

# CHEM 26300 (Chemical Kinetics and Dynamics) Problem Sets

Steven Labalme

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# 1 The Kinetic Theory of Gases

From McQuarrie and Simon (1997).

## Chapter 27

- 4/11: **27-5.** Arrange the following gases in order of increasing root-mean-square speed at the same temperature: O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>, NO<sub>2</sub>, <sup>235</sup>UF<sub>6</sub>, <sup>238</sup>UF<sub>6</sub>.

*Answer.* The root mean square speed is given by

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

Thus, since the temperature is constant by hypothesis, the root mean square speed ordering will be entirely a function of the molar mass (and inversely proportional to it at that). It follows since

$$\begin{aligned} M(\text{O}_2) &= 32.00 \text{ g/mol} \\ M(\text{N}_2) &= 28.02 \text{ g/mol} \\ M(\text{H}_2\text{O}) &= 18.02 \text{ g/mol} \\ M(\text{CO}_2) &= 44.01 \text{ g/mol} \\ M(\text{NO}_2) &= 46.01 \text{ g/mol} \\ M(^{235}\text{UF}_6) &= 349.08 \text{ g/mol} \\ M(^{238}\text{UF}_6) &= 352.04 \text{ g/mol} \end{aligned}$$

that

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

□

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

$$u_{\text{sound}} = \sqrt{\frac{5RT}{3M}}$$

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.

*Answer.* We have that

$$\frac{u_{\text{rms}}}{u_{\text{sound}}} = \frac{\sqrt{3RT/M}}{\sqrt{5RT/3M}}$$

$$\boxed{\frac{u_{\text{rms}}}{u_{\text{sound}}} = \sqrt{9/5}}$$

The root mean square speed for an argon atom at 20 °C is given by

$$u_{\text{rms}}(\text{Ar}) = \sqrt{\frac{3(8.31 \frac{\text{J}}{\text{mol K}})(293 \text{ K})}{0.03995 \frac{\text{kg}}{\text{mol}}}}$$

$$\boxed{u_{\text{rms}}(\text{Ar}) = 428 \text{ m/s}}$$

Similarly, the speed of sound in argon at 20 °C is given by

$$u_{\text{sound}}(\text{Ar}) = \sqrt{\frac{5(8.31 \frac{\text{J}}{\text{mol K}})(293 \text{ K})}{3(0.03995 \frac{\text{kg}}{\text{mol}})}}$$

$$u_{\text{sound}}(\text{Ar}) = 319 \text{ m/s}$$

and thus that

$$\frac{u_{\text{rms}}(\text{Ar})}{u_{\text{sound}}(\text{Ar})} = \frac{428 \text{ m/s}}{319 \text{ m/s}} = 1.34 \approx \sqrt{9/5}$$

as desired.  $\square$

- 27-12.** We can use the equation for  $f(u_x)$  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  $-u_{x0} \leq u_x \leq u_{x0}$  is given by

$$\begin{aligned} \text{Prob}\{-u_{x0} \leq u_x \leq u_{x0}\} &= \sqrt{\frac{m}{2\pi k_B T}} \int_{-u_{x0}}^{u_{x0}} e^{-mu_x^2/2k_B T} du_x \\ &= 2\sqrt{\frac{m}{2\pi k_B T}} \int_0^{u_{x0}} e^{-mu_x^2/2k_B T} du_x \end{aligned}$$

Now let  $mu_x^2/2k_B T = w^2$  to get the cleaner looking expression

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

where  $w_0 = u_{x0}\sqrt{m/2k_B T}$ .

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

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

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

$z$	$\text{erf}(z)$	$z$	$\text{erf}(z)$
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

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

Calculate the probability that  $-\sqrt{2k_B T/m} \leq u_x \leq \sqrt{2k_B T/m}$ .

*Answer.* The probability distribution  $f(u_x)$  of the  $x$ -components of the velocity of a system of molecules is given by

$$f(u_x) = \sqrt{\frac{m}{2\pi k_B T}} e^{-mu_x^2/2k_B T}$$

It follows that the probability that the  $x$ -component of the velocity of a molecule lies between  $u_x$  and  $u_x + du_x$  is  $f(u_x) du_x$ . Thus, to calculate the total probability that the  $x$ -component of the velocity of a molecule lies within the range  $-u_{x0} \leq u_x \leq u_{x0}$ , we can use an integral to sum all of the infinitesimal probabilities  $f(u_x) du_x$  in that range as follows.

$$\begin{aligned}\text{Prob}\{-u_{x0} \leq u_x \leq u_{x0}\} &= \int_{-u_{x0}}^{u_{x0}} f(u_x) du_x \\ &= \sqrt{\frac{m}{2\pi k_B T}} \int_{-u_{x0}}^{u_{x0}} e^{-mu_x^2/2k_B T} du_x \\ &= 2\sqrt{\frac{m}{2\pi k_B T}} \int_0^{u_{x0}} e^{-mu_x^2/2k_B T} du_x\end{aligned}$$

Note that the last equality holds because  $f(u_x) = g(u_x^2)$ , where  $u_x^2$  is an even function and hence  $f$  is even. Now define the function  $w(u_x)$  by

$$w^2 = \frac{mu_x^2}{2k_B T}$$

Since  $w$  is monotonically increasing on the range  $[0, u_{x0}]$ , and

$$\begin{aligned}w(0) &= 0 & w(u_{x0}) &= u_{x0} \sqrt{\frac{m}{2k_B T}} & 2w \frac{dw}{du_x} &= \frac{2mu_x}{2k_B T} \\ & & & & \frac{2wk_B T}{mu_x} dw &= du_x \\ & & & & \frac{2u_x \sqrt{m/2k_B T} k_B T}{mu_x} dw &= du_x \\ & & & & \sqrt{\frac{2k_B T}{m}} dw &= du_x\end{aligned}$$

we may substitute it into the above integral using the  $u$ -substitution method to yield

$$\begin{aligned}\text{Prob}\{-u_{x0} \leq u_x \leq u_{x0}\} &= 2\sqrt{\frac{m}{2\pi k_B T}} \cdot \sqrt{\frac{2k_B T}{m}} \int_{w(0)}^{w(u_{x0})} e^{-w^2} dw \\ &= \frac{2}{\sqrt{\pi}} \int_0^{w_0} e^{-w^2} dw\end{aligned}$$

Naturally, the above equals  $\text{erf}(w_0)$  by the definition of the error function.

Lastly, if  $u_{x0} = \sqrt{2k_B T/m}$ , then

$$w_0 = u_{x0} \sqrt{m/2k_B T} = \sqrt{2k_B T/m} \cdot \sqrt{m/2k_B T} = 1$$

It follows that

$$\begin{aligned}\text{Prob}\{-\sqrt{2k_B T/m} \leq u_x \leq \sqrt{2k_B T/m}\} &= \text{erf}(w_0) \\ &= \text{erf}(1)\end{aligned}$$

$$\boxed{\text{Prob}\{-\sqrt{2k_B T/m} \leq u_x \leq \sqrt{2k_B T/m}\} = 0.84270}$$

□

- 27-20.** Show that the variance of the equation  $I(\nu) \propto e^{-mc^2(\nu-\nu_0)^2/2\nu_0^2 k_B T}$  is given by  $\sigma^2 = \nu_0^2 k_B T/mc^2$ . Calculate  $\sigma$  for the  $3p \ ^2P_{3/2}$  to  $3s \ ^2S_{1/2}$  transition in atomic sodium vapor (see Figure 8.4 on McQuarrie and Simon (1997, p. 307)) at 500 K.

*Answer.* As per MathChapter B of McQuarrie and Simon (1997),  $I(\nu)$  is a Gaussian distribution, i.e., is of the form  $e^{-(x-\langle x \rangle)^2/2\sigma^2}$  where  $\sigma$  is the standard deviation. It follows by comparing this general form with the given equation for  $I(\nu)$  that

$$\sigma^2 = \frac{\nu_0^2 k_B T}{mc^2}$$

From Figure 8.4, we have that

$$\lambda(3p^2P_{3/2} \rightarrow 3s^2S_{1/2}) = 5.8899 \times 10^3 \text{ \AA}$$

Thus,

$$\nu_0 = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{5.8899 \times 10^{-7} \text{ m}} = 5.090 \times 10^{14} \text{ s}^{-1}$$

Therefore, we have that

$$\begin{aligned} \sigma &= \sqrt{\frac{\nu_0^2 R T}{M c^2}} \\ &= \sqrt{\frac{(5.090 \times 10^{14} \frac{1}{\text{s}})^2 (8.31 \frac{\text{J}}{\text{mol K}}) (500 \text{ K})}{(0.02299 \frac{\text{kg}}{\text{mol}}) (2.998 \times 10^8 \frac{\text{m}}{\text{s}})^2}} \\ \sigma &= 7.22 \times 10^8 \text{ s}^{-1} \end{aligned}$$

□

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

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

where  $x_0 = u_0 \sqrt{m/2k_B T}$ . This integral cannot be expressed in terms of any known function and must be integrated numerically. Use Simpson's rule or any other integration routine to evaluate  $\text{Prob}\{u \leq \sqrt{2k_B T/m}\}$ .

*Answer.* As in Problem 27-12, we have that

$$\begin{aligned} \text{Prob}\{u \leq u_0\} &= \int_0^{u_0} F(u) du \\ &= 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} \int_0^{u_0} u^2 e^{-mu^2/2k_B T} du \\ &= 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} \cdot \sqrt{\frac{2k_B T}{m}} \int_{x(0)}^{x(u_0)} \frac{2k_B T x^2}{m} e^{-x^2} dx \\ &= 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} \cdot \left( \frac{2k_B T}{m} \right)^{1/2} \cdot \left( \frac{2k_B T}{m} \right) \int_0^{x_0} x^2 e^{-x^2} dx \\ &= \frac{4}{\sqrt{\pi}} \int_0^{x_0} x^2 e^{-x^2} dx \end{aligned}$$

We now evaluate

$$\text{Prob}\{u \leq \sqrt{2k_B T/m}\} = \frac{4}{\sqrt{\pi}} \int_0^1 x^2 e^{-x^2} dx$$

using Simpson's rule with four subdivisions, each having height  $h = 0.25$ , as follows.

$$\begin{aligned} \text{Prob}\{u \leq \sqrt{2k_B T/m}\} &\approx \frac{4}{\sqrt{\pi}} \cdot \frac{0.25}{3} [g(0) + 4g(0.25) + 2g(0.5) + 4g(0.75) + g(1)] \\ &= \frac{1}{3\sqrt{\pi}} (0 + 4 \cdot 0.059 + 2 \cdot 0.195 + 4 \cdot 0.321 + 0.367) \end{aligned}$$

$$\boxed{\text{Prob}\{u \leq \sqrt{2k_B T/m}\} \approx 0.429}$$

□

- 27-27.** Derive an expression for  $\sigma_\varepsilon^2 = \langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2$  from the equation for  $F(\varepsilon) d\varepsilon$ . Now form the ratio  $\sigma_\varepsilon / \langle \varepsilon \rangle$ . What does this say about the fluctuation in  $\varepsilon$ ?

*Answer.* We know from class that

$$\langle \varepsilon \rangle = \frac{3}{2} k_B T$$

Additionally, we can derive that

$$\begin{aligned} \langle \varepsilon^2 \rangle &= \int_0^\infty \varepsilon^2 F(\varepsilon) d\varepsilon \\ &= \frac{2\pi}{(\pi k_B T)^{3/2}} \int_0^\infty \varepsilon^2 \cdot \varepsilon^{1/2} e^{-\varepsilon/k_B T} d\varepsilon \\ &= \frac{2\pi}{(\pi k_B T)^{3/2}} \int_0^\infty \varepsilon^{5/2} e^{-\varepsilon/k_B T} d\varepsilon \\ &= \frac{2\pi}{(\pi k_B T)^{3/2}} \cdot \frac{(5)(3)(1)}{(2/k_B T)^{(5+1)/2}} \left( \frac{\pi}{1/k_B T} \right)^{1/2} \\ &= \frac{15}{4} (k_B T)^2 \end{aligned}$$

where we have evaluated the integral using Table 27.1 in my notes. Thus, we have that

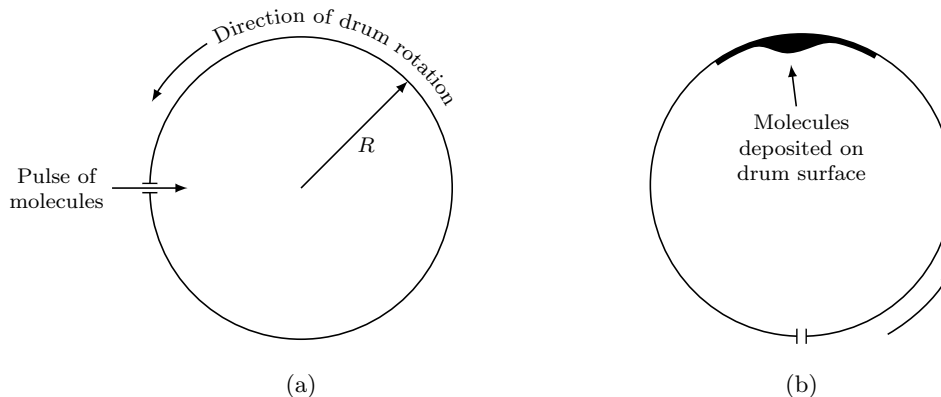
$$\begin{aligned} \sigma_\varepsilon^2 &= \langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2 \\ &= \frac{15}{4} (k_B T)^2 - \frac{9}{4} (k_B T)^2 \\ \sigma_\varepsilon^2 &= \frac{3}{2} (k_B T)^2 \end{aligned}$$

Taking

$$\frac{\sigma_\varepsilon}{\langle \varepsilon \rangle} = \frac{\sqrt{3/2} k_B T}{3 k_B T / 2} = \left( \frac{2}{3} \right)^{1/2}$$

reveals that the fluctuation in  $\varepsilon$  is sizeable with respect to the average energy. □

- 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 enters a rotating hollow drum. Let  $R$  be the radius of the drum,  $\nu$  be the 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.

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

$$I(s) ds = \frac{A}{s^5} e^{-m(4\pi R^2 \nu)^2 / 2k_B T s^2} ds$$

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

*Answer.* Once the molecule enters the drum, it must travel a distance  $2R$  before striking the opposite side. It will cover this distance in  $2R/u$  seconds. Moreover, we know that the drum rotates once every  $\nu$  seconds, so the drum will perform  $2R\nu/u$  of a rotation in  $2R/u$  seconds. Finally, since a point on the inner surface of the drum moves a distance of  $2\pi R$  with every rotation, the inner surface of the drum will move a distance

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

over the course of the molecule's trip across the interior of the drum. Succinctly,

$$s = \frac{2R \text{ meters}}{1} \times \frac{1 \text{ second}}{u \text{ meters}} \times \frac{\nu \text{ rotations}}{1 \text{ second}} \times \frac{2\pi R \text{ meters}}{1 \text{ rotation}} = \frac{4\pi R^2 \nu}{u}$$

The equation for  $dz_{\text{coll}}$  describes the collision frequency of atoms moving in a single direction with a single speed. Since the atoms leave the oven in a single direction, the only variable factor on which  $dz_{\text{coll}}$  depends is  $uF(u) du \propto u^3 e^{-mu^2/2k_B T} du$ , as desired.

Let  $I(u) du$  be the distribution of molecules that strike the inner surface of the cylinder with speed between  $u$  and  $u + du$ . By the above,

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

Since we have that

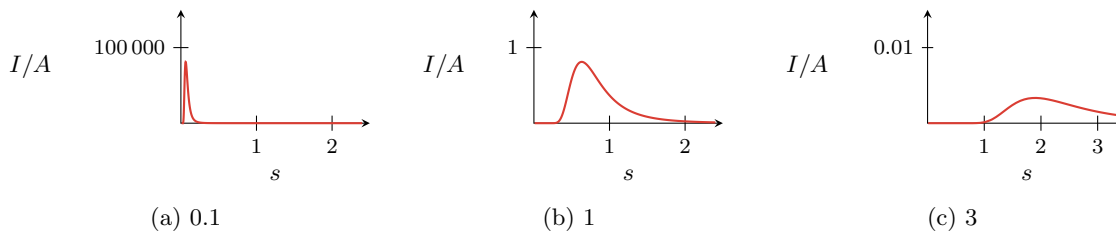
$$u = \frac{4\pi R^2 \nu}{s} \quad du = -\frac{4\pi R^2 \nu}{s^2} ds$$

we know that

$$I(s) ds \propto \left( \frac{4\pi R^2 \nu}{s} \right)^3 e^{-m(4\pi R^2 \nu / s)^2 / 2k_B T} \cdot -\frac{4\pi R^2 \nu}{s^2} ds = \frac{A}{s^5} e^{-m(4\pi R^2 \nu)^2 / 2k_B T s^2} ds$$

where we have incorporated all external constants into the proportionality constant  $A$ .

The following are the desired plots



□



**27-36.** On the average, what is the time between collisions of a xenon atom at 300 K and...

(a) One torr;

*Answer.* The collision frequency is

$$z_A = \sqrt{2} \rho \sigma \langle u \rangle = \sqrt{2} \cdot \frac{PN_A}{RT} \cdot \sigma_{\text{Xe}} \cdot \sqrt{\frac{8RT}{\pi M}}$$

It follows that the time  $t$  between collisions is

$$\begin{aligned} t &= \frac{1}{z_A} \\ &= \frac{\sqrt{\pi RTM}}{4N_A P \sigma_{\text{Xe}}} \\ &= \frac{\sqrt{\pi (8.31 \frac{\text{J}}{\text{mol K}})(300 \text{ K})(0.03995 \frac{\text{kg}}{\text{mol}})}}{4N_A (133 \text{ Pa})(7.50 \times 10^{-19} \text{ m}^2)} \\ &\boxed{t = 7.36 \times 10^{-8} \text{ s}} \end{aligned}$$

□

(b) One bar.

*Answer.* As in part (a), we have that

$$\begin{aligned} t &= \frac{\sqrt{\pi RTM}}{4N_A P \sigma_{\text{Xe}}} \\ &= \frac{\sqrt{\pi (8.31 \frac{\text{J}}{\text{mol K}})(300 \text{ K})(0.03995 \frac{\text{kg}}{\text{mol}})}}{4N_A (10^5 \text{ Pa})(7.50 \times 10^{-19} \text{ m}^2)} \\ &\boxed{t = 9.79 \times 10^{-11} \text{ s}} \end{aligned}$$

□

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

Altitude (km)	Pressure (mbar)	Temperature (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.

*Answer.* The mean free path is given by

$$l = \frac{1}{\sqrt{2} \rho \sigma_{\text{N}_2}} = \frac{RT}{\sqrt{2} P N_A \sigma_{\text{N}_2}}$$

Thus, plugging in

$$R = 8.31 \frac{\text{J}}{\text{mol K}} \qquad \sigma_{\text{N}_2} = 4.50 \times 10^{-19} \text{ m}^2$$

and the pressure and temperature from the above table in bars and kelvins, respectively, we have that

$$\begin{aligned}l(20.0 \text{ km}) &= 8.5 \times 10^{-7} \text{ m} \\l(40.0 \text{ km}) &= 1.8 \times 10^{-5} \text{ m} \\l(60.0 \text{ km}) &= 2.0 \times 10^{-4} \text{ m} \\l(80.0 \text{ km}) &= 3.0 \times 10^{-3} \text{ m}\end{aligned}$$

□

## 2 Kinetic Theory II / Rate Laws

### Chapter 27

From McQuarrie and Simon (1997).

- 4/18: **27-42.** Calculate the pressures at which the mean free path of a hydrogen molecule will be 100  $\mu\text{m}$ , 1.00 mm, and 1.00 m at 20  $^{\circ}\text{C}$ .

*Answer.* For a hydrogen molecule, we have  $\sigma = 2.30 \times 10^{-19} \text{ m}^2$ . This combined with  $T = 293 \text{ K}$ ,  $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ , and the various values of  $l$  yields

$P(100 \mu\text{m}) = 124 \text{ Pa}$ $P(1.00 \text{ mm}) = 12.4 \text{ Pa}$ $P(1.00 \text{ m}) = 0.0124 \text{ Pa}$
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□

- 27-44.** Calculate the frequency of nitrogen-oxygen collisions per  $\text{dm}^3$  in air at the conditions given in Problem 27-40. Assume in this case that 80% of the molecules are nitrogen molecules.

*Answer.* We have that

$$\begin{aligned}
 Z_{\text{N}_2\text{O}_2} &= \sigma_{\text{N}_2\text{O}_2} \langle u_r \rangle \rho_{\text{N}_2} \rho_{\text{O}_2} \\
 &= \pi \left( \frac{d_{\text{N}_2} + d_{\text{O}_2}}{2} \right)^2 \cdot \left( \frac{8k_{\text{B}}T}{\pi\mu} \right)^{1/2} \cdot \frac{P_{\text{N}_2} N_{\text{A}}}{RT} \cdot \frac{P_{\text{O}_2} N_{\text{A}}}{RT} \\
 &= \pi(0.8P)(0.2P) \left[ \frac{N_{\text{A}}(d_{\text{N}_2} + d_{\text{O}_2})}{RT} \right]^2 \cdot \left[ \frac{k_{\text{B}}T(m_{\text{N}_2} + m_{\text{O}_2})}{2\pi m_{\text{N}_2} m_{\text{O}_2}} \right]^{1/2} \\
 &= [0.4PN_{\text{A}}(d_{\text{N}_2} + d_{\text{O}_2})]^2 \left[ \frac{\pi(M_{\text{N}_2} + M_{\text{O}_2})}{2M_{\text{N}_2}M_{\text{O}_2}(RT)^3} \right]^{1/2}
 \end{aligned}$$

Thus, plugging in

$$\begin{aligned}
 d_{\text{N}_2} &= 3.80 \times 10^{-10} \text{ m} & d_{\text{O}_2} &= 3.60 \times 10^{-10} \text{ m} \\
 M_{\text{N}_2} &= 0.02802 \text{ kg mol}^{-1} & M_{\text{O}_2} &= 0.03200 \text{ kg mol}^{-1}
 \end{aligned}$$

as well as  $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$  and the various values of  $P$  and  $T$  from Problem 27-40 in Pascals and Kelvins, respectively, we have that

$Z_{\text{N}_2\text{O}_2}(20.0 \text{ km}) = 1.31 \times 10^{32} \text{ s}^{-1} \text{ m}^{-3}$ $Z_{\text{N}_2\text{O}_2}(40.0 \text{ km}) = 3.32 \times 10^{29} \text{ s}^{-1} \text{ m}^{-3}$ $Z_{\text{N}_2\text{O}_2}(60.0 \text{ km}) = 2.54 \times 10^{27} \text{ s}^{-1} \text{ m}^{-3}$ $Z_{\text{N}_2\text{O}_2}(80.0 \text{ km}) = 9.51 \times 10^{24} \text{ s}^{-1} \text{ m}^{-3}$
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□

- 27-49.** The following equation gives us the frequency of collisions that the molecules of a gas make with a surface area of the walls of the container.

$$z_{\text{coll}} = \frac{1}{A} \frac{dN_{\text{coll}}}{dt} = \frac{\rho \langle u \rangle}{4}$$

Suppose now that 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, independent 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**. The above equation can be applied to calculate the rate of molecular effusion. Show that the above equation can be expressed as

$$\text{effusion flux} = \frac{P}{\sqrt{2\pi m k_B T}} = \frac{P N_A}{\sqrt{2\pi M R T}} \quad (1)$$

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.

*Answer.* There are

$$\frac{\rho \langle u \rangle}{4} = \frac{P N_A}{4 R T} \cdot \left( \frac{8 R T}{\pi M} \right)^{1/2} = \frac{P N_A}{\sqrt{2\pi M R T}}$$

collisions per second per unit area. But since flux is current (i.e., number of would-be collisions) per unit area, the above gives the effusion flux, as desired.

As to the second part of the question, we have from the original equation that

$$\begin{aligned} \frac{dN_{\text{coll}}}{dt} &= \frac{P N_A A}{\sqrt{2\pi M R T}} \\ \frac{dN}{dt} &= \frac{P N_A A}{\sqrt{2\pi M R T}} \end{aligned}$$

where  $dN/dt$  denotes the number of molecules that effuse through a hole of size  $A = \pi(d/2)^2$  per second. Thus, plugging in

$$P = 10^5 \text{ Pa} \quad d = 10^{-5} \text{ m} \quad M = 0.02802 \text{ kg mol}^{-1} \quad R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1} \quad T = 298 \text{ }^\circ\text{C}$$

we have that

$$N = 2.26 \times 10^{17} \text{ s}^{-1}$$

□

- 27-52.** We can use Equation 1 of Problem 25-49 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

$$\text{rate of effusion} = \frac{dN}{dt} = \frac{P A}{\sqrt{2\pi m k_B T}}$$

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

$$\frac{dN}{dt} = \frac{d}{dt} \left( \frac{P V}{k_B T} \right) = \frac{V}{k_B T} \frac{dP}{dt}$$

Now show that

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

where  $\alpha = A\sqrt{k_B T/2\pi m}/V$ . Note that the pressure of the gas decreases exponentially with time.

*Answer.* As per the second part of Problem 27-49, we have

$$\frac{dN}{dt} = \frac{P N_A A}{\sqrt{2\pi M R T}} = \frac{P A}{\sqrt{2\pi m k_B T}}$$

as desired.

If we redefine  $N$  as the number of molecules in the container (i.e., so that  $dN \rightarrow -dN$ ), then it follows that

$$\begin{aligned}\frac{dP}{dt} &= -\frac{k_B T}{V} \frac{dN}{dt} \\ &= -\frac{k_B T}{V} \frac{PN_A A}{\sqrt{2\pi MRT}} \\ &= -\frac{A}{V} \sqrt{\frac{k_B T}{2\pi m}} P \\ &= -\alpha P \\ \int_{P(0)}^{P(t)} \frac{dP}{P} &= \int_0^t -\alpha dt \\ \ln \frac{P(t)}{P(0)} &= e^{-\alpha t} \\ P(t) &= P(0)e^{-\alpha t}\end{aligned}$$

as desired. □

## Chapter 28

*From McQuarrie and Simon (1997).*

**28-7.** Derive the integrated rate law for a reaction that is zero order in reactant concentration.

*Answer.* If the reaction is zero order in reactant concentration, then the (differential) rate law is of the form

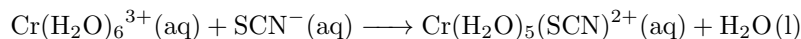
$$\begin{aligned}v(t) &= k[A]^0[B]^0 \dots \\ -\frac{d[A]}{dt} &= k\end{aligned}$$

We may integrate the above from the initial concentration  $[A]_0$  at time  $t = 0$  to the current concentration  $[A]$  at time  $t$  as follows.

$$\begin{aligned}\int_{[A]_0}^{[A]} d[A] &= \int_0^t -k dt \\ \boxed{[A] = -kt + [A]_0}\end{aligned}$$

□

**28-10.** Consider the reaction described by



for which the following initial rate data were obtained at 298.15 K.

$[\text{Cr}(\text{H}_2\text{O})_6^{3+}]_0$ (mol dm <sup>-3</sup> )	$[\text{SCN}^-]_0$ (mol dm <sup>-3</sup> )	$v_0$ (mol dm <sup>-3</sup> s <sup>-1</sup> )
$1.21 \times 10^{-4}$	$1.05 \times 10^{-5}$	$2.11 \times 10^{-11}$
$1.46 \times 10^{-4}$	$2.28 \times 10^{-5}$	$5.53 \times 10^{-11}$
$1.66 \times 10^{-4}$	$1.02 \times 10^{-5}$	$2.82 \times 10^{-11}$
$1.83 \times 10^{-4}$	$3.11 \times 10^{-5}$	$9.44 \times 10^{-11}$

Determine the rate law for the reaction and the rate constant at 298.15 K. Assume the orders are integers.

*Answer.* Let the four trials in the above table be labeled 1 through 4 going down. No two trials have the same measured initial concentration in either reactant, but trials 1 and 3 have fairly close values of  $[\text{SCN}^-]_0$ , so we will approximate these as having the same value of  $[\text{SCN}^-]_0$ . Under this assumption, the method of initial rates gives us

$$m_{\text{Cr}(\text{H}_2\text{O})_6^{3+}} = \frac{\ln(v_1/v_3)}{\ln([\text{Cr}(\text{H}_2\text{O})_6^{3+}]_1/[\text{Cr}(\text{H}_2\text{O})_6^{3+}]_3)} = 0.917 \approx 1$$

Having established this, we can use trials 1 and 4 to determine  $m_{\text{SCN}^-}$  as follows.

$$\begin{aligned} \frac{v_1}{v_4} &= \frac{k[\text{Cr}(\text{H}_2\text{O})_6^{3+}]_1[\text{SCN}^-]_1^{m_{\text{SCN}^-}}}{k[\text{Cr}(\text{H}_2\text{O})_6^{3+}]_4[\text{SCN}^-]_4^{m_{\text{SCN}^-}}} \\ \frac{v_1[\text{Cr}(\text{H}_2\text{O})_6^{3+}]_4}{v_4[\text{Cr}(\text{H}_2\text{O})_6^{3+}]_1} &= \left( \frac{[\text{SCN}^-]_1}{[\text{SCN}^-]_4} \right)^{m_{\text{SCN}^-}} \\ m_{\text{SCN}^-} &= \frac{\ln \left( \frac{v_1[\text{Cr}(\text{H}_2\text{O})_6^{3+}]_4}{v_4[\text{Cr}(\text{H}_2\text{O})_6^{3+}]_1} \right)}{\ln \left( \frac{[\text{SCN}^-]_1}{[\text{SCN}^-]_4} \right)} = 0.999 \approx 1 \end{aligned}$$

It follows that the differential rate law for the reaction is of the form

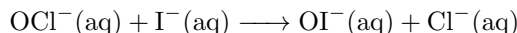
$$-\frac{d[\text{Cr}(\text{H}_2\text{O})_6^{3+}]}{dt} = -\frac{d[\text{SCN}^-]}{dt} = k[\text{Cr}(\text{H}_2\text{O})_6^{3+}][\text{SCN}^-]$$

Thus, we can determine  $k$  by performing a linear regression on a plot of  $-v_0$  vs.  $[\text{Cr}(\text{H}_2\text{O})_6^{3+}][\text{SCN}^-]$ . Indeed, running such a regression gives us the final rate law

$$v = 1.66 \times 10^{-2} [\text{Cr}(\text{H}_2\text{O})_6^{3+}][\text{SCN}^-]$$

□

**28-11.** Consider the base-catalyzed reaction



Use the following initial-rate data to determine the rate law and the corresponding rate constant for the reaction.

$[\text{OCl}^-]$ (mol dm <sup>-3</sup> )	$[\text{I}^-]$ (mol dm <sup>-3</sup> )	$[\text{OH}^-]$ (mol dm <sup>-3</sup> )	$v_0$ (mol dm <sup>-3</sup> s <sup>-1</sup> )
$1.62 \times 10^{-3}$	$1.62 \times 10^{-3}$	0.52	$3.06 \times 10^{-4}$
$1.62 \times 10^{-3}$	$2.88 \times 10^{-3}$	0.52	$5.44 \times 10^{-4}$
$2.71 \times 10^{-3}$	$1.62 \times 10^{-3}$	0.84	$3.16 \times 10^{-4}$
$1.62 \times 10^{-3}$	$2.88 \times 10^{-3}$	0.91	$3.11 \times 10^{-4}$

*Answer.* Let the four trials in the above table be labeled 1 through 4 going down. By a direct application of the method of initial rates,

$$\begin{aligned} m_{\text{I}^-} &= \frac{\ln(v_1/v_2)}{\ln([\text{I}^-]_1/[\text{I}^-]_2)} = 1 \\ m_{\text{OH}^-} &= \frac{\ln(v_2/v_4)}{\ln([\text{OH}^-]_2/[\text{OH}^-]_4)} = -0.999 \approx -1 \end{aligned}$$

Adapting the technique from Problem 28-10 developed for  $m_{\text{SCN}^-}$ , we have that

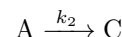
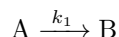
$$m_{\text{OCl}^-} = \frac{\ln \left( \frac{v_1[\text{OH}^-]_1}{v_3[\text{OH}^-]_3} \right)}{\ln \left( \frac{[\text{OCl}^-]_1}{[\text{OCl}^-]_3} \right)} = 0.995 \approx 1$$

Thus, taking another linear regression inspired by the technique of Problem 28-10, we have that the final rate law is

$$v = 60.7 \frac{[\text{OCl}^-][\text{I}^-]}{[\text{OH}^-]}$$

□

**28-17.** Show that if A reacts to form either B or C according to



then

$$[\text{A}] = [\text{A}]_0 e^{-(k_1+k_2)t}$$

Now show that  $t_{1/2}$ , the half-life of A, is given by

$$t_{1/2} = \frac{0.693}{k_1 + k_2}$$

Show that  $[\text{B}]/[\text{C}] = k_1/k_2$  for all times  $t$ . For the set of initial conditions  $[\text{A}] = [\text{A}]_0$ ,  $[\text{B}]_0 = [\text{C}]_0 = 0$ , and  $k_2 = 4k_1$ , plot  $[\text{A}]$ ,  $[\text{B}]$ , and  $[\text{C}]$  as a function of time on the same graph.

*Answer.* For this setup, the differential rate law is

$$-\frac{d[\text{A}]}{dt} = k_1[\text{A}] + k_2[\text{A}]$$

It follows by integrating as in Problem 28-7 that

$$[\text{A}] = [\text{A}]_0 e^{-(k_1+k_2)t}$$

Moving on, the half-life is defined by the following equation, which we can algebraically manipulate into the desired expression.

$$\begin{aligned} [\text{A}]_0/2 &= [\text{A}]_0 e^{-(k_1+k_2)t_{1/2}} \\ 1/2 &= e^{-(k_1+k_2)t_{1/2}} \\ t_{1/2} &= -\frac{\ln(1/2)}{k_1 + k_2} \\ &\approx \frac{0.693}{k_1 + k_2} \end{aligned}$$

Moving on again, we know that

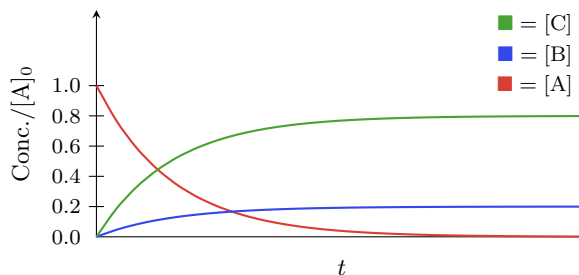
$$\begin{aligned} \frac{d[\text{B}]}{dt} &= k_1[\text{A}] & \frac{d[\text{C}]}{dt} &= k_2[\text{A}] \\ \frac{d[\text{B}]}{dt} &= k_1[\text{A}]_0 e^{-(k_1+k_2)t} & \frac{d[\text{C}]}{dt} &= k_2[\text{A}]_0 e^{-(k_1+k_2)t} \\ \int_0^{[\text{B}]} d[\text{B}] &= \int_0^t k_1[\text{A}]_0 e^{-(k_1+k_2)t} dt & \int_0^{[\text{C}]} d[\text{C}] &= \int_0^t k_2[\text{A}]_0 e^{-(k_1+k_2)t} dt \\ [\text{B}] &= \frac{k_1}{k_1 + k_2} [\text{A}]_0 (1 - e^{-(k_1+k_2)t}) & [\text{C}] &= \frac{k_2}{k_1 + k_2} [\text{A}]_0 (1 - e^{-(k_1+k_2)t}) \end{aligned}$$

Thus,

$$\frac{[\text{B}]}{[\text{C}]} = \frac{\frac{k_1}{k_1+k_2} [\text{A}]_0 (1 - e^{-(k_1+k_2)t})}{\frac{k_2}{k_1+k_2} [\text{A}]_0 (1 - e^{-(k_1+k_2)t})} = \frac{k_1}{k_2}$$

for all  $t$ , as desired.

For the last request, we have the following.



□

**28-24.** In this problem, we will derive the left equation below from the right equation below.

$$kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[A][B]_0}{[B][A]_0} \qquad -\frac{d[A]}{dt} = k[A][B]$$

Use the reaction stoichiometry of the chemical equation  $A + B \longrightarrow \text{products}$  to show that  $[B] = [B]_0 - [A]_0 + [A]$ . Use this result to show that the differential equation on the right above can be written as

$$-\frac{d[A]}{dt} = k[A]([B]_0 - [A]_0 + [A])$$

Now separate the variables and then integrate the resulting equation subject to its initial conditions to obtain the desired result, the integrated equation on the left above.

*Answer.* As per the given chemical equation, every unit of A consumed necessitates that a corresponding unit of B is consumed and vice versa. Mathematically,

$$\begin{aligned} \Delta[B] &= \Delta[A] \\ [B] - [B]_0 &= [A] - [A]_0 \\ [B] &= [B]_0 - [A]_0 + [A] \end{aligned}$$

It follows by direct substitution that

$$-\frac{d[A]}{dt} = k[A]([B]_0 - [A]_0 + [A])$$

Integrating yields

$$\begin{aligned} -\frac{d[A]}{dt} &= k[A]([B]_0 - [A]_0 + [A]) \\ \int_0^t k \, dt &= - \int_{[A]_0}^{[A]} \frac{d[A]}{[A]([B]_0 - [A]_0 + [A])} \\ &= -\frac{1}{[B]_0 - [A]_0} \int_{[A]_0}^{[A]} \left( \frac{d[A]}{[A]} - \frac{d[A]}{[B]_0 - [A]_0 + [A]} \right) \\ kt &= \frac{1}{[A]_0 - [B]_0} \left( \ln \frac{[A]}{[A]_0} - \ln \frac{[B]_0 - [A]_0 + [A]}{[B]_0 - [A]_0 + [A]_0} \right) \\ &= \frac{1}{[A]_0 - [B]_0} \left( \ln \frac{[A]}{[A]_0} - \ln \frac{[B]}{[B]_0} \right) \\ &= \frac{1}{[A]_0 - [B]_0} \ln \frac{[A][B]_0}{[B][A]_0} \end{aligned}$$

as desired, where we have used the method of partial fractions to enable integration. □



**28-25.** The equation

$$kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[A][B]_0}{[B][A]_0}$$

is indeterminate if  $[A]_0 = [B]_0$ . Use L'Hôpital's rule to show that the above equation reduces to one of the following equations when  $[A]_0 = [B]_0$ .

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt \qquad \frac{1}{[B]} = \frac{1}{[B]_0} + kt$$

(Hint: Let  $[A] = [B] + x$  and  $[A]_0 = [B]_0 + x$ .)

*Answer.* The hint is justified since  $[A]_0$  and  $[B]_0$  will be offset by some real number we may call  $x$ , and the difference between  $[A]$  and  $[B]$  at any time  $t$  will naturally be the same in a reaction where both reactant coefficients are one. Taking the hint, we have

$$\begin{aligned} kt &= \frac{1}{[B]_0 + x - [B]_0} \ln \frac{([B] + x)[B]_0}{[B]([B]_0 + x)} \\ &= \frac{1}{x} \ln \frac{([B] + x)[B]_0}{[B]([B]_0 + x)} \\ &= \frac{\ln([B] + x) + \ln[B]_0 - \ln[B] - \ln([B]_0 + x)}{x} \end{aligned}$$

Applying L'Hôpital's rule, we have

$$\begin{aligned} kt &= \lim_{x \rightarrow 0} \frac{\ln([B] + x) + \ln[B]_0 - \ln[B] - \ln([B]_0 + x)}{x} \\ &= \lim_{x \rightarrow 0} \frac{\frac{d}{dx}(\ln([B] + x) + \ln[B]_0 - \ln[B] - \ln([B]_0 + x))}{\frac{d}{dx}(x)} \\ &= \lim_{x \rightarrow 0} \frac{\frac{1}{[B] + x} - \frac{1}{[B]_0 + x}}{1} \\ &= \frac{1}{[B]} - \frac{1}{[B]_0} \end{aligned}$$

as desired. □

## Application

- 1) Name one HW problem you would like to develop into a thought experiment or relate to a literature article.
- 2) Describe how the idea or conclusion from the HW problem applies to the research idea in 1-2 paragraphs (word limit: 300). Once again, this can either be a thought experiment or an experiment found in the literature.
- 3) You do not need to derive any equations in this short discussion. Use your intuition and focus on the big picture.
- 4) Please cite the literature if you link the HW problem to anyone (author names, titles, journal name, volume numbers, and page numbers).

*Answer.* I would like to discuss and build upon Problem 28-25, which begins the process of intuitively rationalizing the rate law for a reaction that is first-order in each reactant and second-order overall. Another way that we can think about it is by noting that by their coefficients, the concentrations of A and B decrease by the same amount  $x$  with each passing instant. We note that because of the structure of the fraction on the right-hand side of the equation, as  $x \rightarrow [B]$ , the change in the denominator will begin to play an outsized

role in determining the value of the fraction. This tempers the rate at which  $[A], [B]$  can change, reflecting the fact that the change in concentration/reaction rate will slow down as one component or the other gets close to being exhausted. Another pattern we can observe is what happens to the rate if we double both initial concentrations. In this case, the fraction out front would change (assuming  $[A]_0 \neq [B]_0$ ), but the fraction within the logarithm would not. This reflects the fact that the initial rate would double, but the curve will be essentially the same, just stretched. Continuing on in such a manner, I believe I gain a better and better understanding for why this equation has such an at-first strange form.  $\square$

## References

McQuarrie, D. A., & Simon, J. D. (1997). *Physical chemistry: A molecular approach*. University Science Books.