

CHEM 26300 (Chemical Kinetics and Dynamics) Problem Sets

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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: O₂, N₂, H₂O, CO₂, NO₂, ²³⁵UF₆, ²³⁸UF₆.

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

$$M(\text{O}_2) = 32.00 \text{ g/mol}$$

$$M(\text{N}_2) = 28.02 \text{ g/mol}$$

$$M(\text{H}_2\text{O}) = 18.02 \text{ g/mol}$$

$$M(\text{CO}_2) = 44.01 \text{ g/mol}$$

$$M(\text{NO}_2) = 46.01 \text{ g/mol}$$

$$M(^{235}\text{UF}_6) = 349.08 \text{ g/mol}$$

$$M(^{238}\text{UF}_6) = 352.04 \text{ g/mol}$$

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

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

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

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

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

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

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 σ 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 σ 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 ε ?

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 1.1 in my notes. Thus, we have that

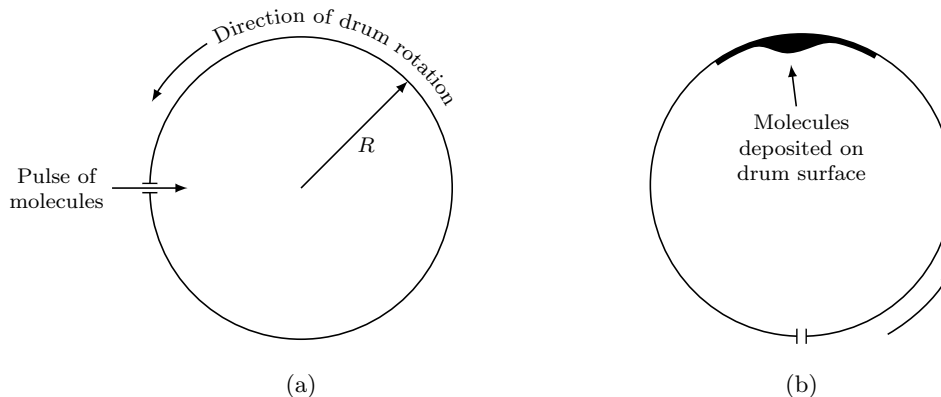
$$\begin{aligned} \sigma_\varepsilon^2 &= \langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2 \\ &= \frac{15}{4} (k_B T)^2 - \frac{9}{4} (k_B T)^2 \\ \sigma_\varepsilon^2 &= \frac{3}{2} (k_B T)^2 \end{aligned}$$

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 ε 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, ν 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_{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 ν 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_{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_{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

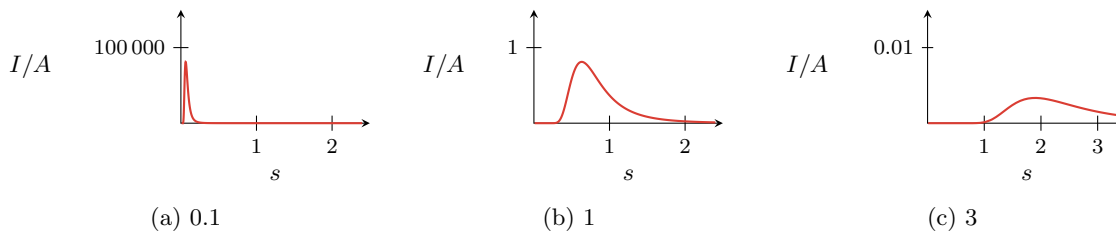
$$u = \frac{4\pi R^2 \nu}{s} \quad du = -\frac{4\pi R^2 \nu}{s^2} ds$$

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

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

It follows that the time t between collisions is

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

□

(b) One bar.

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

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

□

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

$$l = \frac{1}{\sqrt{2}\rho\sigma_{N_2}} = \frac{RT}{\sqrt{2}PN_A\sigma_{N_2}}$$

Thus, plugging in

$$R = 8.31 \frac{\text{J}}{\text{mol K}} \qquad \sigma_{N_2} = 4.50 \times 10^{-19} \text{ m}^2$$

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 μm , 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

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

□

- 27-44.** Calculate the frequency of nitrogen-oxygen collisions per 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

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

□

- 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

$$\frac{dN_{\text{coll}}}{dt} = \frac{P N_A A}{\sqrt{2\pi M R T}}$$

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

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

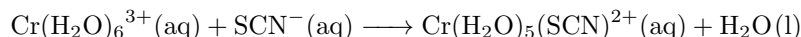
$$\begin{aligned}v(t) &= k[A]^0[B]^0 \dots \\ -\frac{d[A]}{dt} &= k\end{aligned}$$

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 ⁻³)	$[\text{SCN}^-]_0$ (mol dm ⁻³)	v_0 (mol dm ⁻³ s ⁻¹)
1.21×10^{-4}	1.05×10^{-5}	2.11×10^{-11}
1.46×10^{-4}	2.28×10^{-5}	5.53×10^{-11}
1.66×10^{-4}	1.02×10^{-5}	2.82×10^{-11}
1.83×10^{-4}	3.11×10^{-5}	9.44×10^{-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_{SCN^-} as follows.

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

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 the following v_0 vs. $[\text{Cr}(\text{H}_2\text{O})_6^{3+}][\text{SCN}^-]$ data.

$[\text{Cr}(\text{H}_2\text{O})_6^{3+}][\text{SCN}^-]$	v_0
1.27×10^{-9}	2.11×10^{-11}
3.33×10^{-9}	5.53×10^{-11}
1.69×10^{-9}	2.82×10^{-11}
5.69×10^{-9}	9.44×10^{-11}

Indeed, we can run such a regression as follows. First off, note that

$$\begin{aligned} \sum [\text{Cr}(\text{H}_2\text{O})_6^{3+}][\text{SCN}^-] &= (1.27 \times 10^{-9}) + (3.33 \times 10^{-9}) + (1.69 \times 10^{-9}) + (5.69 \times 10^{-9}) \\ &= 1.20 \times 10^{-8} \end{aligned}$$

$$\begin{aligned} \sum v_0 &= (2.11 \times 10^{-11}) + (5.53 \times 10^{-11}) + (2.82 \times 10^{-11}) + (9.44 \times 10^{-11}) \\ &= 1.99 \times 10^{-10} \end{aligned}$$

$$\begin{aligned} \sum ([\text{Cr}(\text{H}_2\text{O})_6^{3+}][\text{SCN}^-] \cdot v_0) &= (1.27 \times 10^{-9})(2.11 \times 10^{-11}) + (3.33 \times 10^{-9})(5.53 \times 10^{-11}) \\ &\quad + (1.69 \times 10^{-9})(2.82 \times 10^{-11}) + (5.69 \times 10^{-9})(9.44 \times 10^{-11}) \\ &= (2.68 \times 10^{-20}) + (1.84 \times 10^{-19}) + (4.77 \times 10^{-20}) + (5.37 \times 10^{-19}) \\ &= 7.96 \times 10^{-19} \end{aligned}$$

$$\begin{aligned} \sum ([\text{Cr}(\text{H}_2\text{O})_6^{3+}][\text{SCN}^-])^2 &= (1.27 \times 10^{-9})^2 + (3.33 \times 10^{-9})^2 + (1.69 \times 10^{-9})^2 + (5.69 \times 10^{-9})^2 \\ &= (1.61 \times 10^{-18}) + (1.11 \times 10^{-17}) + (2.86 \times 10^{-18}) + (3.24 \times 10^{-17}) \\ &= 4.80 \times 10^{-17} \end{aligned}$$

Then we have by plugging into the linear regression slope formula that

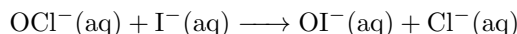
$$\begin{aligned}
 m &= \frac{\sum [\text{Cr}(\text{H}_2\text{O})_6^{3+}][\text{SCN}^-] \cdot \sum v_0 - 4 \sum ([\text{Cr}(\text{H}_2\text{O})_6^{3+}][\text{SCN}^-] \cdot v_0)}{(\sum [\text{Cr}(\text{H}_2\text{O})_6^{3+}][\text{SCN}^-])^2 - 4 \sum ([\text{Cr}(\text{H}_2\text{O})_6^{3+}][\text{SCN}^-])^2} \\
 &= \frac{2.39 \times 10^{-18} - 3.18 \times 10^{-18}}{1.44 \times 10^{-16} - 1.92 \times 10^{-16}} \\
 &= \frac{-7.90 \times 10^{-19}}{-4.8 \times 10^{-17}} \\
 &= 1.65 \times 10^{-2}
 \end{aligned}$$

The result gives us the final rate law

$$v = 1.65 \times 10^{-2} [\text{Cr}(\text{H}_2\text{O})_6^{3+}][\text{SCN}^-]$$

□

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 ⁻³)	$[\text{I}^-]$ (mol dm ⁻³)	$[\text{OH}^-]$ (mol dm ⁻³)	v_0 (mol dm ⁻³ s ⁻¹)
1.62×10^{-3}	1.62×10^{-3}	0.52	3.06×10^{-4}
1.62×10^{-3}	2.88×10^{-3}	0.52	5.44×10^{-4}
2.71×10^{-3}	1.62×10^{-3}	0.84	3.16×10^{-4}
1.62×10^{-3}	2.88×10^{-3}	0.91	3.11×10^{-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_{SCN^-} , we have that

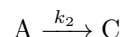
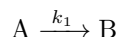
$$m_{\text{OCl}^-} = \frac{\ln\left(\frac{v_1[\text{OH}^-]_1}{v_3[\text{OH}^-]_3}\right)}{\ln\left(\frac{[\text{OCl}^-]_1}{[\text{OCl}^-]_3}\right)} = 0.995 \approx 1$$

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

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

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

Answer. For this setup, the differential rate law is

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

It follows by integrating as in Problem 28-7 that

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

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

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

Moving on again, we know that

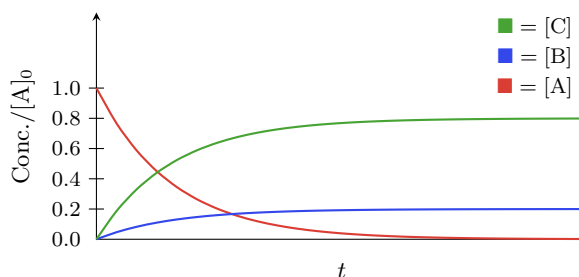
$$\begin{aligned} \frac{d[B]}{dt} &= k_1[A] & \frac{d[C]}{dt} &= k_2[A] \\ \frac{d[B]}{dt} &= k_1[A]_0 e^{-(k_1+k_2)t} & \frac{d[C]}{dt} &= k_2[A]_0 e^{-(k_1+k_2)t} \\ \int_0^{[B]} d[B] &= \int_0^t k_1[A]_0 e^{-(k_1+k_2)t} dt & \int_0^{[C]} d[C] &= \int_0^t k_2[A]_0 e^{-(k_1+k_2)t} dt \\ [B] &= \frac{k_1}{k_1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

Thus,

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

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).

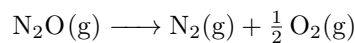
Answer. I would like to discuss and build upon Problem 28-25, which begins the process of intuitively rationalizing the rate law for a reaction that is first-order in each reactant and second-order overall. Another way that we can think about it is by noting that by their coefficients, the concentrations 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. □

3 Rate Laws II / Mechanisms

Chapter 28

From McQuarrie and Simon (1997).

4/25: **28-31.** The following data were obtained for the reaction



$[\text{N}_2\text{O}]_0/\text{mol dm}^{-3}$	1.674×10^{-3}	4.458×10^{-3}	9.300×10^{-3}	1.155×10^{-2}
$t_{1/2}/\text{s}$	1200	470	230	190

Assume the rate law for this reaction is

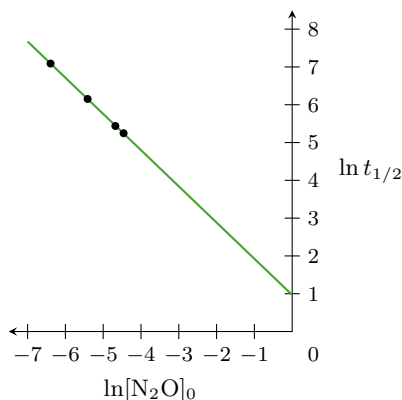
$$-\frac{d[\text{N}_2\text{O}]}{dt} = k[\text{N}_2\text{O}]^n$$

and use the equation for the half-life of an n^{th} -order reaction to determine the reaction order of N_2O by plotting $\ln t_{1/2}$ against $\ln[\text{A}]_0$. Calculate the rate constant for this decomposition reaction.

Answer. We have that

$$\begin{aligned} \ln(kt_{1/2}) &= \ln\left(\frac{1}{n-1} \frac{2^{n-1}-1}{[\text{A}]_0^{n-1}}\right) \\ \ln k + \ln t_{1/2} &= -\ln(n-1) + \ln(2^{n-1}-1) - (n-1)\ln[\text{A}]_0 \\ \ln t_{1/2} &= -(n-1)\ln[\text{A}]_0 + C \end{aligned}$$

where $C = \ln(2^{n-1}-1) - \ln(n-1) - \ln k$ is a constant. Thus, we can determine n by finding the best fit line on a plot of $\ln t_{1/2}$ vs. $\ln[\text{N}_2\text{O}]_0$ as follows.



The resultant line of best fit has slope approximately equal to 1, which means that

$$-(n-1) = 1$$

$$\boxed{n = 2}$$

It follows by plugging our four data points back into the equation

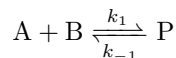
$$k = \frac{1}{(2-1)t_{1/2}} \frac{2^{2-1}-1}{[\text{N}_2\text{O}]_0^{2-1}} = \frac{1}{t_{1/2} \cdot [\text{N}_2\text{O}]_0}$$

and averaging the results that

$$\boxed{k = 0.47 \frac{\text{L}}{\text{mol s}}}$$

□

28-33. Consider the general chemical reaction



If we assume that both the forward and reverse reactions are first order in their respective reactants, the rate law is given by

$$\frac{d[P]}{dt} = k_1[A][B] - k_{-1}[P]$$

Now consider the response of this chemical reaction to a temperature jump. Let $[A] = [A]_{2,eq} + \Delta[A]$, $[B] = [B]_{2,eq} + \Delta[B]$, and $[P] = [P]_{2,eq} + \Delta[P]$, where the subscript “2,eq” refers to the new equilibrium state. Now use the fact that $\Delta[A] = \Delta[B] = -\Delta[P]$ to show that the above rate law becomes

$$\frac{d\Delta[P]}{dt} = k_1[A]_{2,eq}[B]_{2,eq} - k_{-1}[P]_{2,eq} - \{k_1([A]_{2,eq} + [B]_{2,eq}) + k_{-1}\}\Delta[P] + O(\Delta[P]^2)$$

Show that the first terms on the right side of this equation cancel and that the following two equations result.

$$\Delta[P] = \Delta[P]_0 e^{-t/\tau} \qquad \tau = \frac{1}{k_1([A]_{2,eq} + [B]_{2,eq}) + k_{-1}}$$

Answer. We have that

$$\begin{aligned} \frac{d}{dt}([P]_{2,eq} + \Delta[P]) &= k_1([A]_{2,eq} + \Delta[A])([B]_{2,eq} + \Delta[B]) - k_{-1}([P]_{2,eq} + \Delta[P]) \\ \frac{d\Delta[P]}{dt} &= k_1([A]_{2,eq}[B]_{2,eq} + [A]_{2,eq}\Delta[B] + \Delta[A][B]_{2,eq} + \Delta[A]\Delta[B]) - k_{-1}([P]_{2,eq} + \Delta[P]) \\ &= k_1([A]_{2,eq}[B]_{2,eq} - [A]_{2,eq}\Delta[P] - \Delta[P][B]_{2,eq} + \Delta[P]\Delta[P]) - k_{-1}([P]_{2,eq} + \Delta[P]) \\ &= k_1[A]_{2,eq}[B]_{2,eq} - k_{-1}[P]_{2,eq} - \{k_1([A]_{2,eq} + [B]_{2,eq}) + k_{-1}\}\Delta[P] + O(\Delta[P]^2) \end{aligned}$$

as desired, where $d[P]_{2,eq}/dt = 0$ because $[P]_{2,eq}$ is a constant, and we have bundled $k_1\Delta[P]^2$ into the $O(\Delta[P]^2)$ term.

Moreover, the first two terms on the right side of the bottom equation above equal zero since at equilibrium under the new conditions,

$$\frac{d[P]}{dt} = 0 = k_1[A]_{2,eq}[B]_{2,eq} - k_{-1}[P]_{2,eq}$$

Thus, ignoring the $O(\Delta[P]^2)$ term, we have that

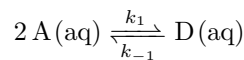
$$\begin{aligned} \frac{d\Delta[P]}{dt} &= -\{k_1([A]_{2,eq} + [B]_{2,eq}) + k_{-1}\}\Delta[P] \\ \frac{d\Delta[P]}{\Delta[P]} &= -\frac{dt}{1/\{k_1([A]_{2,eq} + [B]_{2,eq}) + k_{-1}\}} \\ \int_{\Delta[P]_0}^{\Delta[P]} \frac{d\Delta[P]}{\Delta[P]} &= \int_0^t -\frac{dt}{\tau} \\ \ln \frac{\Delta[P]}{\Delta[P]_0} &= -\frac{t}{\tau} \\ \Delta[P] &= \Delta[P]_0 e^{-t/\tau} \end{aligned}$$

where

$$\tau = \frac{1}{k_1([A]_{2,eq} + [B]_{2,eq}) + k_{-1}}$$

as desired. □

28-36. Consider the chemical reaction described by



If we assume the forward reaction is second order and the reverse reaction is first order, the rate law is given by

$$\frac{d[\text{D}]}{dt} = k_1[\text{A}]^2 - k_{-1}[\text{D}]$$

Now consider the response of this chemical reaction to a temperature jump. Let $[\text{A}] = [\text{A}]_{2,\text{eq}} + \Delta[\text{A}]$ and $[\text{D}] = [\text{D}]_{2,\text{eq}} + \Delta[\text{D}]$, where the subscript “2,eq” refers to the new equilibrium state. Now use the fact that $\Delta[\text{A}] = -2\Delta[\text{D}]$ to show that the rate law becomes

$$\frac{d\Delta[\text{D}]}{dt} = -(4k_1[\text{A}]_{2,\text{eq}} + k_{-1})\Delta[\text{D}] + O(\Delta[\text{D}]^2)$$

Show that if we ignore the $O(\Delta[\text{D}]^2)$ term, then

$$\Delta[\text{D}] = \Delta[\text{D}]_0 e^{-t/\tau}$$

where $\tau = 1/(4k_1[\text{A}]_{2,\text{eq}} + k_{-1})$.

Answer. Proceeding as in Problem 28-33, we have that

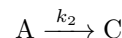
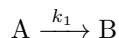
$$\begin{aligned} \frac{d}{dt}([\text{D}]_{2,\text{eq}} + \Delta[\text{D}]) &= k_1([\text{A}]_{2,\text{eq}} + \Delta[\text{A}])^2 - k_{-1}([\text{D}]_{2,\text{eq}} + \Delta[\text{D}]) \\ \frac{d\Delta[\text{D}]}{dt} &= k_1([\text{A}]_{2,\text{eq}}^2 + 2[\text{A}]_{2,\text{eq}}\Delta[\text{A}] + \Delta[\text{A}]^2) - k_{-1}([\text{D}]_{2,\text{eq}} + \Delta[\text{D}]) \\ &= k_1(-4[\text{A}]_{2,\text{eq}}\Delta[\text{D}] + 4\Delta[\text{D}]^2) - k_{-1}\Delta[\text{D}] \\ &= -(4k_1[\text{A}]_{2,\text{eq}} + k_{-1})\Delta[\text{D}] + O(\Delta[\text{D}]^2) \end{aligned}$$

so that integrating yields

$$\Delta[\text{D}] = \Delta[\text{D}]_0 e^{-t/\tau}$$

where $\tau = 1/(4k_1[\text{A}]_{2,\text{eq}} + k_{-1})$. □

28-46. Show that if A reacts to form either B or C according to



then E_a , the observed activation energy for the disappearance of A, is given by

$$E_a = \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2}$$

where E_1 is the activation energy for the first reaction and E_2 is the activation energy for the second reaction.

Answer. We have that

$$k_1 = A_1 e^{-E_1/RT}$$

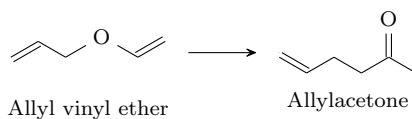
$$k_2 = A_2 e^{-E_2/RT}$$

Thus, since $k = k_1 + k_2$, we can plug into the original form of the Arrhenius equation to determine that

$$\begin{aligned}\frac{E_a}{RT^2} &= \frac{d \ln(k_1 + k_2)}{dT} \\ &= \frac{1}{k_1 + k_2} \frac{d}{dT} \left(A_1 e^{-E_1/RT} + A_2 e^{-E_2/RT} \right) \\ &= \frac{1}{k_1 + k_2} \left(A_1 e^{-E_1/RT} \cdot \frac{E_1}{RT^2} + A_2 e^{-E_2/RT} \cdot \frac{E_2}{RT^2} \right) \\ E_a &= \frac{1}{k_1 + k_2} (k_1 \cdot E_1 + k_2 \cdot E_2) \\ &= \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2}\end{aligned}$$

as desired. □

28-48. The gas-phase rearrangement reaction



has a rate constant of $6.015 \times 10^{-5} \text{ s}^{-1}$ at 420 K and a rate constant of $2.971 \times 10^{-3} \text{ s}^{-1}$ at 470 K. Calculate the values of the Arrhenius parameters A and E_a . Calculate the values of $\Delta^\ddagger H^\circ$ and $\Delta^\ddagger S^\circ$ at 420 K. Assume ideal-gas behavior.

Answer. Let

$$\begin{aligned}k_1 &= 6.015 \times 10^{-5} \text{ s}^{-1} & k_2 &= 2.971 \times 10^{-3} \text{ s}^{-1} \\ T_1 &= 420 \text{ K} & T_2 &= 470 \text{ K}\end{aligned}$$

Then

$$k_1 = A e^{-E_a/RT_1} \qquad k_2 = A e^{-E_a/RT_2}$$

so that

$$\begin{aligned}\frac{k_1}{k_2} &= \frac{A e^{-E_a/RT_1}}{A e^{-E_a/RT_2}} \\ &= e^{E_a/RT_2 - E_a/RT_1} \\ \ln \frac{k_1}{k_2} &= \frac{(T_1 - T_2) E_a}{RT_1 T_2} \\ E_a &= \frac{RT_1 T_2}{T_1 - T_2} \ln \frac{k_1}{k_2} \\ \boxed{E_a = 128.0 \frac{\text{kJ}}{\text{mol}}}\end{aligned}$$

and

$$\begin{aligned}A &= \frac{k_1}{e^{-E_a/RT_1}} \\ \boxed{A = 5.0 \times 10^{11} \text{ s}^{-1}}\end{aligned}$$

Additionally, since this is a unimolecular reaction, we have that

$$E_a = \Delta^\ddagger H^\circ + RT$$

$$\Delta^\ddagger H^\circ = E_a - RT$$

$$\Delta^\ddagger H^\circ = 124.5 \frac{\text{kJ}}{\text{mol}}$$

and

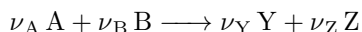
$$A = \frac{e k_B T}{h} e^{\Delta^\ddagger S^\circ / R}$$

$$\Delta^\ddagger S^\circ = R \ln \frac{A h}{e k_B T}$$

$$\Delta^\ddagger S^\circ = -32.1 \frac{\text{J}}{\text{mol K}}$$

at 420 K. □

- 28-49.** The kinetics of a chemical reaction can be followed by a variety of experimental techniques, including optical spectrometry, NMR spectroscopy, conductivity, resistivity, pressure changes, and volume changes. When using these techniques, we do not measure the concentration itself but we know that the observed signal is proportional to the concentration; the exact proportionality constant depends on the experimental technique and the species present in the chemical system. Consider the general reaction given by



where we assume that A is the limiting reagent so that $[A] \rightarrow 0$ as $t \rightarrow \infty$. Let p_i be the proportionality constant for the contribution of species i to S , the measured signal from the instrument. Explain why at any time t during the reaction, S is given by

$$S(t) = p_A[A] + p_B[B] + p_Y[Y] + p_Z[Z] \quad (1)$$

Show that the initial and final readings from the instrument are given by

$$S(0) = p_A[A]_0 + p_B[B]_0 + p_Y[Y]_0 + p_Z[Z]_0 \quad (2)$$

and

$$S(\infty) = p_B \left([B]_0 - \frac{\nu_B}{\nu_A} [A]_0 \right) + p_Y \left([Y]_0 + \frac{\nu_Y}{\nu_A} [A]_0 \right) + p_Z \left([Z]_0 + \frac{\nu_Z}{\nu_A} [A]_0 \right) \quad (3)$$

Combine Equations 1-3 to show that

$$[A] = [A]_0 \frac{S(t) - S(\infty)}{S(0) - S(\infty)}$$

(Hint: Be sure to express $[B]$, $[Y]$, and $[Z]$ in terms of their initial values, $[A]$ and $[A]_0$.)

Answer. If only species X exists *in situ* at time t , then $S(t) \propto [X]$ with proportionality constant p_X , where $[X]$ denotes the concentration of species X at time t . Therefore, since the total signal is the sum of all of the partial signals,

$$S(t) = \sum_X p_X [X] = p_A[A] + p_B[B] + p_Y[Y] + p_Z[Z]$$

It follows by direct substitution that

$$S(0) = p_A[A]_0 + p_B[B]_0 + p_Y[Y]_0 + p_Z[Z]_0 \quad (4)$$

where $[X]_0$ denotes the concentration of species X at time $t = 0$. Additionally, at time $t = \infty$, all of A (the limiting reagent) will have been consumed, and a proportional amount of all other species will have been created or consumed. For instance, if V is the volume of the reaction domain, then dimensional analysis tells us that $[A]_0 \cdot V$ moles of A will react with

$$\frac{[A]_0 \cdot V \text{ moles A}}{1} \times \frac{\nu_B \text{ moles B}}{\nu_A \text{ moles A}} = \frac{\nu_B}{\nu_A} [A]_0 \cdot V \text{ moles B}$$

Another way of looking at this is that the concentration of B will decrease by $\frac{\nu_B}{\nu_A} [A]_0$ over the course of the reaction, i.e., that the final concentration $[B]_\infty$ of B will be given by

$$[B]_\infty = [B]_0 - \frac{\nu_B}{\nu_A} [A]_0$$

Similarly, the concentration of the products will increase by a proportional amount. Thus, we have that

$$\begin{aligned} S(\infty) &= p_A [A]_\infty + p_B [B]_\infty + p_Y [Y]_\infty + p_Z [Z]_\infty \\ &= p_A \cdot 0 + p_B \left([B]_0 - \frac{\nu_B}{\nu_A} [A]_0 \right) + p_Y \left([Y]_0 + \frac{\nu_Y}{\nu_A} [A]_0 \right) + p_Z \left([Z]_0 + \frac{\nu_Z}{\nu_A} [A]_0 \right) \\ &= p_B \left([B]_0 - \frac{\nu_B}{\nu_A} [A]_0 \right) + p_Y \left([Y]_0 + \frac{\nu_Y}{\nu_A} [A]_0 \right) + p_Z \left([Z]_0 + \frac{\nu_Z}{\nu_A} [A]_0 \right) \end{aligned}$$

as desired.

To derive an expression for $[A]$ as a function of $S(t)$, we can first note that there are a number of similar terms between Equations 1, 2, and 3 that would cancel when adding or subtracting. As such, we can determine that

$$\begin{aligned} S(\infty) - S(0) &= p_B \left([B]_0 - \frac{\nu_B}{\nu_A} [A]_0 \right) + p_Y \left([Y]_0 + \frac{\nu_Y}{\nu_A} [A]_0 \right) + p_Z \left([Z]_0 + \frac{\nu_Z}{\nu_A} [A]_0 \right) \\ &\quad - p_A [A]_0 - p_B [B]_0 - p_Y [Y]_0 - p_Z [Z]_0 \\ &= -p_B \frac{\nu_B}{\nu_A} [A]_0 + p_Y \frac{\nu_Y}{\nu_A} [A]_0 + p_Z \frac{\nu_Z}{\nu_A} [A]_0 - p_A [A]_0 \\ S(0) - S(\infty) &= (p_A \nu_A + p_B \nu_B - p_Y \nu_Y - p_Z \nu_Z) \frac{[A]_0}{\nu_A} \end{aligned}$$

and

$$\begin{aligned} S(t) - S(0) &= p_A ([A] - [A]_0) + p_B ([B] - [B]_0) + p_Y ([Y] - [Y]_0) + p_Z ([Z] - [Z]_0) \\ &= p_A \cdot \frac{\nu_A}{\nu_A} ([A] - [A]_0) + p_B \cdot \frac{\nu_B}{\nu_A} ([A] - [A]_0) - p_Y \cdot \frac{\nu_Y}{\nu_A} ([A] - [A]_0) - p_Z \cdot \frac{\nu_Z}{\nu_A} ([A] - [A]_0) \\ &= (p_A \nu_A + p_B \nu_B - p_Y \nu_Y - p_Z \nu_Z) \frac{[A] - [A]_0}{\nu_A} \end{aligned}$$

It follows that

$$\begin{aligned} S(t) - S(\infty) &= [S(t) - S(0)] + [S(0) - S(\infty)] \\ &= (p_A \nu_A + p_B \nu_B - p_Y \nu_Y - p_Z \nu_Z) \frac{[A]}{\nu_A} \end{aligned}$$

so that

$$\begin{aligned} \frac{S(t) - S(\infty)}{S(0) - S(\infty)} &= \frac{(p_A \nu_A + p_B \nu_B - p_Y \nu_Y - p_Z \nu_Z) [A] / \nu_A}{(p_A \nu_A + p_B \nu_B - p_Y \nu_Y - p_Z \nu_Z) [A]_0 / \nu_A} \\ &= \frac{[A]}{[A]_0} \\ [A] &= [A]_0 \frac{S(t) - S(\infty)}{S(0) - S(\infty)} \end{aligned}$$

as desired. □

Chapter 29

From McQuarrie and Simon (1997).

29-5. Solve the differential equation

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

to obtain $[A] = [A]_0 e^{-k_1 t}$, and substitute this result into the differential equation

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

to obtain

$$\frac{d[I]}{dt} + k_2[I] = k_1[A]_0 e^{-k_1 t}$$

This equation is of the form (see the Zwillinger (2003), for example)

$$\frac{dy(x)}{dx} + p(x)y(x) = q(x)$$

a linear, first-order differential equation whose general solution is

$$y(x)e^{h(x)} = \int q(x)e^{h(x)} dx + c$$

where $h(x) = \int p(x) dx$ and c is a constant. Show that this solution leads to

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

Answer. As in Problem 28-33, we can integrate

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

to obtain $[A] = [A]_0 e^{-k_1 t}$. Substituting this into the rate law for the intermediate I yields

$$\begin{aligned} \frac{d[I]}{dt} &= k_1[A]_0 e^{-k_1 t} - k_2[I] \\ \frac{d[I]}{dt} + k_2[I] &= k_1[A]_0 e^{-k_1 t} \end{aligned}$$

Noting that this equation is of the described form with $y(x) = [I](t)$, $p(x) = k_2$, and $q(x) = k_1[A]_0 e^{-k_1 t}$, we can determine that

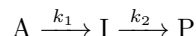
$$\begin{aligned} h(x) &= \int_0^x k_2 dx \\ &= k_2 x \end{aligned}$$

and thus that the general solution is

$$\begin{aligned} [I] \cdot e^{k_2 t} &= \int_0^t k_1[A]_0 e^{-k_1 t} \cdot e^{k_2 t} dt \\ [I] e^{k_2 t} &= k_1[A]_0 \int_0^t e^{(k_2 - k_1)t} dt \\ [I] e^{k_2 t} &= \frac{k_1[A]_0}{k_2 - k_1} (e^{(k_2 - k_1)t} - 1) \\ [I] &= \frac{k_1}{k_2 - k_1} [A]_0 (e^{-k_1 t} - e^{-k_2 t}) \end{aligned}$$

as desired. □

29-7. Consider the reaction mechanism

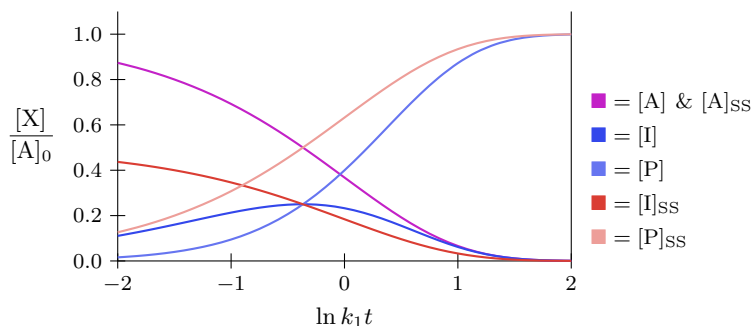


where $[A] = [A]_0$ and $[I]_0 = [P]_0 = 0$ at time $t = 0$. Use the exact solution to this kinetic scheme (below) to plot the time dependence of $[A]/[A]_0$, $[I]/[A]_0$, and $[P]/[A]_0$ versus $\log k_1 t$ for the case $k_2 = 2k_1$.

$$\begin{aligned} [A] &= [A]_0 e^{-k_1 t} \\ [I] &= \frac{k_1}{k_2 - k_1} [A]_0 (e^{-k_1 t} - e^{-k_2 t}) \\ [P] &= [A]_0 - [A] - [I] = [A]_0 \left\{ 1 + \frac{1}{k_1 - k_2} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right\} \end{aligned}$$

On the same graph, plot the time dependence of $[A]/[A]_0$, $[I]/[A]_0$, and $[P]/[A]_0$ using the expressions for $[A]$, $[I]$, and $[P]$ obtained using the steady-state approximation for $[I]$. Based on your results, can you use the steady-state approximation to model the kinetics of this reaction mechanism when $k_2 = 2k_1$?

Answer.



Based on the above graph, the steady-state approximation is not a good model in this case. As we can see, there are substantial differences in the values for $[P]$, and the two curves describing $[I]$ do not even have similar shapes. \square

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 deepen my understanding of Problem 28-46, which considers the observed activation energy as a function of the component activation energies for parallel reactions. One of the first things I noticed when looking at this problem was that the expression I'm deriving is a weighted average of the two component activation energies by the speeds at which said reactions occur. This should make intuitive sense. Consider how often E_1 being supplied to the system results in the formation of a molecule of B. This relative rate should be summed up somewhat by k_1 . A similar statement holds for E_2 , C, and k_2 . Moreover, if we

take $k_2 = 2k_1$ and $E_2 > E_1$ for the sake of having something tangible to work with, we should be able to imagine that supplying E_2 to the system means we are twice as likely to generate a molecule of C as we would be likely to generate a molecule of B upon supplying E_1 to the system. Thus, assuming all quantities of energy are supplied equally, we would observe that supplying slightly more than $(E_1 + E_2)/2$ results in the reaction happening at the optimum production-to-energy input ratio, as predicted by the expression given in Problem 28-46. \square

References

- McQuarrie, D. A., & Simon, J. D. (1997). *Physical chemistry: A molecular approach*. University Science Books.
- Zwillinger, D. (Ed.). (2003). *CRC standard mathematical tables and formulae* (31st). Chapman & Hall/CRC.