Chemistry 2000 Spring 2002 Midterm Examination Solutions

1. (a) The concentrations in experiments 1 and 2 are in a 3:1 ratio, as are the rates. This is therefore a first-order reaction with rate law

$$v = k[(CH_3N)_2].$$

The rate constant can be determined from either experiment:

$$k = \frac{v}{[(CH_3N)_2]} = \frac{6.0 \times 10^{-6} \, mol \, L^{-1} s^{-1}}{2.4 \times 10^{-2} \, mol/L} = 2.5 \times 10^{-4} \, s^{-1}.$$

(b)

$$
\begin{aligned}
v &= \frac{d[C_2H_6]}{dt} \approx \frac{\Delta[C_2H_6]}{\Delta t}. \\
\therefore \Delta t &= \frac{\Delta[C_2H_6]}{v} = \frac{10^{-4} \, mol/L}{6.0 \times 10^{-6} \, mol \, L^{-1} s^{-1}} = 17 \, s.
\end{aligned}
$$

2. If it's a first-order reaction, a graph of $\ln(\text{percent})$ vs t should be a straight line of slope $-k$. In this case, we have

t (min)	2.21	5.16	13.26	22.84	40.52	60.41
$\ln(\%\text{bp})$	4.55	4.42	4.17	3.78	3.14	2.30

My graph is shown in Fig. 1. The data fit a straight line reasonably well, which confirms that the decomposition of bp is a first-order process. The rate constant is found by taking the slope of the line. The line passes through the points $(0, 4.65)$ and $(70, 1.98)$ (estimated from the graph). The slope is therefore

$$\text{slope} = \frac{\Delta y}{\Delta x} = \frac{4.65 - 1.98}{0 - 70 \, min} = -0.0381 \, min^{-1}.$$

Since the slope is $-k$, this means that $k = 0.0381 \, min^{-1}$.

3. (a)

$$
\begin{aligned}
k &= k_\infty e^{-E_a/(RT)} \\
&= (1.2 \times 10^{10} \, L \, mol^{-1} s^{-1}) \exp\left(\frac{-17.5 \times 10^3 \, J/mol}{(8.314472 \, J \, K^{-1} mol^{-1})(243.15 \, K)}\right) \\
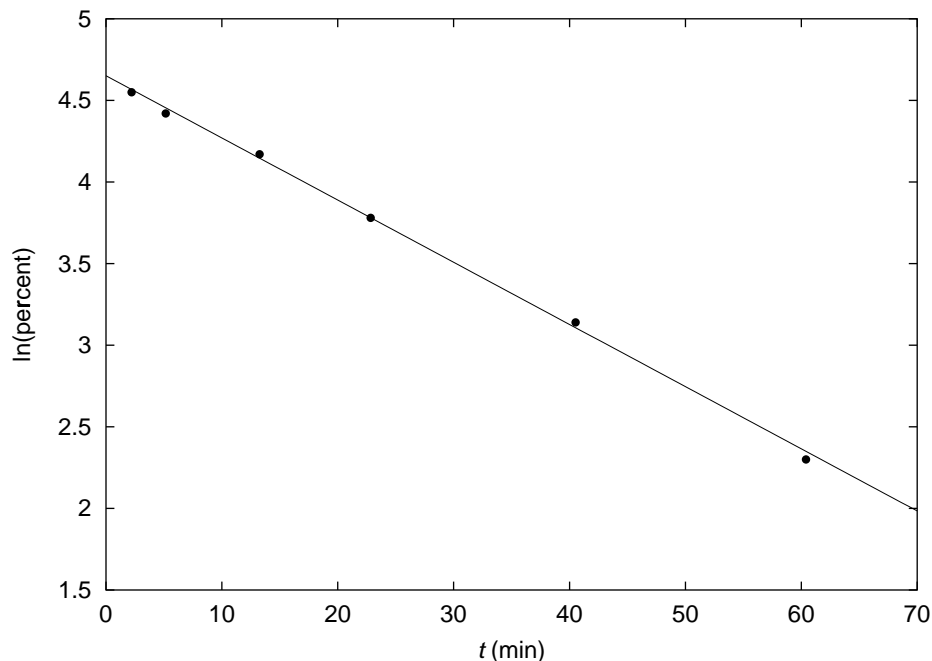&= 2.09 \times 10^6 \, L \, mol^{-1} s^{-1}.
\end{aligned}
$$

Figure 1: Plot of $\ln(\%bp)$ vs t from the data of question 2.

(b) $\dfrac{d[\text{OH}]}{dt} = -k[\text{OH}][\text{CF}_3\text{CH}_2\text{OCHF}_2]$

(c) If the initial concentrations are equal, then by stoichiometry the two concentrations remain equal for all time. Thus $\dfrac{d[\text{OH}]}{dt} = -k[\text{OH}]^2$, which is a simple second-order reaction.

(d) According to the second-order integrated rate law,

$$
\begin{aligned}
t &= \frac{1}{k}\left(\frac{1}{[\text{R}]} - \frac{1}{[\text{R}]_0}\right). \\
[\text{R}] &= 0.10[\text{R}]_0 = 0.00405\,\text{mol/L}. \\
\therefore t &= \frac{1}{2.09 \times 10^6\,\text{L}\,\text{mol}^{-1}\text{s}^{-1}}\left(\frac{1}{0.00405\,\text{mol/L}} - \frac{1}{0.0405\,\text{mol/L}}\right) \\
&= 1.06 \times 10^{-4}\,\text{s}.
\end{aligned}
$$

4.

$$
Q = \frac{(a_{\text{PCl}_3})(a_{\text{Cl}_2})}{a_{\text{PCl}_5}} = \frac{(0.223)(0.111)}{0.177} = 0.140 < K.
$$

This means that the amounts of products will have to increase to reach equilibrium, which in turn means that the reaction is spontaneous as written.

5. Potassium hydroxide is a strong base. Accordingly, $[\text{OH}^-] = 1.3 \times 10^{-4}\,\text{mol/L}$. Since $K_w = (a_{\text{H}^+})(a_{\text{OH}^-})$,

$$
\begin{aligned}
a_{\text{H}^+} &= \frac{K_w}{a_{\text{OH}^-}} = \frac{2.9 \times 10^{-15}}{1.3 \times 10^{-4}} = 2.2 \times 10^{-11}. \\
\therefore \text{pH} &= -\log_{10} a_{\text{H}^+} = 10.65.
\end{aligned}
$$

6. $K = \dfrac{a_{\text{Br}}^2}{a_{\text{Br}_2}} = \dfrac{(P_{\text{Br}}/P^\circ)^2}{P_{\text{Br}_2}/P^\circ}$. We need to know the equilibrium pressures of bromine atoms and molecules. The number of moles of Br_2 at equilibrium is $100 - 1.20\% = 98.8\%$ of the initial number, i.e. $(0.988)(1.05\,\text{mol}) = 1.0374\,\text{mol}$. The number of molecules dissociated is $(0.0120)(1.05\,\text{mol}) = 0.0126\,\text{mol}$. The number of bromine atoms produced is twice as large (by stoichiometry), so $n_{\text{Br}} = 0.0252\,\text{mol}$. The volume of the flask is $(0.980\,\text{L})/(1000\,\text{L/m}^3) = 9.80 \times 10^{-4}\,\text{m}^3$. The temperature is $1600 + 273.15\,\text{K} = 1873\,\text{K}$. The pressures of the reactant and product are therefore

$$
\begin{aligned}
P_{\text{Br}_2} &= \frac{n_{\text{Br}_2} RT}{V} \\
&= \frac{(1.0374\,\text{mol})(8.314472\,\text{J K}^{-1}\text{mol}^{-1})(1873\,\text{K})}{9.80 \times 10^{-4}\,\text{m}^3} \\
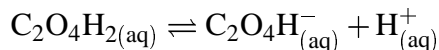&= 1.65 \times 10^7\,\text{Pa} \equiv 163\,\text{atm.} \\
P_{\text{Br}} &= \frac{n_{\text{Br}} RT}{V} \\
&= \frac{(0.0252\,\text{mol})(8.314472\,\text{J K}^{-1}\text{mol}^{-1})(1873\,\text{K})}{9.80 \times 10^{-4}\,\text{m}^3} \\
&= 4.00 \times 10^5\,\text{Pa} \equiv 3.95\,\text{atm.} \\
\therefore K &= \frac{3.95^2}{163} = 9.60 \times 10^{-2}.
\end{aligned}
$$

7. In these problems, we only ever need to worry about the first proton. By Le Chatelier's principle, we know that the acidic environment created by the first proton will inhibit the dissociation of the second proton. The relevant equilibrium is thus

$$
\text{C}_2\text{O}_4\text{H}_{2(\text{aq})} \rightleftharpoons \text{C}_2\text{O}_4\text{H}^-_{(\text{aq})} + \text{H}^+_{(\text{aq})}
$$

for which we have

$$
K_a = \frac{(a_{\text{C}_2\text{O}_4\text{H}^-})(a_{\text{H}^+})}{a_{\text{C}_2\text{O}_4\text{H}_2}}.
$$

The K_a is quite large. It seems extremely likely that we will be able to ignore the autoionization of water. However, we probably should not treat this equilibrium as if little dissociation occurred because of the size of the equilibrium constant. Suppose that the amount of oxalic acid which dissociates, expressed in terms of activities, is x. Then

	$a_{C_2O_4H_2}$	$a_{C_2O_4H^-}$	a_{H^+}
Initial	0.043	0	0
Change	$-x$	x	x
Final	$0.043 - x$	x	x

The K_a expression becomes

$$
\begin{aligned}
6.5 \times 10^{-2} &= \frac{x^2}{0.043 - x}. \\
\therefore 0 &= x^2 + 6.5 \times 10^{-2}x - 2.795 \times 10^{-3}. \\
\therefore x &= \frac{1}{2}\left(-6.5 \times 10^{-2} \pm \sqrt{(6.5 \times 10^{-2})^2 - 4(-2.795 \times 10^{-3})}\right) \\
&= 2.96 \times 10^{-2}. \\
\therefore a_{H^+} &= 2.96 \times 10^{-2}. \\
\therefore \mathrm{pH} &= -\log_{10} a_{H^+} = -\log_{10}(2.96 \times 10^{-2}) = 1.53.
\end{aligned}
$$