{x0}\}\end{aligned}$$

In Problem 27–12 we found that $\text{Prob}\{-u_{x0} \le u_x \le u_{x0}\} = \text{erf}(w_0)$, so

$$\text{Prob}\{|u_x| \ge u_{x0}\} = 1 - \text{erf}(w_0)$$

Notice that $\text{Prob}\{u_x \ge u_{x0}\} = \frac{1}{2}[1 - \text{erf}(w_0)]$ (see Problem 27–14).

27–14. Use the result of Problem 27–12 to calculate $\text{Prob}\{u_x \ge +(k_BT/m)^{1/2}\}$ and $\text{Prob}\{u_x \ge +(2k_BT/m)^{1/2}\}$.

We can write

$$\text{Prob}\{u_x \ge +(k_BT/m)^{1/2}\} = 1 - \text{Prob}\{u_x \le +(k_BT/m)^{1/2}\}$$

Following the procedure used in Problem 27–12, this becomes

$$\text{Prob}\{u_x \ge +(k_BT/m)^{1/2}\} = 1 - \left(\frac{m}{2\pi k_B T}\right)^{1/2} \int_{-\infty}^{(k_BT/m)^{1/2}} e^{-mu_x^2/2k_BT} du_x$$

Letting $w = (m/2k_BT)^{1/2} u_x$ and $w_0 = (m/2k_BT)^{1/2} u_{x0}$, this becomes

$$\begin{aligned}\text{Prob}\{u_x \ge +(k_BT/m)^{1/2}\} &= 1 - \left[\frac{1}{\pi^{1/2}} \int_{-\infty}^0 e^{-w^2} dw + \frac{1}{\pi^{1/2}} \int_0^{w_0 = 1/\sqrt{2}} e^{-w^2} dw\right] \\ &= 1 - \left[\frac{1}{\pi^{1/2}} \left(\frac{\pi}{4}\right)^{1/2} + \frac{1}{2}\text{erf}\left(\frac{1}{\sqrt{2}}\right)\right] \\ &= 0.159\end{aligned}$$

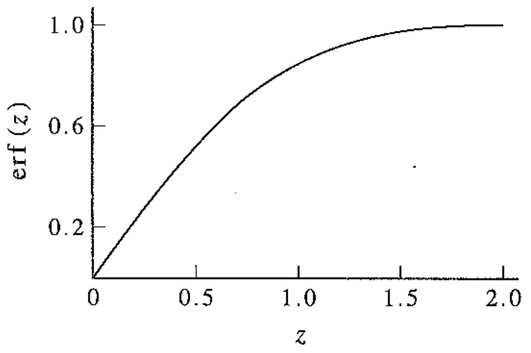
Likewise,

$$\begin{aligned}\text{Prob}\{u_x \geq +(2k_\text{B}T/m)^{1/2}\} &= 1 - \left[\frac{1}{\pi^{1/2}}\int_{-\infty}^{0} e^{-w^2}dw + \frac{1}{\pi^{1/2}}\int_{0}^{w_0=1} e^{-w^2}dw\right]\\ &= 1 - \left[\frac{1}{\pi^{1/2}}\left(\frac{\pi}{4}\right)^{1/2} + \frac{1}{2}\text{erf}\,(1)\right]\\ &= 0.0786\end{aligned}$$

27–15. Use the result of Problem 27–12 to plot the probability that $-u_{x0} \leq u_x \leq u_{x0}$ against $u_{x0}/(2k_\text{B}T/m)^{1/2}$.

We found in Problem 27–12 that the above probability is given by $\text{erf}(w_0)$, where $w_0 = u_{x0}/(2k_\text{B}T/m)^{1/2}$. The required plot will be a plot of $\text{erf}(w_0)$ against w_0 and thus identical to the plot in the following problem.

27–16. Use Simpson's rule or any other numerical integration routine to verify the values of erf(*z*) given in Problem 27–12. Plot erf(*z*) against *z*.



27–17. Derive an expression for the average value of the positive values of u_x.

$$f(u_x) = \left(\frac{m}{2\pi k_\text{B}T}\right)^{1/2} e^{-mu_x^2/2k_\text{B}T} \tag{27.33}$$

As in Equation 27.34, we can write the average value of the positive u_x as

$$\begin{aligned}\langle u_x+\rangle &= \int_0^\infty u_x f(u_x)du_x = \left(\frac{m}{2\pi k_\text{B}T}\right)^{1/2}\int_0^\infty u_x e^{-mu_x^2/2k_\text{B}T}du_x\\ &= \left(\frac{m}{2\pi k_\text{B}T}\right)^{1/2}\frac{2k_\text{B}T}{2m} = \left(\frac{k_\text{B}T}{2\pi m}\right)^{1/2}\end{aligned}$$

27–18. This problem deals with the idea of the *escape velocity* of a particle from a body such as the Earth's surface. Recall from your course in physics that the potential energy of two masses, m_1 and m_2, separated by a distance r is given by

$$V(r) = -\frac{Gm_1m_2}{r}$$

(note the similarity with Coulomb's law) where $G = 6.67 \times 10^{-11}\ \text{J}\cdot\text{m}\cdot\text{kg}^{-1}$ is called the gravitional constant. Suppose a particle of mass m has a velocity u perpendicular to the Earth's surface. Show that the minimum velocity that the particle must have in order to escape the Earth's surface (its *escape velocity*) is given by

$$u = \left(\frac{2GM_\text{earth}}{R_\text{earth}}\right)^{1/2}$$

Given that $M_\text{earth} = 5.98 \times 10^{24}$ kg is the mass of the Earth and $R_\text{earth} = 6.36 \times 10^6$ m is its mean radius, calculate the escape velocity of a hydrogen molecule and a nitrogen molecule. What temperature would each of these molecules have to have so that their average speed exceeds their escape velocity?

The kinetic energy of the particle is equal and opposite to the potential energy between the two bodies when the particle has the minimum velocity required to escape the Earth's surface, so

$$\begin{aligned}\frac{1}{2}mv_\text{escape}^2 &= \frac{GmM_\text{earth}}{R_\text{earth}}\\ v_\text{escape} &= \left(\frac{2GM_\text{earth}}{R_\text{earth}}\right)^{1/2}\end{aligned}$$

where we can consider the distance between the particle and the circumference of the earth negligible compared with the distance between the circumference of the earth and its center of mass. Since the escape velocity is independent of particle size, for both hydrogen and nitrogen

$$v_\text{escape} = \left[\frac{2(6.67 \times 10^{-11}\ \text{J}\cdot\text{m}\cdot\text{kg}^{-1})(5.98 \times 10^{24}\ \text{kg})}{6.36 \times 10^6\ \text{m}}\right]^{1/2} = 11\,200\ \text{m}\cdot\text{s}^{-1}$$

From Equation 27.42,

$$\begin{aligned}T_{\text{escape},\text{H}_2} &= \frac{\pi M v_\text{escape}^2}{8R}\\ &= \frac{\pi(0.002016\ \text{kg}\cdot\text{mol}^{-1})(11\,200\ \text{m}\cdot\text{s}^{-1})^2}{8(8.3145\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})} = 11.9 \times 10^3\ \text{K}\\ T_{\text{escape},\text{N}_2} &= \frac{\pi M v_\text{escape}^2}{8R}\\ &= \frac{\pi(0.02802\ \text{kg}\cdot\text{mol}^{-1})(11\,200\ \text{m}\cdot\text{s}^{-1})^2}{8(8.3145\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})} = 16.6 \times 10^4\ \text{K}\end{aligned}$$

27–19. Repeat the calculation in the previous problem for the moon's surface. Take the mass of the moon to be 7.35×10^{22} kg and its radius to be 1.74×10^6 m.

Now

$$v_\text{min} = \left(\frac{2GM_\text{moon}}{R_\text{moon}}\right)^{1/2} = 2370\ \text{m}\cdot\text{s}^{-1}$$

Again, from Equation 27.42,

$$\begin{aligned} T_{\text{escape},\text{H}_2} &= \frac{\pi M v^2_{\text{escape}}}{8R} \\ &= \frac{\pi(0.002016\ \text{kg}\cdot\text{mol}^{-1})(2370\ \text{m}\cdot\text{s}^{-1})^2}{8(8.3145\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})} = 537\ \text{K} \\ T_{\text{escape},\text{N}_2} &= \frac{\pi M v^2_{\text{escape}}}{8R} \\ &= \frac{\pi(0.02802\ \text{kg}\cdot\text{mol}^{-1})(2370\ \text{m}\cdot\text{s}^{-1})^2}{8(8.3145\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})} = 7460\ \text{K} \end{aligned}$$

27–20. Show that the variance of Equation 27.37 is given by $\sigma^2 = \nu_0^2 k_\text{B}T/mc^2$. Calcuate σ for the $3p\,^2P_{3/2}$ to $3s\,^2S_{1/2}$ transition in atomic sodium vapor (see Figure 8.4) at 500 K.

Equation 27.37 gives $I(\nu)$ as

$$I(\nu) = K \exp\left[\frac{-mc^2(\nu - \nu_0)^2}{2\nu_0^2 k_\text{B}T}\right] \tag{27.37}$$

Compare this equation to that of a general Gaussian curve (Example B–4), with variance $\sigma^2 = a^2$:

$$p(x)dx = c\exp\left[\frac{-(x - x_0)^2}{2a^2}\right]$$

Since we know that $I(\nu)$ has the shape of a Gaussian curve (by comparing the equations), the variance for $I(\nu)$ is given by

$$\sigma^2 = \frac{\nu_0^2 k_\text{B}T}{mc^2} = \frac{\nu_0^2 RT}{Mc^2}$$

The wavelength of the $3p\,^2P_{3/2}$ to $3s\,^2S_{1/2}$ transition is (from Figure 8.4) 5889.9×10^{-10} m. Since $\lambda\nu = c$, $\nu = 5.090 \times 10^{14}\ \text{s}^{-1}$. Substituting, we find

$$\sigma^2 = \frac{(5.090 \times 10^{14}\ \text{s}^{-1})^2(8.3145\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(500\ \text{K})}{(0.02299\ \text{kg}\cdot\text{mol}^{-1})(2.998 \times 10^8\ \text{m}\cdot\text{s}^{-1})^2} = 5.21 \times 10^{17}\ \text{s}^{-2}$$

or $\sigma = 7.22 \times 10^8\ \text{s}^{-1}$.

27–21. Show that the distribution of speeds for a two-dimensional gas is given by

$$F(u)du = \frac{m}{k_\text{B}T} u e^{-mu^2/2k_\text{B}T} du$$

(Recall that the area element in plane polar coordinates is $r dr d\theta$.)

The two-dimensional version of Equation 27.39 is

$$F(u)du = \left(\frac{m}{2\pi k_\text{B}T}\right) e^{-m(u_x^2+u_y^2)/2k_\text{B}T} du_x du_y$$

Using a two-dimensional velocity space, we replace $u_x^2 + u_y^2$ by u^2 and $du_x du_y$ with $2\pi u du$ to obtain

$$F(u)du = \left(\frac{m}{k_\text{B}T}\right) u e^{-mu^2/2k_\text{B}T} du$$

27–22. Use the formula in the previous problem to derive formulas for $\langle u \rangle$ and $\langle u^2 \rangle$ for a two-dimensional gas. Compare your result for $\langle u^2 \rangle$ to $\langle u_x^2 \rangle + \langle u_y^2 \rangle$.

Because u is an intrinsically positive quantity, we can write our integrals over a positive range only. Then, using Equations B.12 and B.13 and Table 27.2 to evaluate the integrals,

$$\begin{aligned} \langle u \rangle &= \int_0^\infty u F(u) du = \frac{m}{k_\text{B}T}\int_0^\infty u^2 e^{-mu^2/2k_\text{B}T} du \\ &= \left(\frac{m}{k_\text{B}T}\right)\left(\frac{2k_\text{B}T}{4m}\right)\left(\frac{2\pi k_\text{B}T}{m}\right)^{1/2} = \left(\frac{\pi k_\text{B}T}{2m}\right)^{1/2} = \left(\frac{\pi RT}{2M}\right)^{1/2} \\ \langle u^2 \rangle &= \int_0^\infty u^2 F(u) du = \frac{m}{k_\text{B}T}\int_0^\infty u^3 e^{-mu^2/2k_\text{B}T} du \\ &= \left(\frac{m}{k_\text{B}T}\right)\frac{1}{2}\left(\frac{2k_\text{B}T}{m}\right)^2 = \frac{2k_\text{B}T}{m} = \frac{2RT}{M} \end{aligned}$$

From Equations 27.5 and 27.6,

$$\langle u_x^2 \rangle = \langle u_y^2 \rangle = \frac{PV}{Nm} = \frac{RT}{Nm} = \frac{k_\text{B}T}{m}$$

So $\langle u^2 \rangle = \langle u_x^2 \rangle + \langle u_y^2 \rangle$.

27–23. Use the formula in Problem 27–21 to calculate the probability that $u \geq u_0$ for a two-dimensional gas.

The probability that $u \geq u_0$ for a two-dimensional gas is given by

$$\text{Prob}\{u \geq u_0\} = \int_{u_0}^\infty F(u)du = \frac{m}{k_\text{B}T}\int_{u_0}^\infty u e^{-mu^2/2k_\text{B}T} du$$

Let $x = (m/2k_\text{B}T)^{1/2}u$, so

$$\begin{aligned} \text{Prob}\{u \geq u_0\} &= \frac{m}{k_\text{B}T}\int_{(m/2k_\text{B}T)^{1/2}u_0}^\infty \left(\frac{2k_\text{B}T}{m}\right)^{1/2} x e^{-x^2}\left(\frac{2k_\text{B}T}{m}\right)^{1/2} dx \\ &= 2\int_{(m/2k_\text{B}T)^{1/2}u_0}^\infty x e^{-x^2} dx = 2\left(-\frac{1}{2}\right) e^{-x^2}\Big|_{(m/2k_\text{B}T)^{1/2}u_0}^\infty \\ &= e^{-mu_0^2/2k_\text{B}T} \end{aligned}$$

27–24. Show that the probability that a molecule has a speed less than or equal to u_0 is given by

$$\text{Prob}\{u \leq u_0\} = \frac{4}{\pi^{1/2}}\int_0^{x_0} x^2 e^{-x^2} dx$$

where $x_0 = (m/2k_BT)^{1/2}u_0$. This integral cannot be expressed in closed form and must be integrated numerically. Use Simpson's rule or any other integration routine to evaluate Prob$\{u \le (2k_BT/m)^{1/2}\}$.

We use Equation 27.40 for $F(u)du$:

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

The probability that $u \le u_0$ is given by $\int_0^{u_0} F(u)du$, so

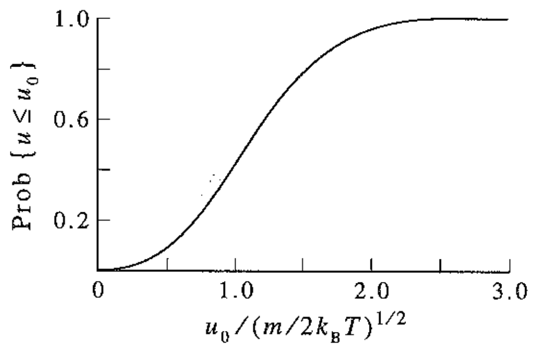
$$\begin{aligned}\text{Prob}\{u \le u_0\} &= 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2}\int_0^{u_0} u^2 e^{-mu^2/2k_BT}du\\ &= 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2}\int_0^{x=x_0}\left(\frac{2k_BT}{m}\right)x^2e^{-x^2}\left(\frac{2k_BT}{m}\right)^{1/2}dx\\ &= \frac{4}{\pi^{1/2}}\int_0^{x_0} x^2e^{-x^2}dx\end{aligned}$$

where we have let $x^2 = mu^2/2k_BT$ and $x_0 = (m/2k_BT)^{1/2}u_0$. To evaluate Prob$\{u \le (2k_BT/m)^{1/2}\}$, we let $x_0 = 1$, so

$$\text{Prob}\{u \le (2k_BT/m)^{1/2}\} = \frac{4}{\pi^{1/2}}\int_0^1 x^2e^{-x^2}dx = 0.4276$$

27–25. Using Simpson's rule or any other integration routine, plot Prob$\{u \le u_0\}$ against $u_0/(m/2k_BT)^{1/2}$. (see Problem 27–24.)

We use the numerical integration package in *Mathematica* to plot Prob$\{u \le u_0\}$ against $u_0/(m/2k_BT)^{1/2}$.



Note that Prob$\{u \le u_0\}$ goes to unity as $\left(\frac{2k_BT}{m}\right)^{1/2}u_0$ goes to infinity.

27–26. What is the most probable kinetic energy for a molecule in the gas phase?

The most probable kinetic energy for a molecule can be found by setting the derivative of $F(\varepsilon)$ equal to zero. Using Equation 27.44, we find

$$\begin{aligned}\frac{dF}{d\varepsilon} &= \frac{2\pi}{(\pi k_BT)^{3/2}}\left[\frac{\varepsilon^{-1/2}e^{-\varepsilon/k_BT}}{2} - \frac{e^{-\varepsilon/k_BT}\varepsilon^{1/2}}{k_BT}\right]\\ 0 &= \frac{2\pi e^{-\varepsilon/k_BT}}{(\pi k_BT)^{3/2}}\left[\frac{1}{2\varepsilon^{1/2}} - \frac{\varepsilon^{1/2}}{k_BT}\right]\\ \varepsilon &= \frac{k_BT}{2}\end{aligned}$$

27–27. Derive an expression for $\sigma_\varepsilon^2 = \langle\varepsilon^2\rangle - \langle\varepsilon\rangle^2$ from Equation 27.44. Now form the ratio $\sigma_\varepsilon/\langle\varepsilon\rangle$. What does this say about the fluctuations in ε?

$$F(\varepsilon)d\varepsilon = \frac{2\pi}{(\pi k_BT)^{3/2}}\varepsilon^{1/2}e^{-\varepsilon/k_BT}d\varepsilon \tag{27.44}$$

Using Equations B.12 and B.13,

$$\begin{aligned}\langle\varepsilon\rangle &= \frac{2\pi}{(\pi k_BT)^{3/2}}\int_0^\infty \varepsilon^{3/2}e^{-\varepsilon/k_BT}d\varepsilon\\ &= \frac{2\pi}{(\pi k_BT)^{3/2}}\left[\frac{3}{(2/k_BT)^2}\right](\pi k_BT)^{1/2} = \frac{3}{2}k_BT\\ \langle\varepsilon^2\rangle &= \frac{2\pi}{(\pi k_BT)^{3/2}}\int_0^\infty \varepsilon^{5/2}e^{-\varepsilon/k_BT}d\varepsilon\\ &= \frac{2}{(k_BT)^{3/2}\pi^{1/2}}\left[\frac{15}{(2/k_BT)^3}\right](\pi k_BT)^{1/2} = \frac{15}{4}(k_BT)^2\\ \sigma_\varepsilon^2 &= \langle\varepsilon^2\rangle - \langle\varepsilon\rangle^2 = \frac{15-9}{4}(k_BT)^2 = \frac{3}{2}(k_BT)^2\\ \sigma_\varepsilon &= \left(\frac{3}{2}\right)^{1/2}k_BT\\ \frac{\sigma_\varepsilon}{\langle\varepsilon\rangle} &= \left(\frac{2}{3}\right)^{1/2}\end{aligned}$$

This says that the fluctuations in ε are large compared to ε.

27–28. Compare the most probable speed of a molecule that collides with a small surface area with the most probable speed of a molecule in the bulk of the gas phase.

From Figure 27.6, we can see that the most probable speed of a molecule that collides with a small surface area is greater than the most probable speed of a molecule in the bulk of the gas. We have found (Equation 27.43) that u_{mp} for a molecule in the bulk of a gas is $(2k_BT/m)^{1/2}$. For a molecule colliding with a small surface area, we must find the u for which the probability of the molecule hitting the surface area is at a maximum, which is the u for which $d[uF(u)]/du = 0$.

$$\begin{aligned} uF(u) &= u^3 e^{-mu^2/2k_\mathrm{B}T} \\ \frac{d[uF(u)]}{du} &= \left[3u^2 - 2\frac{mu^4}{2k_\mathrm{B}T}\right] e^{-mu^2/2k_\mathrm{B}T} \\ \frac{2mu_\mathrm{mp}^4}{2k_\mathrm{B}T} &= 3u_\mathrm{mp}^2 \\ u_\mathrm{mp} &= \left(\frac{3k_\mathrm{B}T}{m}\right)^{1/2} \end{aligned}$$

The ratio of the most probable speeds is

$$\frac{u_\mathrm{mp}(\text{bulk})}{u_\mathrm{mp}(\text{small area})} = \left(\frac{2}{3}\right)^{1/2}$$

27–29. Use Equation 27.48 to calculate the collision frequency per unit area for helium at 100 K and 10^{-6} torr.

This is much like Example 27–6. The number density is

$$\begin{aligned} \rho = \frac{N_\mathrm{A}P}{RT} &= \frac{(6.022 \times 10^{23}\ \mathrm{mol^{-1}})(10^{-6}\ \mathrm{torr}/760\ \mathrm{atm\cdot torr^{-1}})}{(0.082058\ \mathrm{dm^3\cdot atm\cdot mol^{-1}\cdot K^{-1}})(100\ \mathrm{K})} \\ &= 9.656 \times 10^{13}\ \mathrm{dm^{-3}} = 9.656 \times 10^{16}\ \mathrm{m^{-3}} \end{aligned}$$

and $\langle u \rangle$ is (Equation 27.42)

$$\begin{aligned} \langle u \rangle = \left(\frac{8RT}{\pi M}\right)^{1/2} &= \left[\frac{8(8.314\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}})(100\ \mathrm{K})}{\pi(4.0026 \times 10^{-3}\ \mathrm{kg})}\right]^{1/2} \\ &= 727\ \mathrm{m\cdot s^{-1}} \end{aligned}$$

Then, from Equation 27.48,

$$z_\mathrm{coll} = \rho\frac{\langle u \rangle}{4} = 1.76 \times 10^{19}\ \mathrm{m^{-2}\cdot s^{-1}}$$

27–30. Calculate the average speed of a molecule that strikes a small surface area. How does this value compare to the average speed of all the molecules?

The distribution of the speed of molecules that strike a small surface area goes as $u^3 e^{-mu^2/2k_\mathrm{B}T}$. This is not necessarily normalized, so to find the average speed of all the molecules we must divide the integral $\int u^4 e^{-mu^2/2k_\mathrm{B}T}du$ by the integral over all space of the speed of molecules that strike a small surface area:

$$\begin{aligned} \langle u \rangle &= \frac{\int_0^\infty u^4 e^{-mu^2/2k_\mathrm{B}T}du}{\int_0^\infty u^3 e^{-mu^2/2k_\mathrm{B}T}du} \\ &= \left[\frac{3}{8}\left(\frac{2k_\mathrm{B}T}{m}\right)^2\left(\frac{2\pi k_\mathrm{B}T}{m}\right)^{1/2}\right]\left[\frac{1}{2}\left(\frac{2k_\mathrm{B}T}{m}\right)^2\right]^{-1} \\ &= \frac{3}{4}\left(\frac{2\pi k_\mathrm{B}T}{m}\right)^{1/2} = \left(\frac{9\pi k_\mathrm{B}T}{8m}\right)^{1/2} \end{aligned}$$

This is larger than the average speed of the molecules in the bulk of the gas, given in Equation 27.42 as $(8k_\mathrm{B}T/\pi m)^{1/2}$. The ratio is

$$\frac{\langle u \rangle_\mathrm{wall}}{\langle u \rangle_\mathrm{bulk}} = \left(\frac{9\pi^2}{64}\right)^{1/2} = \frac{3\pi}{8}$$

27–31. How long will it take for an initially clean surface to become 1.0% covered if it is bathed by an atmosphere of nitrogen at 77 K and one bar? Assume that every nitrogen molecule that strikes the surface sticks and that a nitrogen molecule covers an area of $1.1 \times 10^5\ \mathrm{pm}^2$.

As in Example 27–6,

$$\begin{aligned} \rho &= \frac{P}{k_\mathrm{B}T} = \frac{10^5\ \mathrm{Pa}}{(1.3806 \times 10^{-23}\ \mathrm{J\cdot K^{-1}})(77\ \mathrm{K})} = 9.406 \times 10^{25}\ \mathrm{m^{-3}} \\ \langle u \rangle &= \left(\frac{8RT}{\pi M}\right)^{1/2} = \left[\frac{8(8.314\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}})(77\ \mathrm{K})}{\pi(0.02802\ \mathrm{kg\cdot mol^{-1}})}\right]^{1/2} = 241.2\ \mathrm{m\cdot s^{-1}} \end{aligned}$$

Then

$$z_\mathrm{coll} = \rho\frac{\langle u \rangle}{4} = 5.67 \times 10^{27}\ \mathrm{m^{-2}\cdot s^{-1}}$$

This is the rate at which particles hit a surface of one square meter. For 1.0 % of the surface to be covered, 0.010 square meter must be covered. Since each molecule covers an area of $1.1 \times 10^5\ \mathrm{pm}^2$,

$$\frac{0.010\ \mathrm{m^2}}{1.1 \times 10^{-19}\ \mathrm{m^2}} = 9.09 \times 10^{16}\text{molecules}$$

must collide within the square meter.

$$\frac{9.09 \times 10^{16}\ \text{molecules}}{5.67 \times 10^{27}\ \text{molecule}\cdot\mathrm{s^{-1}}} = 1.60 \times 10^{-11}\ \mathrm{s}$$

or 1.60×10^{-11} s for 1.0% of each square meter of surface to be covered.

27–32. Calculate the number of methane molecules at 25°C and one torr that strike a 1.0 cm^2 surface in one millisecond.

First find z_coll:

$$\begin{aligned} \rho &= \frac{P}{k_\mathrm{B}T} = \frac{(1\ \mathrm{torr})\ (101325\ \mathrm{Pa}/760\ \mathrm{torr})}{(1.3806 \times 10^{-23}\ \mathrm{J\cdot K^{-1}})(298.15\ \mathrm{K})} = 3.24 \times 10^{22}\ \mathrm{m^{-3}} \\ \langle u \rangle &= \left(\frac{8RT}{\pi M}\right)^{1/2} = \left[\frac{8(8.314\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}})(298.15\ \mathrm{K})}{\pi(0.01604\ \mathrm{kg})}\right]^{1/2} = 627\ \mathrm{m\cdot s^{-1}} \\ z_\mathrm{coll} &= \rho\frac{\langle u \rangle}{4} = 5.08 \times 10^{24}\ \mathrm{m^{-2}\cdot s^{-1}} \end{aligned}$$

The number of methane molecules striking a 1 cm^2 surface in 1 ms is given by

$$z_\mathrm{coll}(1 \times 10^{-4}\ \mathrm{m^{-2}})(1.0 \times 10^{-3}\ \mathrm{s^{-1}}) = 5.08 \times 10^{17}\ \text{molecules}$$

27–33. Consider the velocity selector shown in Figure 27.9. Let the distance between successive disks be h, the rotational frequency be ν (in units of Hz), and the angle between the slits of successive disks be θ (in degrees). Derive the following condition for a molecule traveling with speed u to pass through successive slits:

$$u = \frac{360\nu h}{\theta}$$

Typical values of h and θ are 2 cm and 2°, respectively, so $u = 3.6\nu$. By varying ν from 0 to about 500 Hz, you can select speeds from 0 to over 1500 $\text{m}\cdot\text{s}^{-1}$.

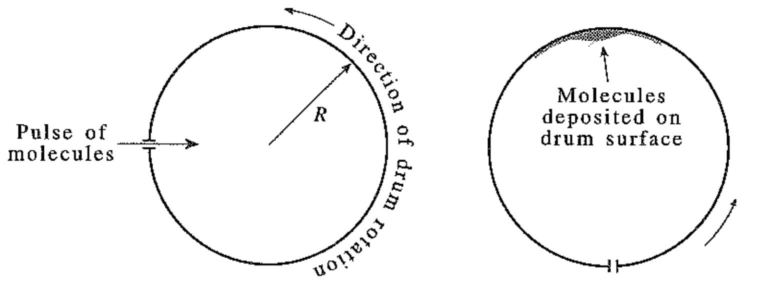
Let $h = ut$, so that t is the time it takes for the molecule to travel between two disks. In order for the molecule to pass through both slits, the disks must have rotated by θ in time t. Since ν measures the number of revolutions per second of the disks, and there are 360° in one revolution, we can write $\theta = 360\nu t$, where θ is measured in degrees. Then

$$\frac{h}{u} = \frac{\theta}{360\nu} \qquad \text{and so} \qquad u = \frac{360\nu h}{\theta}$$

27–34. The figure below illustrates another method that has been used to determine the distribution of molecular speeds. A pulse of molecules collimated from a hot oven enter a rotating hollow drum. Let R be the radius of the drum, ν be its rotational frequency, and s be the distance through which the drum rotates during the time it takes for a molecule to travel from the entrance slit to the inner surface of the drum. Show that

$$s = \frac{4\pi R^2\nu}{u}$$

where u is the speed of the molecule.


Pulse of molecules
R
Direction of drum rotation
Molecules deposited on drum surface

(a) (b)

Use Equation 27.46 to show that the distribution of molecular speeds emerging from the oven is proportional to $u^3e^{-mu^2/2k_\text{B}T}du$. Now show that the distribution of molecules striking the inner surface of the cylinder is given by

$$I(s)ds = \frac{A}{s^5}e^{-m(4\pi R^2\nu)^2/2k_\text{B}Ts^2}ds$$

where A is simply a proportionality constant. Plot I versus s for various values of $4\pi R^2\nu/(2k_\text{B}T/m)^{1/2}$, say 0.1, 1, and 3. Experimental data are quantitatively described by the above equation.

The molecule travels the length of the drum, $2R$, in time t, so $2R = ut$. The distance s that the drum rotates in time t is given by $R\theta$, where θ is the degree to which the drum has been rotated. Since ν measures the number of revolutions per second of the disks, and there are 2π radians in one revolution, we can write $\theta = 2\pi\nu t$, where θ is measured in degrees. Then

$$s = R\theta = 2R\pi\nu t = 2R\pi\nu\left(\frac{2R}{u}\right) = \frac{4\pi R^2\nu}{u}$$

Equation 27.46 gives an expression for the number of collisions per time per unit area for molecules having speeds ranging from u to $u + du$. Therefore it is proportional to the distribution of molecular speeds in a pulse of molecules hitting a small unit area, and (defining this distribution as $I(u)du$)

$$I(u)du \propto u^3e^{-mu^2/2k_\text{B}T}du$$

Using the expression found for s, we can write

$$ds = -\frac{4\pi R^2\nu}{u^2}du$$

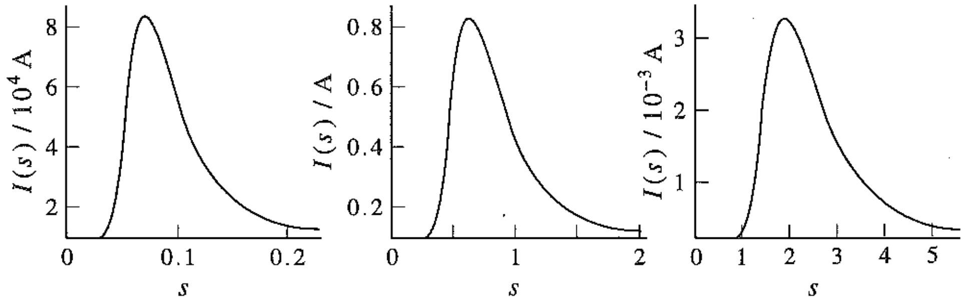
Now we can express $I(u)du$ in terms of s, as

$$I(s)ds \propto -\frac{u^5}{4\pi R^2\nu}e^{-mu^2/2k_\text{B}T}ds$$

$$I(s)ds \propto -\left(\frac{4\pi R^2\nu}{s}\right)^5\frac{1}{4\pi R^2\nu}e^{-m(4\pi R^2\nu)^2/2k_\text{B}Ts^2}ds$$

$$I(s)ds = \frac{A}{s^5}e^{-m(4\pi R^2\nu)^2/2k_\text{B}Ts^2}ds$$

where A is a proportionality constant.



Note the different scales on the x and y-axes needed for different values of $4\pi R^2\nu/(2k_\text{B}T/m)^{1/2}$.

27–35. Use Equation 27.49 to calculate the collision frequency of a single hydrogen molecule at 25°C and (a) one torr and (b) one bar.

Use Equation 27.49, substituting $\sigma = 0.230 \times 10^{-18}\ \text{m}^2$ from Table 27.3:

$$\begin{aligned} z_\text{A} &= \rho\sigma\left(\frac{8RT}{\pi M}\right)^{1/2} \\ &= \rho(0.230\times10^{-18}\ \text{m}^2)\left[\frac{8(8.3145\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(298.15\ \text{K})}{\pi(0.00202\ \text{kg}\cdot\text{mol}^{-1})}\right]^{1/2} = \rho(4.070\times10^{-16}\ \text{m}^3\cdot\text{s}^{-1}) \end{aligned}$$

At 1 torr,

$$\rho = \frac{P}{k_BT} = \frac{(1\text{ torr})}{(1.3806 \times 10^{-23}\text{ J·K}^{-1})(298.15\text{ K})}\left(\frac{101325\text{ Pa}}{760\text{ torr}}\right) = 3.24 \times 10^{22}\text{ m}^{-3}$$

$$z_A = \rho(4.070 \times 10^{-16}\text{ m}^3\text{·s}^{-1}) = 1.32 \times 10^7\text{ s}^{-1}$$

At 1 bar,

$$\rho = \frac{P}{k_BT} = \frac{(1\text{ bar})}{(1.3806 \times 10^{-23}\text{ J·K}^{-1})(298.15\text{ K})}\left(\frac{1 \times 10^5\text{ Pa}}{1\text{ bar}}\right) = 2.43 \times 10^{25}\text{ m}^{-3}$$

$$z_A = \rho(4.070 \times 10^{-16}\text{ m}^3\text{·s}^{-1}) = 9.89 \times 10^9\text{ s}^{-1}$$

27–36. On the average, what is the time between collisions of a xenon atom at 300 K and (a) one torr and (b) one bar.

Use Equation 27.49, substituting $\sigma = 0.750 \times 10^{-18}\text{ m}^2$ from Table 27.3:

$$\begin{aligned} z_A &= \rho\sigma\left(\frac{8RT}{\pi M}\right)^{1/2} \\ &= \rho(0.750 \times 10^{-18}\text{ m}^2)\left[\frac{8(8.3145\text{ J·mol}^{-1}\text{·K}^{-1})(300\text{ K})}{\pi(0.13130\text{ kg·mol}^{-1})}\right]^{1/2} \\ &= \rho(1.650 \times 10^{-16}\text{ m}^3\text{·s}^{-1}) \end{aligned}$$

At 1 torr,

$$\rho = \frac{P}{k_BT} = \frac{(1\text{ torr})}{(1.3806 \times 10^{-23}\text{ J·K}^{-1})(300\text{ K})}\left(\frac{101325\text{ Pa}}{760\text{ torr}}\right) = 3.22 \times 10^{22}\text{ m}^{-3}$$

$$z_A = \rho(1.650 \times 10^{-16}\text{ m}^3\text{·s}^{-1}) = 5.31 \times 10^6\text{ s}^{-1}$$

$$z_A^{-1} = 1.88 \times 10^{-7}\text{ s}$$

(Recall that z_A^{-1} is the measure of the average time between collisions.) At 1 bar,

$$\rho = \frac{P}{k_BT} = \frac{(1\text{ bar})}{(1.3806 \times 10^{-23}\text{ J·K}^{-1})(300\text{ K})}\left(\frac{1 \times 10^5\text{ Pa}}{1\text{ bar}}\right) = 2.41 \times 10^{25}\text{ m}^{-3}$$

$$z_A = \rho(1.650 \times 10^{-16}\text{ m}^3\text{·s}^{-1}) = 3.98 \times 10^9\text{ s}^{-1}$$

$$z_A^{-1} = 2.51 \times 10^{-10}\text{ s}$$

27–37. What is the probability that an oxygen molecule at 25°C and one bar will travel (a) 1.00×10^{-5} mm, (b) 1.00×10^{-3} mm, and (c) 1.00 mm without undergoing a collision?

Use Equation 27.55:

$$\int_0^d p(x)dx = \frac{1}{l}\int_0^d e^{-x/l}dx = 1 - e^{-d/l}$$

$$p(x) = 1 - e^{-d/l}$$

The probability of the oxygen molecule not colliding is $1 - p(x)$, since $p(x)$ is the probability of collision. We can use Equation 27.51 for l:

$$\begin{aligned} l &= \frac{RT}{2^{1/2}N_A\sigma P} \\ &= \frac{(8.3145\text{ J·K}^{-1}\text{·mol}^{-1})(300\text{ K})}{2^{1/2}(6.022 \times 10^{23}\text{ mol}^{-1})(0.410 \times 10^{-18}\text{ m}^2)(1.00 \times 10^5\text{ Pa})} \\ &= 7.143 \times 10^{-8}\text{ m} = 7.143 \times 10^{-5}\text{ mm} \end{aligned}$$

a. $\text{Prob} = \exp\left(\frac{-1.00 \times 10^{-5}}{7.143 \times 10^{-5}}\right) = 0.869$

b. $\text{Prob} = \exp\left(\frac{-1.00 \times 10^{-3}}{7.143 \times 10^{-5}}\right) = 8.32 \times 10^{-7}$

c. $\text{Prob} = \exp\left(\frac{-1.00}{7.143 \times 10^{-5}}\right) \approx 0$

27–38. Repeat the calculation in the previous problem for a pressure of one torr.

Again, we can use Equation 27.51 for l:

$$\begin{aligned} l &= \frac{RT}{2^{1/2}N_A\sigma P} \\ &= \frac{(8.3145\text{ J·K}^{-1}\text{·mol}^{-1})(300\text{ K})}{2^{1/2}(6.022 \times 10^{23}\text{ mol}^{-1})(0.410 \times 10^{-18}\text{ m}^2)(1.00\text{ torr})}\left(\frac{760\text{ torr}}{101325\text{ Pa}}\right) \\ &= 5.36 \times 10^{-5}\text{ m} = 5.36 \times 10^{-2}\text{ mm} \end{aligned}$$

a. $\text{Prob} = \exp\left(\frac{-1.00 \times 10^{-5}}{5.36 \times 10^{-2}}\right) \approx 1.00$

b. $\text{Prob} = \exp\left(\frac{-1.00 \times 10^{-3}}{5.36 \times 10^{-2}}\right) = 0.982$

c. $\text{Prob} = \exp\left(\frac{-1.00}{5.36 \times 10^{-2}}\right) = 7.84 \times 10^{-9}$

27–39. At an altitude of 150 km, the pressure is about 2×10^{-6} torr and the temperature is about 500 K. Assuming for simplicity that the air consists entirely of nitrogen, calculate the mean free path under these conditions. What is the average collision frequency?

Using Equation 27.51,

$$\begin{aligned} l &= \frac{RT}{2^{1/2}N_A\sigma P} \\ &= \frac{(8.3145\text{ J·mol}^{-1}\text{·K}^{-1})(500\text{ K})}{2^{1/2}(6.022 \times 10^{23}\text{ mol}^{-1})(0.450 \times 10^{-18}\text{ m}^2)(2 \times 10^{-6}\text{ torr})}\left(\frac{760\text{ torr}}{101325\text{ Pa}}\right) \\ &= 40.7\text{ m} \end{aligned}$$

Then

$$z_A = \frac{\langle u \rangle}{l} = \left(\frac{8RT}{\pi M}\right)^{1/2}\frac{1}{l} = \frac{615\text{ m·s}^{-1}}{40.7\text{ m}} = 15.1\text{ s}^{-1}$$

27–40. The following table gives the pressure and temperature of the Earth's upper atmosphere as a function of altitude:

altitude/km	P/mbar	T/K
20.0	56	220
40.0	3.2	260
60.0	0.28	260
80.0	0.013	180

Assuming for simplicity that air consists entirely of nitrogen, calculate the mean free path at each of these conditions.

Again, use Equation 27.51 to express l in terms of T and P:

$$\begin{aligned}l &= \frac{R}{2^{1/2}N_A\sigma}\left(\frac{T}{P}\right)\\ &= \frac{8.3145\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}}{2^{1/2}(6.022\times10^{23}\ \mathrm{mol^{-1}})(0.450\times10^{-18}\ \mathrm{m^2})}\left(\frac{1\ \mathrm{Pa}}{100\ \mathrm{mbar}}\right)\left(\frac{T}{P}\right)\\ &= (2.1699\times10^{-7}\ \mathrm{K\cdot mbar^{-1}})\frac{T}{P}\end{aligned}$$

We can substitute the values given in the table to calculate the mean free path for each altitude:

altitude/km	l/m
20.0	8.52×10^{-7}
40.0	1.76×10^{-5}
60.0	2.01×10^{-4}
80.0	3.00×10^{-3}

27–41. Interstellar space has an average temperature of about 10 K and an average density of hydrogen atoms of about one hydrogen atom per cubic meter. Compute the mean free path of a hydrogen atom in interstellar space. Take the diameter of a hydrogen atom to be 100 pm.

We defined $\sigma = \pi d^2$ in Section 27–6, so $\sigma = \pi(100\times10^{-12}\ \mathrm{m})^2 = 3.142\times10^{-20}\ \mathrm{m^2}$. The density of hydrogen atoms is $1\ \mathrm{m^{-3}}$, so, from the equations directly preceding Equation 27.51,

$$l = \frac{1}{2^{1/2}\sigma\rho} = \frac{1}{2^{1/2}(3.14\times10^{-20}\ \mathrm{m^2})(1\ \mathrm{m^{-3}})} = 2\times10^{19}\ \mathrm{m}$$

27–42. Calculate the pressures at which the mean free path of a hydrogen molecule will be 100 μm, 1.00 mm, and 1.00 m at 20°C.

Using Equation 27.51 and σ from Table 27.3, we find

$$P = \frac{RT}{2^{1/2}N_A\sigma l} = \frac{(8.314\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}})(293.15\ \mathrm{K})}{2^{1/2}(6.022\times10^{23}\ \mathrm{mol^{-1}})(0.230\times10^{-18}\ \mathrm{m^2})}l^{-1}$$

$$P/\mathrm{Pa} = \frac{0.0124}{l/\mathrm{m}}$$

l/m	P/Pa	P/bar
1.00×10^{-4}	124	1.24×10^{-3}
1.00×10^{-3}	12.4	1.24×10^{-4}
1.00	0.0124	1.24×10^{-7}

27–43. Derive an expression for the distance, d, at which a fraction f of the molecules will have been scattered from a beam consisting initially of n_0 molecules. Plot d against f.

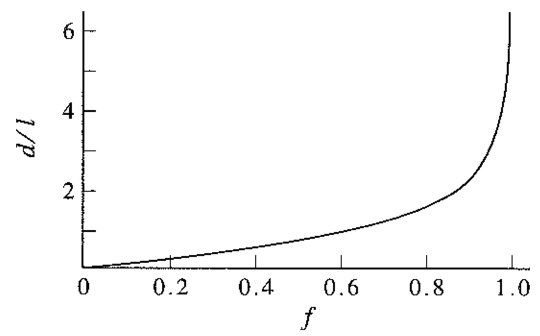
The probability of one of the n_0 molecules colliding between 0 and d is (Equation 27.55)

$$\text{Prob} = f = \int_0^d p(x)dx = \int_0^d \frac{1}{l}e^{-x/l}dx = 1 - e^{-d/l}$$

Solving for d in terms of f gives

$$d = -l\ln(1-f)$$

Below is a plot of d versus f.



27–44. Calculate the frequency of nitrogen–oxygen collisions per dm³ in air at the conditions given in Problem 27–40. Assume in this case that 80% of the molecules are nitrogen molecules.

We use Equations 27.58 to find σ_{N_2,O_2}, ρ_{N_2}, and ρ_{O_2} in terms of P and T:

$$\begin{aligned}\sigma_{N_2,O_2} &= \pi\left(\frac{d_{N_2}+d_{O_2}}{2}\right)^2\\ &= \pi\left(\frac{380\times10^{-12}\ \mathrm{m}+360\times10^{-12}\ \mathrm{m}}{2}\right)^2 = 4.30\times10^{-19}\ \mathrm{m^2}\\ \langle u_r\rangle &= \left(\frac{8k_BT}{\pi\mu}\right)^{1/2} = \left[\frac{8(8.3145\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}})(0.06002\ \mathrm{kg})T}{\pi(0.02802\ \mathrm{kg})(0.03200\ \mathrm{kg})}\right]^{1/2}\\ &= 37.65T^{1/2}\\ \rho_{N_2} &= \frac{N_AP_{N_2}}{RT} = \frac{(6.022\times10^{23}\ \mathrm{mol^{-1}})(0.80P)}{(8.3145\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}})T} = 5.79\times10^{22}\left(\frac{P}{T}\right)\\ \rho_{O_2} &= \frac{N_AP_{N_2}}{RT} = \frac{(6.022\times10^{23}\ \mathrm{mol^{-1}})(0.20P)}{(8.3145\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}})T} = 1.44\times10^{22}\left(\frac{P}{T}\right)\end{aligned}$$

where P is measured in Pa and T is measured in K. Substituting into Equation 27.57, we find

$$Z_{\mathrm{N_2,O_2}} = \sigma_{\mathrm{N_2,O_2}}\langle u_r\rangle\rho_{\mathrm{N_2}}\rho_{\mathrm{O_2}} = (4.30\times10^{-19}\ \mathrm{m^2})(37.65T^{1/2})(5.79\times10^{22})(1.44\times10^{22})\left(\frac{P}{T}\right)^2$$

altitude/km	$P/100$ Pa	T/K	$Z_{\mathrm{N_2,O_2}}/\mathrm{s^{-1}\cdot m^{-3}}$
20.0	56	220	1.31×10^{32}
40.0	3.2	260	3.32×10^{29}
60.0	0.28	260	2.54×10^{27}
80.0	0.013	180	9.51×10^{24}

27–45. Use Equation 27.58 to show that

$$\langle u_r\rangle = (\langle u_{\mathrm{A}}\rangle^2 + \langle u_{\mathrm{B}}\rangle^2)^{1/2}$$

Begin with Equation 27.58 and write μ as $m_{\mathrm{A}}m_{\mathrm{B}}/(m_{\mathrm{A}}+m_{\mathrm{B}})$:

$$\langle u_r\rangle = \left(\frac{8\pi k_{\mathrm{B}}T}{\pi\mu}\right)^{1/2} = \left[\frac{8\pi k_{\mathrm{B}}T}{\pi}\left(\frac{m_{\mathrm{A}}+m_{\mathrm{B}}}{m_{\mathrm{A}}m_{\mathrm{B}}}\right)\right]^{1/2} = \left[\frac{8\pi k_{\mathrm{B}}T}{\pi m_{\mathrm{B}}} + \frac{8\pi k_{\mathrm{B}}T}{\pi m_{\mathrm{A}}}\right]^{1/2} = \left[\langle u_{\mathrm{B}}\rangle^2 + \langle u_{\mathrm{A}}\rangle^2\right]^{1/2}$$

27–46. Modify the derivation of Equation 27.49 to consider the collision frequency of a molecule of type A with B molecules in a mixture of A and B. Derive Equation 27.57 directly from your answer.

The molecule of type A will sweep out a cylinder of diameter $2d_{\mathrm{A}}$. Since the type B molecules have a radius d_{B}, the effective target radius is given by $(d_{\mathrm{A}}+d_{\mathrm{B}})/2$. The number density of the B molecules is given by ρ_{B} and we replace m by μ, so the average speed is given by $\langle u_r\rangle$. Equation 27.49 then becomes

$$z_{\mathrm{A}} = \rho_{\mathrm{B}}\langle u_r\rangle\pi\left(\frac{d_{\mathrm{A}}+d_{\mathrm{B}}}{2}\right)^2 = \rho_{\mathrm{B}}\langle u_r\rangle\sigma_{\mathrm{AB}}$$

Since $Z_{\mathrm{AB}} = \rho_{\mathrm{A}}z_{\mathrm{A}}$, we find

$$Z_{\mathrm{AB}} = \sigma_{\mathrm{AB}}\langle u_r\rangle\rho_{\mathrm{A}}\rho_{\mathrm{B}} \tag{27.57}$$

27–47. Consider a mixture of methane and nitrogen in a 10.0 dm^3 container at 300 K with partial pressures $P_{\mathrm{CH_4}} = 65.0$ mbar and $P_{\mathrm{N_2}} = 30.0$ mbar. Use the equation that you derived in the previous problem to calculate the collision frequency of a methane molecule with nitrogen molecules. Also calculate the frequency of methane–nitrogen collisions per dm^3.

First find the necessary values of ρ, σ, and $\langle u_r\rangle$:

$$\rho_{\mathrm{CH_4}} = \frac{P_{\mathrm{CH_4}}}{k_{\mathrm{B}}T} = \frac{6500\ \mathrm{Pa}}{(1.3806\times10^{-23}\ \mathrm{J\cdot K^{-1}})(300\ \mathrm{K})} = 1.57\times10^{24}\ \mathrm{m^{-3}}$$

$$\rho_{\mathrm{N_2}} = \frac{P_{\mathrm{CH_4}}}{k_{\mathrm{B}}T} = \frac{3000\ \mathrm{Pa}}{(1.3806\times10^{-23}\ \mathrm{J\cdot K^{-1}})(300\ \mathrm{K})} = 7.24\times10^{23}\ \mathrm{m^{-3}}$$

$$\sigma_{\mathrm{CH_4,N_2}} = \pi\left(\frac{410\times10^{-12}\ \mathrm{m} + 380\times10^{-12}\ \mathrm{m}}{2}\right)^2 = 4.90\times10^{-19}\ \mathrm{m^2}$$

$$\langle u_r\rangle = \left[\frac{8RT(m_1+m_2)}{\pi m_1m_2}\right]^{1/2} = \left[\frac{8R(300\ \mathrm{K})(0.044062\ \mathrm{kg})}{\pi(0.02802\ \mathrm{kg})(0.016042\ \mathrm{kg})}\right]^{1/2} = 789\ \mathrm{m\cdot s^{-1}}$$

Now, using the equations from the previous problem,

$$z_{\mathrm{CH_4}} = \rho_{\mathrm{N_2}}\sigma_{\mathrm{CH_4,N_2}}\langle u_r\rangle = 2.80\times10^8\ \mathrm{s^{-1}}$$

$$Z_{\mathrm{CH_4,N_2}} = \rho_{\mathrm{CH_4}}z_{\mathrm{CH_4}} = 4.40\times10^{32}\ \mathrm{m^{-3}\cdot s^{-1}}$$

27–48. Calculate the average relative kinetic energy with which the molecules in a gas collide.

We know that the normalized average kinetic energy is given by

$$\langle\varepsilon_{\mathrm{K}}\rangle = \frac{\int\varepsilon f(\varepsilon)d\varepsilon}{\int f(\varepsilon)d\varepsilon}$$

where $f(\varepsilon)d\varepsilon$ is the distribution of kinetic energy. We can substitute $\varepsilon_r e^{-\varepsilon_r/k_{\mathrm{B}}T}$ for $f(\varepsilon)$ to write

$$\langle\varepsilon_{\mathrm{K}}\rangle = \frac{\int\varepsilon_r^2e^{-\varepsilon_r/k_{\mathrm{B}}T}d\varepsilon_r}{\int\varepsilon_re^{-\varepsilon_r/k_{\mathrm{B}}T}d\varepsilon_r} = \frac{2(k_{\mathrm{B}}T)^3}{(k_{\mathrm{B}}T)^2} = 2k_{\mathrm{B}}T$$

The following four problems deal with molecular effusion.

27–49. Equation 27.48 gives us the frequency of collisions that the molecules of a gas make with a surface area of the walls of the container. Suppose now we make a very small hole in the wall. If the mean free path of the gas is much larger than the width of the hole, any molecule that strikes the hole will leave the container without undergoing any collisions along the way. In this case, the molecules leave the container individually, independently of the others. The rate of flow through the hole will be small enough that the remaining gas is unaffected, and remains essentially in equilibrium. This process is called *molecular effusion*. Equation 27.48 can be applied to calculate the rate of molecular effusion. Show that Equation 27.48 can be expressed as

$$\text{effusion flux} = \frac{P}{(2\pi mk_{\mathrm{B}}T)^{1/2}} = \frac{N_{\mathrm{A}}P}{(2\pi MRT)^{1/2}} \tag{1}$$

where P is the pressure of the gas. Calculate the number of nitrogen molecules that effuse per second through a round hole of 0.010 mm diameter if the gas is at 25°C and one bar.

We begin with Equation 27.48:

$$\begin{aligned} z_{\mathrm{coll}} &= \frac{1}{4}\rho\langle u\rangle = \frac{1}{4}\left(\frac{P}{k_{\mathrm{B}}T}\right)\left(\frac{8k_{\mathrm{B}}T}{\pi m}\right)^{1/2} \\ &= \frac{P}{(2\pi mk_{\mathrm{B}}T)^{1/2}} = \frac{N_{\mathrm{A}}P}{(2\pi MRT)^{1/2}} \\ &= \frac{(6.022\times10^{23}\ \mathrm{mol^{-1}})^{1/2}(10^5\ \mathrm{Pa})}{[2\pi(0.02802\ \mathrm{kg\cdot mol^{-1}})(1.38\times10^{-23}\ \mathrm{J\cdot K^{-1}})(298\ \mathrm{K})]^{1/2}} \\ &= 2.88\times10^{27}\ \mathrm{m^{-2}\cdot s^{-1}} \end{aligned}$$

This will be the effusion flux of the gas. For a round hole of 0.010 mm diameter,

$$\text{molecules per second} = z_{\text{coll}}[\pi(0.005\times10^{-3}\text{ m})^2] = 2.26\times10^{17}\text{ s}^{-1}$$

27–50. Equation 1 of the previous problem can be used to determine vapor pressures of substances with very low vapor pressures. This was done by Irving Langmuir to measure the vapor pressure of tungsten at various temperatures in his investigation of tungsten filaments in light bulbs and vacuum tubes. (Langmuir, who was awarded the Nobel Prize in chemistry in 1932, worked for General Electric.) He estimated the rate of effusion by weighing the tungsten filament at the beginning and the end of each experimental run. Langmuir did these experiments around 1913, but his data appear in the *CRC Handbook of Chemistry and Physics* to this day. Use the following data to determine the vapor pressure of tungsten at each temperature and then determine the molar enthalpy of vaporization of tungsten.

T/K	effusion flux/$\text{g}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$
1200	3.21×10^{-23}
1600	1.25×10^{-14}
2000	1.76×10^{-9}
2400	4.26×10^{-6}
2800	1.10×10^{-3}
3200	6.38×10^{-3}

Note that the flux is given in units of $\text{g}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$, so we divide the flux by 1000 to have units of $\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$. Using Equation 1 of Problem 27–49 gives

$$P = (2\pi m k_{\text{B}} T)^{1/2}\times\frac{\text{effusion flux}}{1000\text{ g}\cdot\text{kg}^{-1}}$$
$$= AT^{1/2}\times\text{effusion flux}$$

Because we are going to plot $\ln P$ against $1/T$, we can write the above equation as

$$\ln P = \ln A + \ln T^{1/2} + \ln(\text{effusion flux})$$

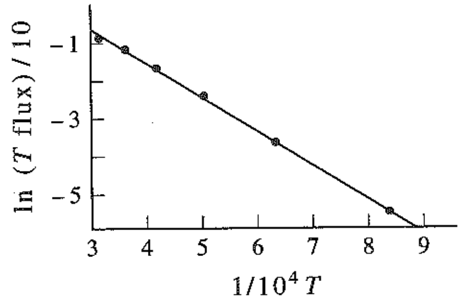
and, because A is a constant, we do not need to evaluate it. Thus we form the table of values

T/K	$T^{1/2}\times$ effusion flux
1200	1.11×10^{-21}
1600	5.00×10^{-13}
2000	7.87×10^{-8}
2400	2.08×10^{-4}
2800	5.89×10^{-2}
3200	0.361

Since $P\propto T^{1/2}\times$ effusion flux, the slope of the best-fit line to $\ln P$ versus $1/T$ will be equal to the slope of the best-fit line to $\ln(T^{1/2}\times\text{effusion flux})$ versus $1/T$. Recall (Chapter 23) that

$$\ln P = -\frac{\Delta_{\text{vap}}H}{RT} + \text{constant}$$

Therefore, the slope of the best-fit line to either plot described above will be equal to $-\Delta_{\text{vap}}H/R$.



The slope of this plot is −92830, and so $\Delta_{\text{vap}}H = 92830R = 772\text{ kJ}\cdot\text{mol}^{-1}$.

27–51. The vapor pressure of mercury can be determined by the effusion technique described in the previous problem. Given that 0.126 mg of mercury passed through a small hole of area 1.65 mm² in 2.25 hours at 0°C, calculate the vapor pressure of mercury in torr.

$$\text{effusion} = \left(\frac{0.126\times10^{-3}\text{ g}}{200.6\text{ g}\cdot\text{mol}^{-1}}\right)(6.022\times10^{23}\text{ molecule}\cdot\text{mol}^{-1})\left(\frac{1}{1.65\times10^{-6}\text{ m}^2}\right)$$
$$\times\left(\frac{1}{2.25\text{ hr}}\right)\left(\frac{1\text{ hr}}{3600\text{ s}}\right)$$
$$= 2.83\times10^{19}\text{ molecule}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$$
$$P = \text{effusion}\times(2\pi m k_{\text{B}} T)^{1/2}$$
$$= (2.83\times10^{19}\text{ molecule}\cdot\text{m}^{-2}\cdot\text{s}^{-1})\left[2\pi\left(\frac{0.2006\text{ kg}\cdot\text{mol}^{-1}}{6.022\times10^{23}\text{ molecule}\cdot\text{mol}^{-1}}\right)\right.$$
$$\left.\times(1.38\times10^{-23}\text{ J}\cdot\text{K}^{-1})(273.15\text{ K})\right]^{1/2}$$
$$= 2.51\times10^{-3}\text{ Pa}\left(\frac{760\text{ torr}}{101325\text{ Pa}}\right) = 1.89\times10^{-5}\text{ torr}$$

27–52. We can use Equation 1 of Problem 27–49 to derive an expression for the pressure as a function of time for an ideal gas that is effusing from its container. First show that

$$\text{rate of effusion} = -\frac{dN}{dt} = \frac{PA}{(2\pi m k_{\text{B}} T)^{1/2}}$$

where N is the number of molecules effusing and A is the area of the hole. At constant T and V,

$$-\frac{dN}{dt} = \frac{d}{dt}\left(\frac{PV}{k_{\text{B}}T}\right) = \frac{V}{k_{\text{B}}T}\frac{dP}{dt}$$

Now show that

$$P(t) = P(0)e^{-\alpha t}$$

where $\alpha = (k_{\text{B}}T/2\pi m)^{1/2}A/V$. Note that the pressure of the gas decreases exponentially with time.

The rate of effusion is given by dN/dt, since this represents how many molecules effuse per unit time. From Problem 27–49, we know the rate of effusion per unit area (effusion flux), so multiplying by the area of the hole from which effusion occurs will give the rate of effusion and

$$\text{rate of effusion} = -\frac{dN}{dt} = \frac{PA}{(2\pi m k_{\text{B}} T)^{1/2}}$$

For an ideal gas, $nN_A = PV/k_BT$ and so $N = PV/k_BT$. If T and V are held constant, we find

$$\frac{dN}{dt} = \frac{d}{dt}\left(\frac{PV}{k_BT}\right) = \frac{V}{k_BT}\frac{dP}{dt}$$

Use the first equation for rate of effusion to write

$$-\frac{V}{k_BT}\frac{dP}{dt} = \frac{PA}{(2\pi m k_BT)^{1/2}}$$

$$-\frac{dP}{dt} = \left(\frac{k_BT}{2\pi m}\right)^{1/2}\frac{A}{V}P = \alpha P$$

The solution to this equation is (as in the derivation of Equation 27.53)

$$P(t) = P(0)e^{-\alpha t}$$

27–53. How would you interpret the velocity distribution

$$h(v_x, v_y, v_z) = \left(\frac{m}{2\pi k_BT}\right)^{3/2}\exp\left[-\frac{m}{2k_BT}\left\{(v_x - a)^2 + (v_y - b)^2 + (v_z - c)^2\right\}\right]$$

This is the velocity distribution relative to an overall translational motion of the system with velocity $a\mathbf{i} + b\mathbf{j} + c\mathbf{k}$.

CHAPTER 28

Chemical Kinetics I: Rate Laws

PROBLEMS AND SOLUTIONS

28–1. For each of the following chemical reactions, calculate the equilibrium extent of reaction at 298.15 K and one bar. (See Section 26–4.)

a. $H_2(g) + Cl_2(g) \rightleftharpoons 2\,HCl(g)$ $\quad \Delta_rG^\circ = -190.54\ \text{kJ}\cdot\text{mol}^{-1}$

Initial amounts: one mole of $H_2(g)$ and $Cl_2(g)$ and no HCl(g).

b. $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$ $\quad \Delta_rG^\circ = 173.22\ \text{kJ}\cdot\text{mol}^{-1}$

Initial amounts: one mole of $N_2(g)$ and $O_2(g)$ and no NO(g).

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a. At equilibrium, there will be $(1 - \xi_{eq})$ moles of $H_2(g)$ and $Cl_2(g)$, and $2\xi_{eq}$ moles of HCl(g). We can write the partial pressures of each species at equilibrium as

$$P_{H_2} = P_{Cl_2} = \frac{(1 - \xi_{eq})}{2}P \qquad \text{and} \qquad P_{HCl} = \frac{2\xi_{eq}}{2}P = \xi_{eq}P$$

where P is the total pressure. We can then write K_P, by definition, as

$$K_P = \frac{P_{HCl}^2}{P_{H_2}P_{Cl_2}} = \frac{(2\xi_{eq})^2}{(1 - \xi_{eq})^2}$$

Equating $\ln K_P$ to $-\Delta_rG^\circ/RT$ (Equation 26.11) allows us to write

$$\ln K_P = \frac{190.54\ \text{kJ}\cdot\text{mol}^{-1}}{(8.3145 \times 10^{-3}\ \text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(298.15\ \text{K})} = 76.862$$

$$K_P = 2.40 \times 10^{33}$$

$$\frac{(2\xi_{eq})^2}{(1 - \xi_{eq})^2} = 2.40 \times 10^{33}$$

Solving this equation for ξ_{eq} gives a value of $\xi_{eq} = 1$ mol.

b. At equilibrium, there will be $(1 - \xi_{eq})$ moles of $N_2(g)$ and $O_2(g)$, and $2\xi_{eq}$ moles of NO(g). We can write the partial pressures of each species at equilibrium as

$$P_{N_2} = P_{O_2} = \frac{(1 - \xi_{eq})}{2}P \qquad \text{and} \qquad P_{NO} = \frac{2\xi_{eq}}{2}P = \xi_{eq}P$$