Chemistry 2710 Spring 2006 Test 1 Solutions

1. The general integrated rate law is

$$x^{1-n} = x_0^{1-n} + kt(n-1).$$

For $n = 1/2$, this specializes to

$$x^{1/2} = x_0^{1/2} - \frac{1}{2}kt.$$

To get k, we would plot $x^{1/2}$ vs t. The rate constant is related to the slope m by $m = -\frac{1}{2}k$, so $k = -2m$.

2. The total pressure is

$$P = P_{C_2H_6} + P_{C_2H_4} + P_{H_2}.$$

The stoichiometric relationships between the pressures are as follows:

$$P_{C_2H_4} = P_{H_2} = P_0 - P_{C_2H_6},$$

where P_0 is the initial pressure. Therefore

$$\begin{aligned} P &= P_{C_2H_6} + 2\left(P_0 - P_{C_2H_6}\right) \\ &= 2P_0 - P_{C_2H_6}. \\ \therefore P_{C_2H_6} &= 2P_0 - P \\ &= 2\left(3.0 \times 10^5\,\text{Pa}\right) - 5.0 \times 10^5\,\text{Pa} = 1.0 \times 10^5\,\text{Pa}. \end{aligned}$$

Since this is a second-order reaction,

$$\begin{aligned} \frac{1}{P_{C_2H_6}} &= \frac{1}{P_0} + kt. \\ \therefore t &= \frac{1}{k}\left(\frac{1}{P_{C_2H_6}} - \frac{1}{P_0}\right) \\ &= \frac{1}{9.55 \times 10^{-2}\,\text{Pa}^{-1}\text{s}^{-1}}\left(\frac{1}{1.0 \times 10^5\,\text{Pa}} - \frac{1}{3.0 \times 10^5\,\text{Pa}}\right) \\ &= 7.0 \times 10^{-5}\,\text{s}. \end{aligned}$$

3. (a) For convenience, denote tritium by T.

$$\begin{aligned}
n_{\mathrm{T}} &= \frac{0.034\,\mathrm{g}}{3.016\,049\,267\,5\,\mathrm{g/mol}} = 1.1 \times 10^{-2}\,\mathrm{mol}. \\
k &= \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{4500\,\mathrm{d}} = 1.5 \times 10^{-4}\,\mathrm{d}^{-1}. \\
v &= k n_{\mathrm{T}} = (1.5 \times 10^{-4}\,\mathrm{d}^{-1})(1.1 \times 10^{-2}\,\mathrm{mol}) \\
&= 1.7 \times 10^{-6}\,\mathrm{mol/d}.
\end{aligned}$$

(b) Since $v \propto n_{\mathrm{T}}$, v also obeys the first-order rate law. Thus,

$$\begin{aligned}
t &= -\frac{1}{k} \ln\left(\frac{v}{v_0}\right). \\
v &= \frac{(1.7 \times 10^{-6}\,\mathrm{mol/d})(6.022\,142 \times 10^{23}\,\mathrm{counts/mol})}{(60\,\mathrm{min/h})(24\,\mathrm{h/d})} \\
&= 7.3 \times 10^{14}\,\mathrm{counts/min}. \\
\therefore t &= -\frac{1}{1.5 \times 10^{-4}\,\mathrm{d}^{-1}} \ln\left(\frac{1000\,\mathrm{counts/min}}{7.3 \times 10^{14}\,\mathrm{counts/min}}\right) \\
&= 1.8 \times 10^{5}\,\mathrm{d} \equiv 485\,\mathrm{y}.
\end{aligned}$$

4. (a) If the reaction is elementary, then according to the law of mass action, it should obey second-order kinetics. The simplest way to show that it does is to draw a graph of $1/[C_2F_4]$ vs t. See figure 1. The data fit a line beautifully, confirming the second-order relationship. The rate constant is the slope of the line, which we find by linear regression:

$$k = 8.01 \times 10^{-2}\,\mathrm{L\,mol^{-1}min^{-1}}.$$

(b)

$$\begin{aligned}
k_{+} &= \frac{8.01 \times 10^{-2}\,\mathrm{L\,mol^{-1}min^{-1}}}{60\,\mathrm{s/min}} = 1.34 \times 10^{-3}\,\mathrm{L\,mol^{-1}s^{-1}}. \\
K &= \frac{k_{+}}{k_{-}} = \frac{1.34 \times 10^{-3}\,\mathrm{L\,mol^{-1}s^{-1}}}{9.6 \times 10^{-13}\,\mathrm{s^{-1}}} = 1.4 \times 10^{9}\,\mathrm{L/mol}.
\end{aligned}$$

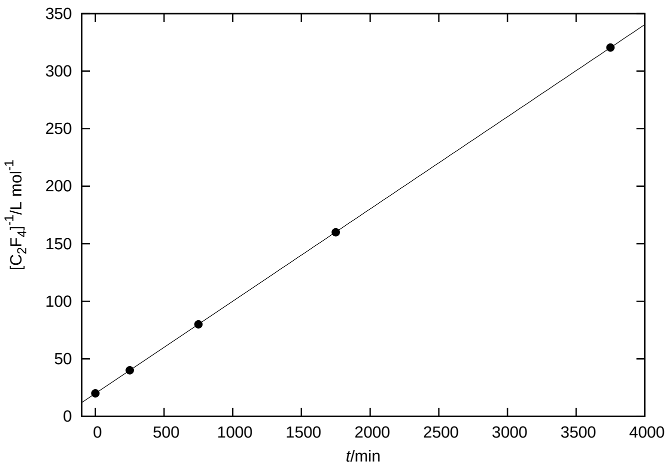

Figure 1: Second-order plot for question 4.

5.

$$\begin{aligned}
\frac{da}{dt} &= -k_1 a - 2k_2 a^2. \\
\therefore \frac{da}{k_1 a + 2k_2 a^2} &= -dt. \\
\therefore -\int_0^t dt' &= \int_{a_0}^{a} \frac{da'}{k_1 a' + 2k_2 (a')^2} = \int_{a_0}^{a} \frac{da'}{a'\,(k_1 + 2k_2 a')}.
\end{aligned}$$

To carry out the integral on the right using the integral given on the exam paper, make the following assignments:

$$\begin{array}{lll}
x \leftarrow a', & a \leftarrow 0, & b \leftarrow 1, \\
c \leftarrow k_1, & e \leftarrow 2k_2. &
\end{array}$$

We can now finish the integral:

$$\begin{aligned}
-t &= \frac{1}{-k_1} \ln\left(\frac{k_1 + 2k_2 a'}{a'}\right)\Bigg|_{a_0}^{a} \\
\therefore t &= \frac{1}{k_1}\left[\ln\frac{k_1 + 2k_2 a}{a} - \ln\frac{k_1 + 2k_2 a_0}{a_0}\right].
\end{aligned}$$