

# 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

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

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

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

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

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

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

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

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  $\sigma$  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

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

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 1.1 in my notes. Thus, we have that

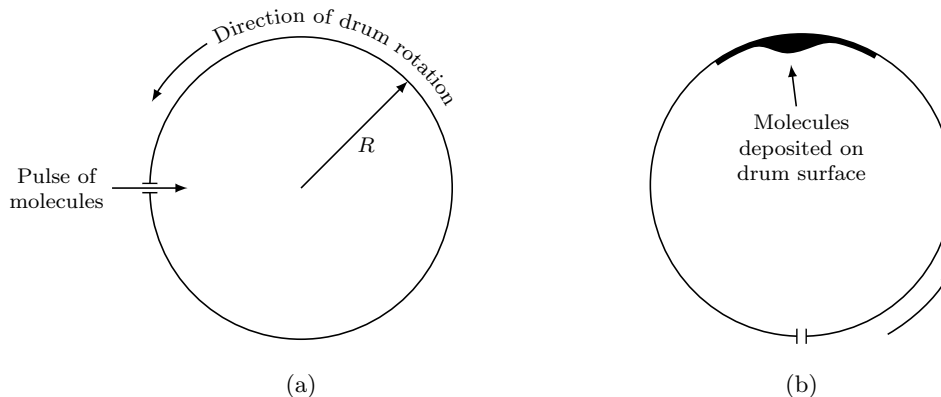
$$\begin{aligned} \sigma_\varepsilon^2 &= \langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2 \\ &= \frac{15}{4} (k_B T)^2 - \frac{9}{4} (k_B T)^2 \\ \sigma_\varepsilon^2 &= \frac{3}{2} (k_B T)^2 \end{aligned}$$

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  $\varepsilon$  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

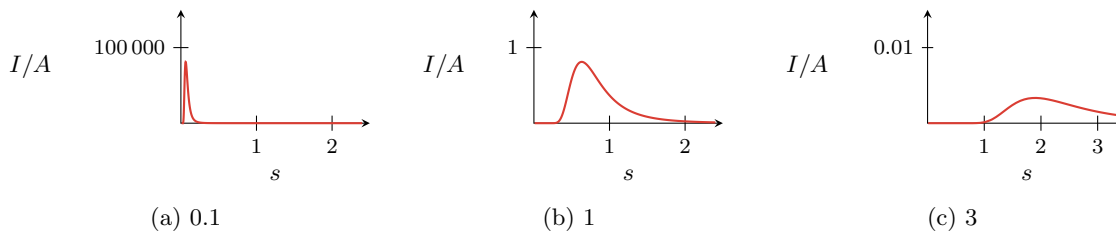
$$u = \frac{4\pi R^2 \nu}{s} \quad du = -\frac{4\pi R^2 \nu}{s^2} ds$$

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

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

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  $\mu\text{m}$ , 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

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

□

- 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

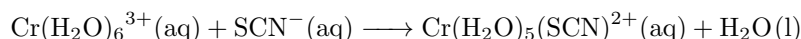
$$\begin{aligned}v(t) &= k[A]^0[B]^0 \dots \\ -\frac{d[A]}{dt} &= k\end{aligned}$$

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.

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

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.

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

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

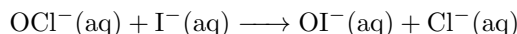
$$\begin{aligned}
 m &= \frac{\sum [\text{Cr}(\text{H}_2\text{O})_6^{3+}][\text{SCN}^-] \cdot \sum v_0 - 4 \sum ([\text{Cr}(\text{H}_2\text{O})_6^{3+}][\text{SCN}^-] \cdot v_0)}{(\sum [\text{Cr}(\text{H}_2\text{O})_6^{3+}][\text{SCN}^-])^2 - 4 \sum ([\text{Cr}(\text{H}_2\text{O})_6^{3+}][\text{SCN}^-])^2}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

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 <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

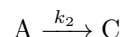
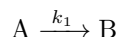
$$m_{\text{OCl}^-} = \frac{\ln\left(\frac{v_1[\text{OH}^-]_1}{v_3[\text{OH}^-]_3}\right)}{\ln\left(\frac{[\text{OCl}^-]_1}{[\text{OCl}^-]_3}\right)} = 0.995 \approx 1$$

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

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

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

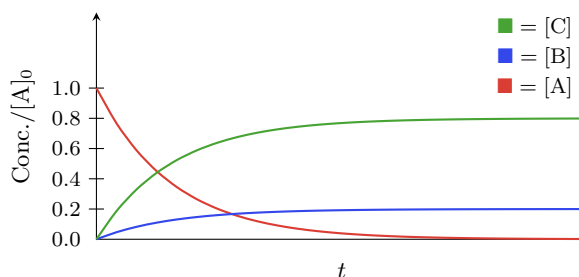
$$\begin{aligned} \frac{d[B]}{dt} &= k_1[A] & \frac{d[C]}{dt} &= k_2[A] \\ \frac{d[B]}{dt} &= k_1[A]_0 e^{-(k_1+k_2)t} & \frac{d[C]}{dt} &= k_2[A]_0 e^{-(k_1+k_2)t} \\ \int_0^{[B]} d[B] &= \int_0^t k_1[A]_0 e^{-(k_1+k_2)t} dt & \int_0^{[C]} d[C] &= \int_0^t k_2[A]_0 e^{-(k_1+k_2)t} dt \\ [B] &= \frac{k_1}{k_1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

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).

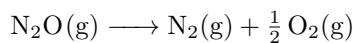
*Answer.* I would like to discuss and build upon Problem 28-25, which begins the process of intuitively rationalizing the rate law for a reaction that is first-order in each reactant and second-order overall. Another way that we can think about it is by noting that by their coefficients, the concentrations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



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

Assume the rate law for this reaction is

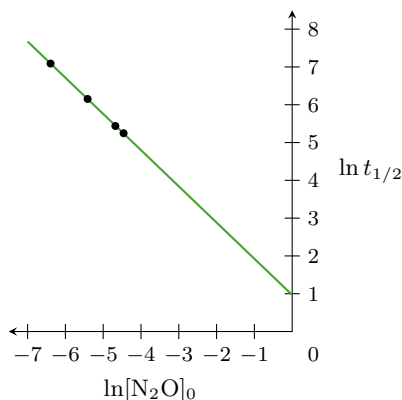
$$-\frac{d[\text{N}_2\text{O}]}{dt} = k[\text{N}_2\text{O}]^n$$

and use the equation for the half-life of an  $n^{\text{th}}$ -order reaction to determine the reaction order of  $\text{N}_2\text{O}$  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

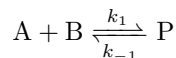
$$k = \frac{1}{(2-1)t_{1/2}} \frac{2^{2-1}-1}{[\text{N}_2\text{O}]_0^{2-1}} = \frac{1}{t_{1/2} \cdot [\text{N}_2\text{O}]_0}$$

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.

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

*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

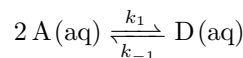
$$\begin{aligned} \frac{d\Delta[P]}{dt} &= -\{k_1([A]_{2,eq} + [B]_{2,eq}) + k_{-1}\}\Delta[P] \\ \frac{d\Delta[P]}{\Delta[P]} &= -\frac{dt}{1/\{k_1([A]_{2,eq} + [B]_{2,eq}) + k_{-1}\}} \\ \int_{\Delta[P]_0}^{\Delta[P]} \frac{d\Delta[P]}{\Delta[P]} &= \int_0^t -\frac{dt}{\tau} \\ \ln \frac{\Delta[P]}{\Delta[P]_0}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

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

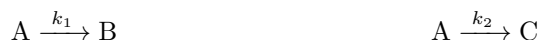
$$\begin{aligned} \frac{d}{dt}([\text{D}]_{2,\text{eq}} + \Delta[\text{D}]) &= k_1([\text{A}]_{2,\text{eq}} + \Delta[\text{A}])^2 - k_{-1}([\text{D}]_{2,\text{eq}} + \Delta[\text{D}]) \\ \frac{d\Delta[\text{D}]}{dt} &= k_1([\text{A}]_{2,\text{eq}}^2 + 2[\text{A}]_{2,\text{eq}}\Delta[\text{A}] + \Delta[\text{A}]^2)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

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

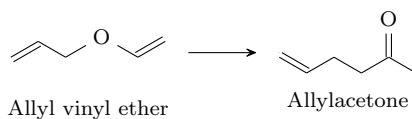
$$k_1 = A_1 e^{-E_1/RT} \qquad \qquad k_2 = A_2 e^{-E_2/RT}$$

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

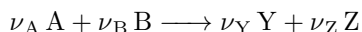
$$A = \frac{e k_B T}{h} e^{\Delta^\ddagger S^\circ / R}$$

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

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

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

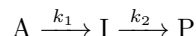
$$\begin{aligned} h(x) &= \int_0^x k_2 dx \\ &= k_2 x \end{aligned}$$

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

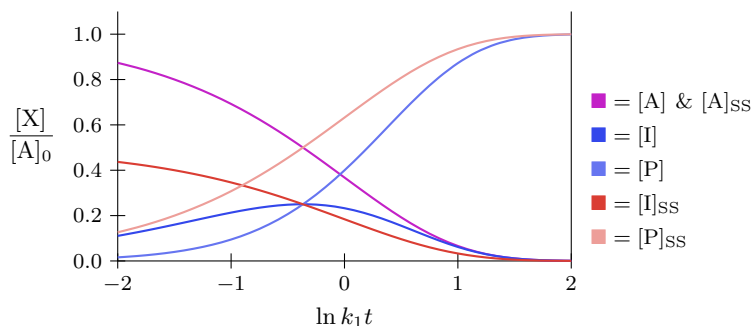


where  $[A] = [A]_0$  and  $[I]_0 = [P]_0 = 0$  at time  $t = 0$ . Use the exact solution to this kinetic scheme (below) to plot the time dependence of  $[A]/[A]_0$ ,  $[I]/[A]_0$ , and  $[P]/[A]_0$  versus  $\log k_1 t$  for the case  $k_2 = 2k_1$ .

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

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

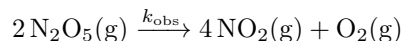
take  $k_2 = 2k_1$  and  $E_2 > E_1$  for the sake of having something tangible to work with, we should be able to imagine that supplying  $E_2$  to the system means we are twice as likely to generate a molecule of C as we would be likely to generate a molecule of B upon supplying  $E_1$  to the system. 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.  $\square$

## 4 Mechanisms II / Gas-Phase Reactions

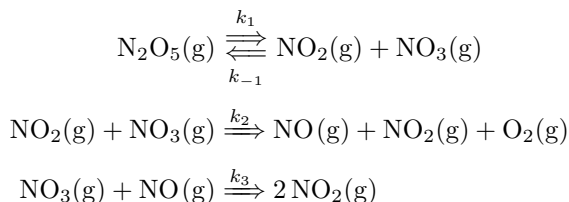
### Chapter 29

From McQuarrie and Simon (1997).

5/9: **29-11.** Consider the decomposition reaction of  $\text{N}_2\text{O}_5(\text{g})$



A proposed mechanism for this reaction is



Assume that the steady-state approximation applies to both the  $\text{NO}(\text{g})$  and  $\text{NO}_3(\text{g})$  reaction intermediates to show that this mechanism is consistent with the experimentally observed rate law

$$\frac{d[\text{O}_2]}{dt} = k_{\text{obs}}[\text{N}_2\text{O}_5]$$

Express  $k_{\text{obs}}$  in terms of the rate constants for the individual steps of the reaction mechanism.

*Answer.* We have that

$$\begin{aligned} \frac{d[\text{O}_2]}{dt} &= k_2[\text{NO}_2][\text{NO}_3] \\ \frac{d[\text{NO}]}{dt} &= k_2[\text{NO}_2][\text{NO}_3] - k_3[\text{NO}_3][\text{NO}] \\ \frac{d[\text{NO}_3]}{dt} &= k_1[\text{N}_2\text{O}_5] - k_{-1}[\text{NO}_2][\text{NO}_3] - k_2[\text{NO}_2][\text{NO}_3] - k_3[\text{NO}_3][\text{NO}] \end{aligned}$$

Applying the steady-state approximation to  $\text{NO}$  yields

$$\begin{aligned} 0 &= k_2[\text{NO}_2][\text{NO}_3] - k_3[\text{NO}_3][\text{NO}] \\ [\text{NO}] &= \frac{k_2}{k_3}[\text{NO}_2] \end{aligned}$$

Hence,

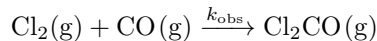
$$\begin{aligned} 0 &= k_1[\text{N}_2\text{O}_5] - k_{-1}[\text{NO}_2][\text{NO}_3] - k_2[\text{NO}_2][\text{NO}_3] - k_3[\text{NO}_3][\text{NO}] \\ &= k_1[\text{N}_2\text{O}_5] - k_{-1}[\text{NO}_2][\text{NO}_3] - k_2[\text{NO}_2][\text{NO}_3] - k_2[\text{NO}_3][\text{NO}_2] \\ &= k_1[\text{N}_2\text{O}_5] - (k_{-1} + 2k_2)[\text{NO}_2][\text{NO}_3] \\ [\text{NO}_2][\text{NO}_3] &= \frac{k_1}{k_{-1} + 2k_2}[\text{N}_2\text{O}_5] \end{aligned}$$

Therefore, we have that

$$\boxed{\frac{d[\text{O}_2]}{dt} = \underbrace{\frac{k_1 k_2}{k_{-1} + 2k_2}}_{k_{\text{obs}}} [\text{N}_2\text{O}_5]}$$

□

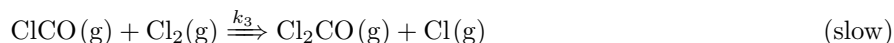
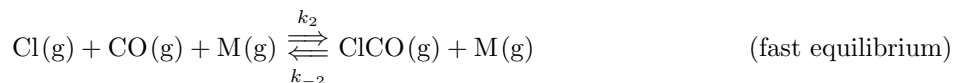
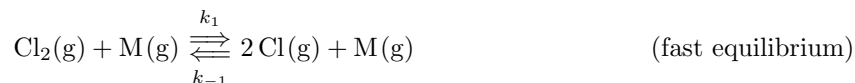
**29-12.** The rate law for the reaction



between  $\text{CO}(\text{g})$  and  $\text{Cl}_2(\text{g})$  to form phosgene ( $\text{Cl}_2\text{CO}$ ) is

$$\frac{d[\text{Cl}_2\text{CO}]}{dt} = k_{\text{obs}}[\text{Cl}_2]^{3/2}[\text{CO}]$$

Show that the following mechanism is consistent with this rate law.



where M is any gas molecule present in the reaction container. Express  $k_{\text{obs}}$  in terms of the rate constants for the individual steps of the reaction mechanism.

*Answer.* We have that

$$\frac{d[\text{Cl}_2\text{CO}]}{dt} = k_3[\text{ClCO}][\text{Cl}_2]$$

Suppose we attempt to find an expression for  $[\text{ClCO}]$  in terms of  $[\text{Cl}_2]$  and  $[\text{CO}]$  via differential equations and the steady-state approximation. Unfortunately, this approach will fail because we have an analogous situation to  $k_1 \gg k_2$ , i.e., the concentration of  $\text{ClCO}$  will build up quickly and decay slowly. Critically, the concentration of  $\text{ClCO}$  will not be steady, so we may not apply the steady-state approximation to our differential equations, and solving them analytically will be a huge hassle, if it is even possible.

As such, we look for another approach. One observation we may make is that the first two elementary reactions in the mechanism will equilibrate quickly, so we may take their equilibrium constants to be constant for the duration of the reaction and later relate them to rate constants via the principle of detailed balance. Attempting this, we find that

$$\begin{aligned} K_{c,1} &= \frac{[\text{Cl}]^2[\text{M}]}{[\text{Cl}_2][\text{M}]} & K_{c,2} &= \frac{[\text{ClCO}][\text{M}]}{[\text{Cl}][\text{CO}][\text{M}]} \\ &= \frac{[\text{Cl}]^2}{[\text{Cl}_2]} & &= \frac{[\text{ClCO}]}{[\text{Cl}][\text{CO}]} \\ [\text{Cl}] &= K_{c,1}^{1/2}[\text{Cl}_2]^{1/2} & [\text{ClCO}] &= K_{c,2}[\text{Cl}][\text{CO}] \end{aligned}$$

It follows since

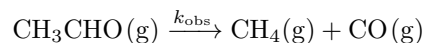
$$K_{c,1} = \frac{k_1}{k_{-1}} \quad K_{c,2} = \frac{k_2}{k_{-2}}$$

that

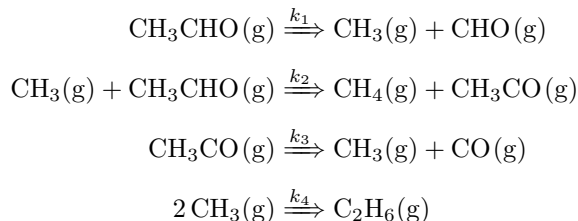
$$\begin{aligned} \frac{d[\text{Cl}_2\text{CO}]}{dt} &= k_3[\text{ClCO}][\text{Cl}_2] \\ &= k_3 K_{c,2}[\text{Cl}][\text{CO}][\text{Cl}_2] \\ &= k_3 K_{c,2} K_{c,1}^{1/2}[\text{Cl}_2]^{1/2}[\text{CO}][\text{Cl}_2] \\ \boxed{\frac{d[\text{Cl}_2\text{CO}]}{dt} &= k_3 \underbrace{\left(\frac{k_2}{k_{-2}}\right) \left(\frac{k_1}{k_{-1}}\right)^{1/2}}_{k_{\text{obs}}} [\text{Cl}_2]^{3/2}[\text{CO}]} \end{aligned}$$

□

**29-28.** Consider the mechanism for the thermal decomposition of acetaldehyde



given as follows.



Show that  $E_{\text{obs}}$ , the measured Arrhenius activation energy for the overall reaction, is given by

$$E_{\text{obs}} = E_2 + \frac{1}{2}(E_1 - E_4)$$

where  $E_i$  is the activation energy of the  $i^{\text{th}}$  step of the reaction mechanism. How is  $A_{\text{obs}}$ , the measured Arrhenius pre-exponential factor for the overall reaction, related to the Arrhenius pre-exponential factors for the individual steps of the reaction mechanism?

*Answer.* We have from Problem 29-24 that

$$k_{\text{obs}} = k_2 \left( \frac{k_1}{2k_4} \right)^{1/2}$$

As in Example 29-7, we may write

$$k_{\text{obs}} = A_{\text{obs}} e^{-E_{\text{obs}}/RT} \quad k_1 = A_1 e^{-E_1/RT} \quad k_2 = A_2 e^{-E_2/RT} \quad k_4 = A_4 e^{-E_4/RT}$$

Note that we could also write such an equation for  $k_3$ , but we do not need to because as per the first equation above, there would be no place to substitute it. Regardless, moving on we also naturally have the differential forms of the above equations

$$\frac{d \ln k_{\text{obs}}}{dT} = \frac{E_{\text{obs}}}{RT^2} \quad \frac{d \ln k_1}{dT} = \frac{E_1}{RT^2} \quad \frac{d \ln k_2}{dT} = \frac{E_2}{RT^2} \quad \frac{d \ln k_4}{dT} = \frac{E_4}{RT^2}$$

Thus,

$$\begin{aligned}\frac{E_{\text{obs}}}{RT^2} &= \frac{d \ln k_{\text{obs}}}{dT} \\ &= \frac{d}{dT} \left( \ln k_2 \left( \frac{k_1}{2k_4} \right)^{1/2} \right) \\ &= \frac{d}{dT} \left( \ln k_2 + \frac{1}{2} (\ln k_1 - \ln 2 - \ln k_4) \right) \\ &= \frac{d \ln k_2}{dT} + \frac{1}{2} \left( \frac{d \ln k_1}{dT} - \frac{d \ln 2}{dT} - \frac{d \ln k_4}{dT} \right) \\ &= \frac{E_2}{RT^2} + \frac{1}{2} \left( \frac{E_1}{RT^2} - 0 - \frac{E_4}{RT^2} \right)\end{aligned}$$

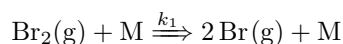
$$E_{\text{obs}} = E_2 + \frac{1}{2}(E_1 - E_4)$$

It follows that

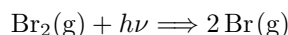
$$\begin{aligned}
 A_{\text{obs}} e^{-E_{\text{obs}}/RT} &= A_2 e^{-E_2/RT} \left( \frac{A_1 e^{-E_1/RT}}{2A_4 e^{-E_4/RT}} \right)^{1/2} \\
 &= A_2 \left( \frac{A_1}{2A_4} \right)^{1/2} e^{-E_2/RT} \left( e^{-(E_1-E_4)/RT} \right)^{1/2} \\
 &= A_2 \left( \frac{A_1}{2A_4} \right)^{1/2} e^{-E_2/RT} e^{-\frac{1}{2}(E_1-E_4)/RT} \\
 &= A_2 \left( \frac{A_1}{2A_4} \right)^{1/2} e^{-[E_2 + \frac{1}{2}(E_1-E_4)]/RT} \\
 &= A_2 \left( \frac{A_1}{2A_4} \right)^{1/2} e^{-E_{\text{obs}}/RT} \\
 \boxed{A_{\text{obs}} = A_2 \left( \frac{A_1}{2A_4} \right)^{1/2}}
 \end{aligned}$$

□

- 29-33.** It is possible to initiate chain reactions using photochemical reactions. For example, in place of the thermal initiation reaction for the  $\text{Br}_2(\text{g}) + \text{H}_2(\text{g})$  chain reaction



we could have the photochemical initiation reaction



If we assume that all the incident light is absorbed by the  $\text{Br}_2$  molecules and that the quantum yield for photodissociation is 1.00, then how does the photochemical rate of dissociation of  $\text{Br}_2$  depend on  $I_{\text{abs}}$ , the number of photons per unit time per unit volume? How does  $d[\text{Br}]/dt$ , the rate of formation of  $\text{Br}$ , depend on  $I_{\text{abs}}$ ? If you assume that the chain reaction is initiated only by the photochemical generation of  $\text{Br}$ , then how does  $d[\text{HBr}]/dt$  depend on  $I_{\text{abs}}$ ?

*Answer.* Take the standard volume to be one liter and the standard unit of time to be one second. We are given that  $I_{\text{abs}}$  photons are supplied to every liter of reaction volume every second. Since every one of these photons is absorbed by a  $\text{Br}_2$  molecule by hypothesis and every one of these excited  $\text{Br}_2$  molecules dissociates by the definition of quantum yield 1.00, it follows that  $I_{\text{abs}}$  molecules of  $\text{Br}_2$  dissociate in every liter of reaction volume every second. Consequently, we may divide by Avogadro's number to learn that  $I_{\text{abs}}/N_{\text{A}}$  moles of  $\text{Br}_2$  dissociate in every liter of reaction volume every second. Another way of putting this is that the change in molar concentration of bromine due to photodissociation every second  $-d[\text{Br}_2]/dt$  is given by  $I_{\text{abs}}/N_{\text{A}}$ . In an equation, the photochemical rate of dissociation of  $\text{Br}_2$  depends on  $I_{\text{abs}}$  via

$$\boxed{-\frac{d[\text{Br}_2]}{dt} = \frac{I_{\text{abs}}}{N_{\text{A}}}}$$

We have from the definition of the rate of reaction that

$$v = -\frac{1}{1} \frac{d[\text{Br}_2]}{dt} = \frac{1}{2} \frac{d[\text{Br}]}{dt}$$

Thus, the rate of formation of  $\text{Br}$  solely due to photodissociation is

$$\begin{aligned}
 \frac{1}{2} \frac{d[\text{Br}]}{dt} &= \frac{I_{\text{abs}}}{N_{\text{A}}} \\
 \boxed{\frac{d[\text{Br}]}{dt} &= \frac{2I_{\text{abs}}}{N_{\text{A}}}}
 \end{aligned}$$

We now have a slightly different mechanism to the first time we analyzed the  $\text{Br}_2(\text{g}) + \text{H}_2(\text{g})$  chain reaction. In particular, the thermal initiation step has been replaced by our photochemical initiation step, and we take the termination step to be the reverse reaction to the initiation step. As such, we may write the modified rate equations

$$\begin{aligned}\frac{d[\text{HBr}]}{dt} &= k_2[\text{Br}][\text{H}_2] - k_{-2}[\text{HBr}][\text{H}] + k_3[\text{H}][\text{Br}_2] \\ \frac{d[\text{H}]}{dt} &= k_2[\text{Br}][\text{H}_2] - k_{-2}[\text{HBr}][\text{H}] - k_3[\text{H}][\text{Br}_2] \\ \frac{d[\text{Br}]}{dt} &= \frac{2I_{\text{abs}}}{N_{\text{A}}} - k_{-1}[\text{Br}]^2 - k_2[\text{Br}][\text{H}_2] + k_{-2}[\text{HBr}][\text{H}] + k_3[\text{H}][\text{Br}_2]\end{aligned}$$

Applying the steady-state approximation to the two intermediate species, we find that

$$\begin{aligned}0 &= k_2[\text{Br}][\text{H}_2] - k_{-2}[\text{HBr}][\text{H}] - k_3[\text{H}][\text{Br}_2] \\ 0 &= \frac{2I_{\text{abs}}}{N_{\text{A}}} - k_{-1}[\text{Br}]^2 - k_2[\text{Br}][\text{H}_2] + k_{-2}[\text{HBr}][\text{H}] + k_3[\text{H}][\text{Br}_2]\end{aligned}$$

Substituting the opposite of the former equation into the latter yields

$$\begin{aligned}0 &= \frac{2I_{\text{abs}}}{N_{\text{A}}} - k_{-1}[\text{Br}]^2 - 0 \\ [\text{Br}] &= \left( \frac{2I_{\text{abs}}}{k_{-1}N_{\text{A}}} \right)^{1/2}\end{aligned}$$

Resubstituting this expression into the SS approximation for  $[\text{H}]$  yields

$$\begin{aligned}0 &= k_2[\text{Br}][\text{H}_2] - k_{-2}[\text{HBr}][\text{H}] - k_3[\text{H}][\text{Br}_2] \\ &= k_2 \left( \frac{2I_{\text{abs}}}{k_{-1}N_{\text{A}}} \right)^{1/2} [\text{H}_2] - (k_{-2}[\text{HBr}] + k_3[\text{Br}_2])[\text{H}] \\ [\text{H}] &= \left( \frac{2I_{\text{abs}}}{k_{-1}N_{\text{A}}} \right)^{1/2} \frac{k_2[\text{H}_2]}{k_{-2}[\text{HBr}] + k_3[\text{Br}_2]}\end{aligned}$$

Substituting these two expressions back into the original differential equation for  $[\text{HBr}]$  yields

$$\begin{aligned}\frac{d[\text{HBr}]}{dt} &= k_2[\text{Br}][\text{H}_2] - k_{-2}[\text{HBr}][\text{H}] + k_3[\text{H}][\text{Br}_2] \\ &= k_2 \left( \frac{2I_{\text{abs}}}{k_{-1}N_{\text{A}}} \right)^{1/2} [\text{H}_2] - (k_{-2}[\text{HBr}] - k_3[\text{Br}_2]) \left( \frac{2I_{\text{abs}}}{k_{-1}N_{\text{A}}} \right)^{1/2} \frac{k_2[\text{H}_2]}{k_{-2}[\text{HBr}] + k_3[\text{Br}_2]} \\ &= k_2 \left( \frac{2I_{\text{abs}}}{k_{-1}N_{\text{A}}} \right)^{1/2} [\text{H}_2] \left\{ 1 - \frac{k_{-2}[\text{HBr}] - k_3[\text{Br}_2]}{k_{-2}[\text{HBr}] + k_3[\text{Br}_2]} \right\} \\ &= k_2 \left( \frac{2I_{\text{abs}}}{k_{-1}N_{\text{A}}} \right)^{1/2} [\text{H}_2] \left\{ \frac{k_{-2}[\text{HBr}] + k_3[\text{Br}_2]}{k_{-2}[\text{HBr}] + k_3[\text{Br}_2]} - \frac{k_{-2}[\text{HBr}] - k_3[\text{Br}_2]}{k_{-2}[\text{HBr}] + k_3[\text{Br}_2]} \right\} \\ &= k_2 \left( \frac{2I_{\text{abs}}}{k_{-1}N_{\text{A}}} \right)^{1/2} [\text{H}_2] \left\{ \frac{2k_3[\text{Br}_2]}{k_{-2}[\text{HBr}] + k_3[\text{Br}_2]} \right\}\end{aligned}$$

$$\boxed{\frac{d[\text{HBr}]}{dt} = \left( \frac{2I_{\text{abs}}}{k_{-1}N_{\text{A}}} \right)^{1/2} \frac{2k_2[\text{H}_2]}{(k_{-2}/k_3)[\text{HBr}]/[\text{Br}_2] + 1}}$$

where we have arranged the last expression so that every molar concentration and rate constant appears at most once, increasing the clarity with which the reader can see what's proportional to what.  $\square$



**29-35.** The ability of enzymes to catalyze reactions can be hindered by **inhibitor molecules**. One of the mechanisms by which an inhibitor molecule works is by competing with the substrate molecule for binding to the active site of the enzyme. We can include this inhibition reaction in a modified Michaelis-Menton mechanism for enzyme catalysis.



In Reaction 2, I is the inhibitor molecule and EI is the enzyme-inhibitor complex. We will consider the case where Reaction 2 is always in equilibrium. Determine the rate laws for [S], [ES], [EI], and [P]. Show that if the steady-state assumption is applied to ES, then

$$[\text{ES}] = \frac{[\text{E}][\text{S}]}{K_m}$$

where  $K_m = (k_{-1} + k_3)/k_1$  is the Michaelis constant. Now show that the material balance for the enzyme gives

$$[\text{E}]_0 = [\text{E}] + \frac{[\text{E}][\text{S}]}{K_m} + [\text{E}][\text{I}]K_I$$

where  $K_I = [\text{EI}]/[\text{E}][\text{I}]$  is the equilibrium constant for Reaction 2. Use this result to show that the initial reaction rate is given by

$$v = \frac{d[\text{P}]}{dt} = \frac{k_3[\text{E}]_0[\text{S}]}{K_m + [\text{S}] + K_m K_I [\text{I}]} \approx \frac{k_3[\text{E}]_0[\text{S}]_0}{K'_m + [\text{S}]_0} \quad (4)$$

where  $K'_m = K_m(1 + K_I[\text{I}])$ . Note that the second expression in Equation 4 has the same functional form as the Michaelis-Menton equation. Does Equation 4 reduce to the expected result when  $[\text{I}] \rightarrow 0$ ?

*Answer.* The four desired rate laws are

$$\begin{aligned} \frac{d[\text{S}]}{dt} &= -k_1[\text{E}][\text{S}] + k_{-1}[\text{ES}] \\ \frac{d[\text{ES}]}{dt} &= k_1[\text{E}][\text{S}] - (k_{-1} + k_3)[\text{ES}] \\ \frac{d[\text{EI}]}{dt} &= k_2[\text{E}][\text{I}] - k_{-2}[\text{EI}] \\ \frac{d[\text{P}]}{dt} &= k_3[\text{ES}] \end{aligned}$$

Applying the steady-state approximation to the rate law describing [ES] yields

$$0 = k_1[\text{E}][\text{S}] - (k_{-1} + k_3)[\text{ES}]$$

$$[\text{ES}] = \frac{k_1}{k_{-1} + k_3} [\text{E}][\text{S}]$$

$$[\text{ES}] = \frac{[\text{E}][\text{S}]}{K_m}$$

where we have defined  $K_m$  as in the statement of the problem.

According to the proposed mechanism, an enzyme molecule can exist in three forms: As an unbound enzyme E, as an enzyme-substrate complex ES, and as an enzyme-inhibitor complex EI. Thus, since no enzyme is created or destroyed (as an idealized catalyst), we know that at any given time,

$$\begin{aligned} [E]_0 &= [E] + [ES] + [EI] \\ &= [E] + \frac{[E][S]}{K_m} + [E][I] \frac{[EI]}{[E][I]} \\ \boxed{[E]_0 &= [E] + \frac{[E][S]}{K_m} + [E][I]K_I} \end{aligned}$$

where we have invoked the final result of applying the SS approximation to ES to make the middle substitution in the second equality, and we have defined  $K_I$  as in the statement of the problem.

It follows that

$$\begin{aligned} [E]_0 &= [E] + \frac{[E][S]}{K_m} + [E][I]K_I \\ &= \frac{K_m + [S] + K_m K_I [I]}{K_m} [E] \\ \frac{[E]}{K_m} &= \frac{[E]_0}{K_m + [S] + K_m K_I [I]} \end{aligned}$$

so that

$$\begin{aligned} \frac{d[P]}{dt} &= k_3 [ES] \\ &= k_3 \frac{[E][S]}{K_m} \\ \boxed{\frac{d[P]}{dt} &= \frac{k_3 [E]_0 [S]}{K_m + [S] + K_m K_I [I]}} \end{aligned}$$

Moreover, if we approximate  $[S] \approx [S]_0$  (a good approximation if there is an excess of substrate) and define  $K'_m$  as in the statement of the problem, the above equation reduces to

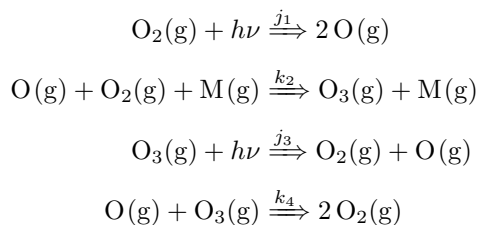
$$\frac{d[P]}{dt} \approx \frac{k_3 [E]_0 [S]_0}{K'_m + [S]_0}$$

Lastly, if  $[I] \rightarrow 0$ , then  $[EI] \rightarrow 0$  so that

$$K'_m = K_m(1 + K_I[I]) = K_m \left( 1 + \frac{[EI]}{[E]} \right) = K_m$$

thereby confirming that Equation 4 reduces as desired. □

**29-47.** A mechanism for ozone creation and destruction in the stratosphere is



where we have used the symbol  $j$  to indicate that the rate constant is for a photochemical reaction. Determine the rate expressions for  $d[\text{O}]/dt$  and  $d[\text{O}_3]/dt$ . Assume that both  $\text{O}(\text{g})$  and  $\text{O}_3(\text{g})$  can be treated by the steady-state approximation and thereby show that

$$[\text{O}] = \frac{2j_1[\text{O}_2] + j_3[\text{O}_3]}{k_2[\text{O}_2][\text{M}] + k_4[\text{O}_3]} \quad (1)$$

and

$$[\text{O}_3] = \frac{k_2[\text{O}][\text{O}_2][\text{M}]}{j_3 + k_4[\text{O}]} \quad (2)$$

Now substitute Equation 1 into Equation 2 and solve the resulting quadratic formula for  $[\text{O}_3]$  to obtain

$$[\text{O}_3] = [\text{O}_2] \frac{j_1}{2j_3} \left\{ \left( 1 + \frac{4j_3k_2}{j_1k_4} [\text{M}] \right)^{1/2} - 1 \right\}$$

Typical values for these parameters at an altitude of 30 km are  $j_1 = 2.51 \times 10^{-12} \text{ s}^{-1}$ ,  $j_3 = 3.16 \times 10^{-4} \text{ s}^{-1}$ ,  $k_2 = 1.99 \times 10^{-33} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ ,  $k_4 = 1.26 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $[\text{O}_2] = 3.16 \times 10^{17} \text{ molecule cm}^{-3}$ , and  $[\text{M}] = 3.98 \times 10^{17} \text{ molecule cm}^{-3}$ . Find  $[\text{O}_3]$  and  $[\text{O}]$  at an altitude of 30 km using Equations 1 and 2. Was the use of the steady-state assumption justified?

*Answer.* The two desired rate laws are

$$\begin{aligned} \frac{d[\text{O}]}{dt} &= 2j_1[\text{O}_2] - k_2[\text{O}][\text{O}_2][\text{M}] + j_3[\text{O}_3] - k_4[\text{O}][\text{O}_3] \\ \frac{d[\text{O}_3]}{dt} &= k_2[\text{O}][\text{O}_2][\text{M}] - j_3[\text{O}_3] - k_4[\text{O}][\text{O}_3] \end{aligned}$$

Applying the steady-state approximation to the rate laws yields

$$\begin{aligned} 0 &= 2j_1[\text{O}_2] - k_2[\text{O}][\text{O}_2][\text{M}] + j_3[\text{O}_3] - k_4[\text{O}][\text{O}_3] \\ &= 2j_1[\text{O}_2] + j_3[\text{O}_3] - (k_2[\text{O}_2][\text{M}] + k_4[\text{O}_3])[\text{O}] \end{aligned}$$

$$[\text{O}] = \frac{2j_1[\text{O}_2] + j_3[\text{O}_3]}{k_2[\text{O}_2][\text{M}] + k_4[\text{O}_3]}$$

and

$$\begin{aligned} 0 &= k_2[\text{O}][\text{O}_2][\text{M}] - j_3[\text{O}_3] - k_4[\text{O}][\text{O}_3] \\ &= k_2[\text{O}][\text{O}_2][\text{M}] - (j_3 + k_4[\text{O}])[\text{O}_3] \end{aligned}$$

$$[\text{O}_3] = \frac{k_2[\text{O}][\text{O}_2][\text{M}]}{j_3 + k_4[\text{O}]}$$

Performing the desired substitution yields

$$\begin{aligned} [\text{O}_3] &= \frac{k_2[\text{O}][\text{O}_2][\text{M}]}{j_3 + k_4[\text{O}]} \\ j_3[\text{O}_3] + k_4[\text{O}_3][\text{O}] &= k_2[\text{O}][\text{O}_2][\text{M}] \\ j_3[\text{O}_3] &= (k_2[\text{O}_2][\text{M}] - k_4[\text{O}_3])[\text{O}] \\ j_3[\text{O}_3] &= (k_2[\text{O}_2][\text{M}] - k_4[\text{O}_3]) \frac{2j_1[\text{O}_2] + j_3[\text{O}_3]}{k_2[\text{O}_2][\text{M}] + k_4[\text{O}_3]} \\ k_2j_3[\text{O}_2][\text{M}][\text{O}_3] + j_3k_4[\text{O}_3]^2 &= 2j_1k_2[\text{O}_2]^2[\text{M}] + k_2j_3[\text{O}_2][\text{M}][\text{O}_3] - 2j_1k_4[\text{O}_2][\text{O}_3] - j_3k_4[\text{O}_3]^2 \\ 0 &= -2j_3k_4[\text{O}_3]^2 - 2j_1k_4[\text{O}_2][\text{O}_3] + 2j_1k_2[\text{O}_2]^2[\text{M}] \\ [\text{O}_3] &= \frac{2j_1k_4[\text{O}_2] \pm \sqrt{4j_1^2k_4^2[\text{O}_2]^2 + 16j_1k_2j_3k_4[\text{O}_2]^2[\text{M}]}}{-4j_3k_4} \end{aligned}$$

$$\begin{aligned}
&= -\frac{j_1[\text{O}_2]}{2j_3} \pm \sqrt{\frac{[\text{O}_2]^2(4j_1^2k_4^2 + 16j_1k_2j_3k_4[\text{M}])}{16j_3^2k_4^2}} \\
&= -\frac{j_1[\text{O}_2]}{2j_3} \pm [\text{O}_2] \sqrt{\frac{j_1^2}{4j_3^2} + \frac{j_1k_2[\text{M}]}{j_3k_4}} \\
&= -\frac{j_1[\text{O}_2]}{2j_3} \pm [\text{O}_2] \sqrt{\frac{j_1^2}{4j_3^2} \left(1 + \frac{4k_2j_3[\text{M}]}{j_1k_4}\right)} \\
&= -\frac{j_1[\text{O}_2]}{2j_3} \pm \frac{j_1[\text{O}_2]}{2j_3} \sqrt{1 + \frac{4k_2j_3[\text{M}]}{j_1k_4}} \\
&= [\text{O}_2] \frac{j_1}{2j_3} \left\{ \pm \left(1 + \frac{4j_3k_2}{j_1k_4}[\text{M}]\right)^{1/2} - 1 \right\} \\
\boxed{[\text{O}_3] = [\text{O}_2] \frac{j_1}{2j_3} \left\{ \left(1 + \frac{4j_3k_2}{j_1k_4}[\text{M}]\right)^{1/2} - 1 \right\}}
\end{aligned}$$

where we choose the plus sign in the last step because otherwise we would have a negative concentration of  $\text{O}_3$ .

Using the above equation and the parameters given in the problem, we can determine by direct substitution that the concentration of ozone at an altitude of 30 km is

$$\begin{aligned}
[\text{O}_3] &= (3.16 \times 10^{17}) \frac{2.51 \times 10^{-12}}{2(3.16 \times 10^{-4})} \left\{ \left(1 + \frac{4(3.16 \times 10^{-4})(1.99 \times 10^{-33})}{(2.51 \times 10^{-12})(1.26 \times 10^{-15})}(3.98 \times 10^{17})\right)^{1/2} - 1 \right\} \\
&= (3.16 \times 10^{17}) \frac{2.51 \times 10^{-12}}{2(3.16 \times 10^{-4})} \left\{ (1 + 3.17 \times 10^8)^{1/2} - 1 \right\} \\
&= (3.16 \times 10^{17}) \frac{2.51 \times 10^{-12}}{2(3.16 \times 10^{-4})} \left\{ (3.17 \times 10^8)^{1/2} - 1 \right\} \\
&= (3.16 \times 10^{17}) \frac{2.51 \times 10^{-12}}{2(3.16 \times 10^{-4})} \{1.780 \times 10^4 - 1\} \\
&= (3.16 \times 10^{17}) \frac{2.51 \times 10^{-12}}{2(3.16 \times 10^{-4})} (1.780 \times 10^4) \\
\boxed{[\text{O}_3] = 2.23 \times 10^{13} \frac{\text{molecule}}{\text{cm}^3}}
\end{aligned}$$

It follows by Equation 1 that at 30 km,

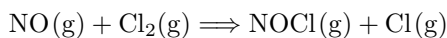
$$\begin{aligned}
[\text{O}] &= \frac{2(2.51 \times 10^{-12})(3.16 \times 10^{17}) + (3.16 \times 10^{-4})(2.23 \times 10^{13})}{(1.99 \times 10^{-33})(3.16 \times 10^{17})(3.98 \times 10^{17}) + (1.26 \times 10^{-15})(2.23 \times 10^{13})} \\
&= \frac{1.59 \times 10^6 + 7.05 \times 10^9}{2.50 \times 10^2 + 2.81 \times 10^{-2}} \\
&= \frac{7.05 \times 10^9}{2.50 \times 10^2} \\
\boxed{[\text{O}] = 2.82 \times 10^7 \frac{\text{molecule}}{\text{cm}^3}}
\end{aligned}$$

Since both  $[\text{O}_3]$  and  $[\text{O}]$  are small relative to the total number of molecules present, it is safe to say that the species are typically destroyed as quickly as they are formed. As such, the use of the steady-state approximation was justified.  $\square$

## Chapter 30

From McQuarrie and Simon (1997).

**30-1.** Calculate the hard-sphere collision theory rate constant for the reaction



at 300 K. The collision diameters of NO and Cl<sub>2</sub> are 370 pm and 540 pm, respectively. The Arrhenius parameters for the reaction are  $A = 3.981 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $E_a = 84.9 \text{ kJ mol}^{-1}$ . Calculate the ratio of the hard-sphere collision theory rate constant to the experimental rate constant at 300 K.

*Answer.* According to hard-sphere collision theory, the rate constant for the above reaction is given by

$$\begin{aligned} k &= \sigma_{(\text{NO Cl}_2)} \langle u_r \rangle \\ &= \pi d_{(\text{NO Cl}_2)}^2 \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} \\ &= \pi \left( \frac{d_{\text{NO}} + d_{\text{Cl}_2}}{2} \right)^2 \left( \frac{8k_B T (m_{\text{NO}} + m_{\text{Cl}_2})}{\pi m_{\text{NO}} m_{\text{Cl}_2}} \right)^{1/2} \end{aligned}$$

Plugging in

$$\begin{aligned} d_{\text{NO}} &= 3.70 \times 10^{-10} \text{ m} \\ d_{\text{Cl}_2} &= 5.40 \times 10^{-10} \text{ m} \\ T &= 300 \text{ K} \\ m_{\text{NO}} &= 4.983 \times 10^{-26} \text{ kg} \\ m_{\text{Cl}_2} &= 1.177 \times 10^{-25} \text{ kg} \end{aligned}$$

yields

$$\begin{aligned} k &= \pi \left( \frac{3.70 \times 10^{-10} + 5.40 \times 10^{-10}}{2} \right)^2 \left( \frac{8(1.381 \times 10^{-23})(300)(4.983 \times 10^{-26} + 1.177 \times 10^{-25})}{\pi(4.983 \times 10^{-26})(1.177 \times 10^{-25})} \right)^{1/2} \\ &= \pi \left( \frac{9.10 \times 10^{-10}}{2} \right)^2 \left( \frac{8(1.381 \times 10^{-23})(300)(1.675 \times 10^{-25})}{\pi(4.983 \times 10^{-26})(1.177 \times 10^{-25})} \right)^{1/2} \\ &= 3.57 \times 10^{-16} \frac{\text{m}^3}{\text{s}} \end{aligned}$$

$$\boxed{k = 2.15 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}}$$

The experimental rate constant is given by the Arrhenius equation as follows.

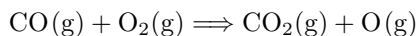
$$\begin{aligned} k' &= A e^{-E_a/RT} \\ &= (3.981 \times 10^9) e^{-(84900)/(8.3145)(300)} \\ &= (3.981 \times 10^9) e^{-34.0} \\ &= (3.981 \times 10^9)(2 \times 10^{-15}) \\ &= 8 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1} \end{aligned}$$

Thus, the ratio of  $k$  to  $k'$  is

$$\boxed{\frac{k}{k'} = 3 \times 10^{16}}$$

□

**30-5.** Consider the following bimolecular reaction at 3000 K.



The experimentally determined Arrhenius pre-exponential factor is  $A = 3.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , and the activation energy is  $E_a = 213.4 \text{ kJ mol}^{-1}$ . The hard-sphere collision diameter of  $\text{O}_2$  is 360 pm and that for CO is 370 pm. Calculate the value of the hard sphere line-of-centers model rate constant at 3000 K and compare it with the experimental rate constant. Also compare the calculated and experimental  $A$  values.

*Answer.* According to the hard sphere line-of-centers model, the rate constant for the above reaction is given by

$$k = \langle u_r \rangle \sigma_{(\text{CO O}_2)} e^{-E_0/k_B T}$$

where

$$\begin{aligned} \langle u_r \rangle &= \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} & \sigma_{(\text{CO O}_2)} &= \pi d_{(\text{CO O}_2)}^2 & e^{-E_0/k_B T} &= e^{-(E_a - k_B T/2)/k_B T} \\ &= \left( \frac{8k_B T(m_{\text{CO}} + m_{\text{O}_2})}{\pi m_{\text{CO}} m_{\text{O}_2}} \right)^{1/2} & &= \pi \left( \frac{d_{\text{CO}} + d_{\text{O}_2}}{2} \right)^2 & &= e^{-E_a/k_B T + 1/2} \end{aligned}$$

Plugging in

$$\begin{aligned} T &= 3000 \text{ K} \\ m_{\text{CO}} &= 4.651 \times 10^{-26} \text{ kg} \\ m_{\text{O}_2} &= 5.314 \times 10^{-26} \text{ kg} \\ d_{\text{CO}} &= 3.70 \times 10^{-10} \text{ m} \\ d_{\text{O}_2} &= 3.60 \times 10^{-10} \text{ m} \\ E_a &= 3.544 \times 10^{-19} \text{ J} \end{aligned}$$

yields

$$\begin{aligned} \langle u_r \rangle &= \left( \frac{8(1.381 \times 10^{-23})(3000)(4.651 \times 10^{-26} + 5.314 \times 10^{-26})}{\pi(4.651 \times 10^{-26})(5.314 \times 10^{-26})} \right)^{1/2} \\ &= \left( \frac{8(1.381 \times 10^{-23})(3000)(9.965 \times 10^{-26})}{\pi(4.651 \times 10^{-26})(5.314 \times 10^{-26})} \right)^{1/2} \\ &= (4.254 \times 10^6)^{1/2} \\ &= 2062.5 \frac{\text{m}}{\text{s}} \end{aligned}$$

for the average relative speed,

$$\begin{aligned} \sigma_{(\text{CO O}_2)} &= \pi \left( \frac{3.70 \times 10^{-10} + 3.60 \times 10^{-10}}{2} \right)^2 \\ &= \pi \left( \frac{7.30 \times 10^{-10}}{2} \right)^2 \\ &= 4.19 \times 10^{-19} \text{ m}^2 \end{aligned}$$

for the collision cross section, and

$$\begin{aligned} e^{-E_0/k_B T} &= e^{-(3.544 \times 10^{-19})/(1.381 \times 10^{-23})(3000) + 1/2} \\ &= e^{-8.554 + 1/2} \\ &= e^{-8.054} \\ &= 3.18 \times 10^{-4} \end{aligned}$$

for the exponential term.

It follows that

$$\begin{aligned} k &= (2062.5)(4.19 \times 10^{-19})(3.18 \times 10^{-4}) \\ &= 2.75 \times 10^{-19} \frac{\text{m}^3}{\text{s}} \end{aligned}$$

$$\boxed{k = 1.66 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}}$$

The experimental rate constant is given by the Arrhenius equation as follows.

$$\begin{aligned} k' &= Ae^{-E_a/RT} \\ &= (3.5 \times 10^9) e^{-(213\,400)/(8.3145)(3000)} \\ &= (3.5 \times 10^9) e^{-8.555} \\ &= (3.5 \times 10^9)(1.93 \times 10^{-4}) \\ &= 6.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \end{aligned}$$

Thus, the theoretical rate constant is between two and three orders of magnitude greater than the experimental rate constant, as shown by their ratio.

$$\boxed{\frac{k}{k'} = 250}$$

Additionally, we can determine the theoretical Arrhenius pre-exponential factor to be

$$\begin{aligned} A' &= \langle u_r \rangle \sigma_{(\text{CO O}_2)} e^{1/2} \\ &= (2062.5)(4.19 \times 10^{-19}) e^{1/2} \\ &= 1.42 \times 10^{-15} \frac{\text{m}^3}{\text{s}} \\ &= 8.55 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1} \end{aligned}$$

Thus, the theoretical Arrhenius pre-exponential factor is also between two and three orders of magnitude greater than the experimental Arrhenius pre-exponential factor, as shown by their ratio.

$$\boxed{\frac{A'}{A} = 250}$$

In fact, the ratios  $k : k'$  and  $A' : A$  are identical to two significant figures. □

## 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 further explore the chemical knowledge underlying Problem 29-28, the thermal decomposition of acetaldehyde. McQuarrie and Simon (1997) have mentioned numerous times that few reactions have been studied in sufficient depth that scientists feel truly confident in the proposed mechanism

and rate law. As such, it is interesting to note that even though the thermal decomposition of acetaldehyde is discussed in their textbook and forms the basis for a series of problems, the manner in which McQuarrie and Simon (1997) characterize it is inaccurate according to the latest theory, which was published over three decades before their textbook.

Indeed, due to the obvious similarities, it appears likely that McQuarrie and Simon (1997) distilled and simplified their proposed mechanism for the thermal decomposition of acetaldehyde from the **Rice-Herzfeld mechanism** (Rice & Herzfeld, 1934, p. 288). The Rice-Herzfeld mechanism was the first proposed mechanism to account for the three-halves-order kinetics of the thermal decomposition of *pure* acetaldehyde. However, in a reexamination thirty years later, Eusuf and Laidler (1964) determined that the Rice-Herzfeld mechanism fails to account for significant increases in reaction order in the presence of foreign inert gases (e.g.,  $\text{N}_2$ ). As such, they proposed a mechanism with a greater emphasis on collision partners and showed it to be consistent with all experimental data collected on the reaction since 1934. For me, this is a fascinating glimpse into the scientific method and how the concepts I'm learning about are still under development today.  $\square$

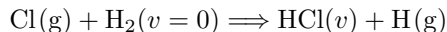


## 5 Gas-Phase Reactions II

### Chapter 30

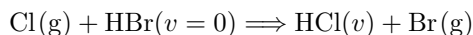
From McQuarrie and Simon (1997).

5/18: **30-18.** Consider the reaction



where  $D_e(\text{H}_2) - D_e(\text{HCl}) = 12.4 \text{ kJ mol}^{-1}$ . Assume there is no activation barrier to the reaction. Model the reactants as hard spheres (no vibrational motion) and calculate the minimum value of the relative speed required for the reaction to occur. If we model  $\text{H}_2(\text{g})$  and  $\text{HCl}(\text{g})$  as hard-sphere harmonic oscillators with  $\tilde{\nu}_{\text{H}_2} = 4159 \text{ cm}^{-1}$  and  $\tilde{\nu}_{\text{HCl}} = 2886 \text{ cm}^{-1}$ , calculate the minimum value of the relative speed required for the reaction to occur.

**30-22.** Consider the reaction



where the relative translational energy of the reactants is  $9.21 \text{ kJ mol}^{-1}$ , the difference  $D_e(\text{HBr}) - D_e(\text{HCl}) = -67.2 \text{ kJ mol}^{-1}$ , and the activation energy for this reaction is about  $6 \text{ kJ mol}^{-1}$ .

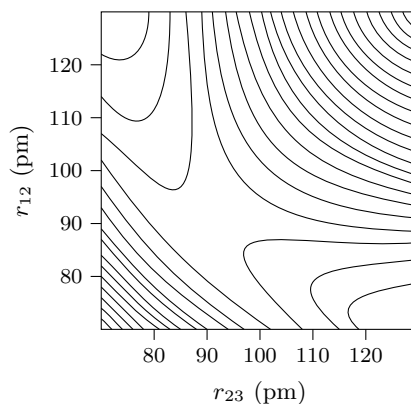
Determine the range of possible vibrational states of the product molecule  $\text{HCl}(\text{g})$ . The spectroscopic constants for  $\text{HBr}(\text{g})$  and  $\text{HCl}(\text{g})$  are

	$\tilde{\nu}_e \text{ (cm}^{-1}\text{)}$	$\tilde{\nu}_e \tilde{x}_e \text{ (cm}^{-1}\text{)}$
HBr	2648.98	45.22
HCl	2990.95	52.82

Draw a diagram for this reaction that is similar to that shown in Figure 6.5 of my notes (Figure 30.8 of McQuarrie and Simon (1997)) for the  $\text{F(g)} + \text{D}_2(\text{g})$  reaction.

**30-31.** Consider the product velocity distribution for the reaction between  $\text{K(g)}$  and  $\text{I}_2(v=0)$  at a relative translational energy of  $15.13 \text{ kJ mol}^{-1}$  shown in Figure 30.13. Assume that the vibrational motion of  $\text{I}_2(\text{g})$  and  $\text{KI(g)}$  is harmonic with  $\tilde{\nu}_{\text{I}_2} = 213 \text{ cm}^{-1}$  and  $\tilde{\nu}_{\text{KI}} = 185 \text{ cm}^{-1}$ . Given that  $D_e(\text{I}_2) - D_e(\text{KI}) = -171 \text{ kJ mol}^{-1}$ , determine the maximum vibrational quantum number for the product  $\text{KI(g)}$ . Now determine the speed of a  $\text{KI}(v=0)$  molecule relative to the center of mass. Repeat the calculation for the  $\text{KI}(v=1)$  molecule. Do the data in the contour map support a conclusion that  $\text{KI(g)}$  is produced in a distribution of vibrational levels?

**30-44.** Below is a drawing of the contour plot of the potential-energy surface of the collinear  $\text{H(g)} + \text{H}_2(\text{g})$  reaction in the vicinity of the transition state. We take  $r_{12}$  and  $r_{23}$  to be the bond length of the  $\text{H}_2$  reactant and product, respectively. Label the location of the transition state. Draw a dashed line that indicates the lowest energy path for the reaction. Draw a two-dimensional representation of the reaction path in which you plot  $V(r_{12}, r_{23})$  as a function of  $r_{12} - r_{23}$ .



## Application

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- 4) Please cite the literature if you link the HW problem to anyone (author names, titles, journal name, volume numbers, and page numbers).

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