

CHM 3400 – Problem Set 8

Due date: Friday, April 3rd, via email, by 5:00pm.

Do all of the following problems. Show your work.

“We should not worry if students don’t know everything, but only if they know everything badly.”

- Peter Kapista

1) The following experimental data were obtained for a particular irreversible reaction at $T = 25.0\text{ }^{\circ}\text{C}$. It is assumed that the reaction obeys a rate law of the form

$$\text{rate} = -d[A]/dt = k [A]^p [B]^q \quad (1.1)$$

Trial	[A] _{initial} (mol/L)	[B] _{initial} (mol/L)	(Rate) _{initial} (mol/L·min)
1	0.00100	0.00100	2.6×10^{-8}
2	0.00100	0.00200	1.2×10^{-7}
3	0.00100	0.00400	3.9×10^{-7}
4	0.00100	0.01000	2.4×10^{-6}
5	0.00200	0.00200	1.5×10^{-7}
6	0.00400	0.00200	1.1×10^{-7}
7	0.01000	0.00200	1.6×10^{-7}

Based on the above data find p, q, and k (including correct units).

2) The data below show the concentration of N_2O_5 versus time for the reaction



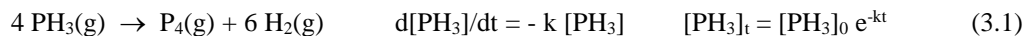
time (s)	[N ₂ O ₅] (mol/L)	time (s)	[N ₂ O ₅] (mol/L)
0.0	1.000	125.0	0.377
25.0	0.822	150.0	0.310
50.0	0.677	175.0	0.255
75.0	0.557	200.0	0.210
100.0	0.458		

The reaction obeys a rate law of the form

$$\text{Rate} = -d[\text{N}_2\text{O}_5]/dt = k [\text{N}_2\text{O}_5]^p$$

where p is the order of the reaction. Determine the order of the reaction, the value for the rate constant (including correct units), and the half-life for the reaction. Also predict the concentration of N_2O_5 at $t = 250.0\text{ s}$.

3) The thermal decomposition of phosphine (PH_3) into phosphorus and molecular hydrogen is a first order reaction

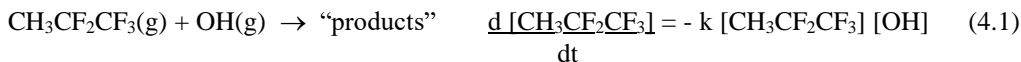


The half-life of the reaction is $t_{1/2} = 35.0\text{ s}$ at $T = 680.\text{ }^{\circ}\text{C}$. Find the following:

- The first order rate constant for the reaction.
- The time required for 95.0 % of the initial phosphine to disappear.

4) Because of their harmful effect on ozone in the stratosphere, chlorofluorocarbons (CFCs), commonly used in air conditioners and refrigerators, have been replaced by compounds such as hydrofluorocarbons (HFCs) that are more reactive in the troposphere and therefore less likely to migrate to the stratosphere and cause damage to the ozone layer. One such compound is $\text{CH}_3\text{CF}_2\text{CF}_3$ (HFC-245cb).

The main removal process for these types of compounds in the troposphere is by reaction with OH radical



Accurate values for the bimolecular rate constant for this reaction are required to model the chemistry of HFC-245cb in the troposphere and determine the half-life for the compound for typical tropospheric conditions.

The above reaction was studied in the laboratory at $T = 298$. K under pseudo-first order conditions, where $[\text{HFC-245cb}]_0 \gg [\text{OH}]_0$, and the following results were found (note $k' = k [\text{HFC-245cb}]_0$, $1 \mu\text{s} = 10^{-6} \text{ s}$).

$[\text{HFC-245cb}]_0$ (molecule/cm ³)	k' (s ⁻¹)	$[\text{HFC-245cb}]_0$ (molecules/cm ³)	k' (s ⁻¹)
2.14×10^{10}	38.3×10^{-6}	7.26×10^{10}	$103. \times 10^{-6}$
4.78×10^{10}	70.2×10^{-6}	9.35×10^{10}	$145. \times 10^{-6}$

Based on these data, find the value for k at $T = 298$. K. Give your final answer in units of cm³/molecule•s.

5) Another hydrofluorocarbon used as a CFC substitute is $\text{CH}_3\text{CH}_2\text{F}$. In a 2003 research paper, Kozlov and coworkers obtained the following data for the temperature dependence of the bimolecular rate constant for the reaction



T (K)	k (cm ³ /molecule•s)
210.	7.94×10^{-14}
220.	9.62×10^{-14}
230.	10.58×10^{-14}
250.	13.48×10^{-14}
272.	17.47×10^{-14}

a) Assuming the above data obey the Arrhenius equation, give an appropriate plot of the data, and from that data plot determine the Arrhenius parameters A (pre-exponential factor) and E_a (activation energy), including correct units.

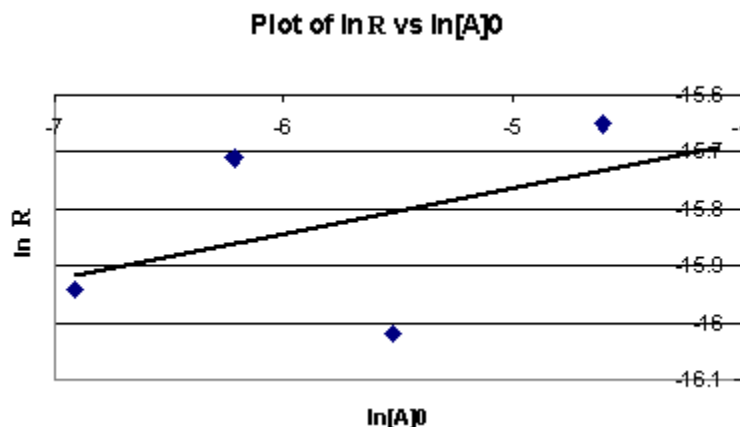
b) Based on your answer in a, calculate the value of k for the above reaction at $T = 300$. K.

Solutions.

1) To find p, we plot $\ln R$ vs $\ln[A]_0$ for trials 2, 5, 6, and 7 (where $[B]_0$ is constant)

trial	$\ln[A]_0$	$\ln R$
2	- 6.908	- 15.94
5	- 6.215	- 15.71
6	- 5.521	- 16.02
7	- 4.605	- 15.65

The data are plotted below



The best fit to the data gives $\ln R = 0.081 \ln[A]_0 - 15.36$

So $p = 0.081$, or, rounded off to the nearest reasonable value, $p = 0$.

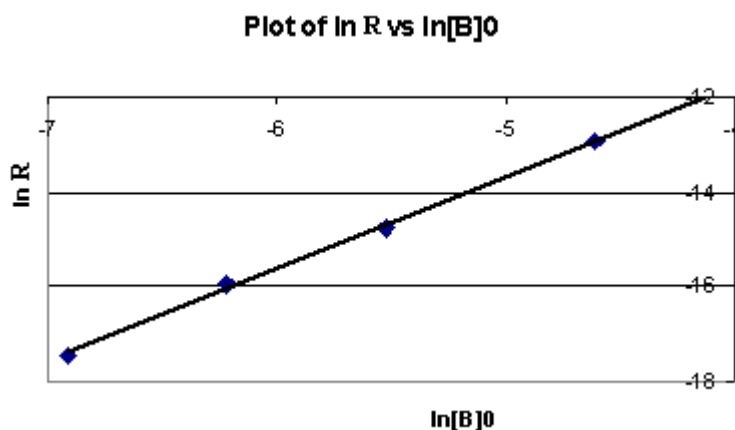
To find q, we plot $\ln R$ vs $\ln[B]_0$ for trials 1, 2, 3, and 4 (where $[A]_0$ is constant)

trial	$\ln[B]_0$	$\ln k$
1	- 6.908	- 17.47
2	- 6.215	- 15.94
3	- 5.521	- 14.76
4	- 4.605	- 12.94

The data are plotted on the next page.

The best fit to the data gives $\ln R = 1.942 \ln[B]_0 - 3.99$

So $q = 1.942$, or, rounded off to the nearest reasonable value, $q = 2$.



The rate law therefore is $\text{Rate} = k [\text{B}]^2$. From the initial rate data, we may find k using

$$k = (\text{Rate})_i / [\text{B}]_0^2$$

trial	k (L/mol•min)
1	0.0260
2	0.0300
3	0.0244
4	0.0240
5	0.0375
6	0.0275
7	0.0400
	AVE $k = 0.030 \text{ L/mol}\cdot\text{min}$

2) The general procedure used in these types of problems is as follows

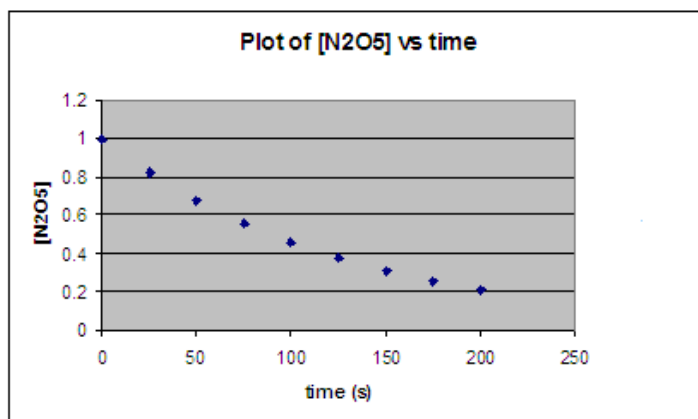
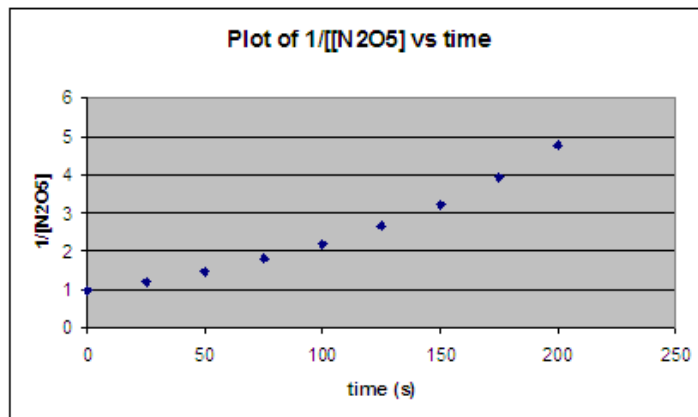
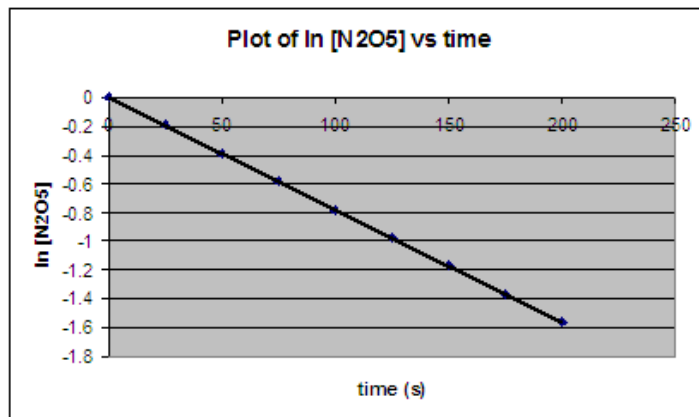
- 1) plot $\ln(\text{concentration})$ vs time. A straight line means a 1st order reaction.
- 2) plot $1/(\text{concentration})$ vs time. A straight line means a 2nd order reaction.
- 3) plot concentration vs time. A straight line means a 0th order reaction.

If none of these gives a straight line, then the reaction order is different than 1st, 2nd, or 0th order. (Note that there are more general methods that can be used to determine the experimental order, but they have not been discussed in the book and so will not be discussed here).

The values needed to do the necessary plots are given in the table below..

time	[N ₂ O ₅]	ln [N ₂ O ₅]	1/[N ₂ O ₅]
0.	1.000	0.000	1.000
25.	0.822	- 0.196	1.217
50.	0.677	- 0.390	1.477
75.	0.557	- 0.585	1.795
100.	0.458	- 0.781	2.183
125.	0.377	- 0.976	2.653
150.	0.310	- 1.171	3.226
175.	0.255	- 1.366	3.922
200.	0.210	- 1.561	4.762

I will give all of the plots discussed above, though usually we would plot them in order, as suggested above, and stop if a linear plot was found.



Note that of the three plots the only one that gives a linear relationship is the plot of $\ln [N_2O_5]$ vs time. Therefore the reaction is first order. So $k = -(\text{slope})$

Based on fitting the data in the plot of $\ln [N_2O_5]$ vs time, I get

$$\text{slope} = -0.0078 \text{ s}^{-1}$$

$$\text{So } k = -(\text{slope}) = 0.0078 \text{ s}^{-1}$$

At $t = 250. \text{ s}$,

$$\ln [N_2O_5] = (-0.0078 \text{ s}^{-1})(250. \text{ s}) = -1.95$$

$$[N_2O_5] = e^{-1.95} = 0.142 \text{ mol/L}$$

3) a) To calculate the rate constant, k , from the half-life of a first-order reaction, we use the relationship

$$t_{1/2} = \frac{\ln(2)}{k}$$

$$k = \frac{\ln(2)}{t_{1/2}} = \frac{\ln(2)}{35.0\text{s}} = 0.0198 \text{ s}^{-1}$$

b) The relationship between the concentration of a reactant at different times in a first-order reaction is given in the text. We are asked to determine the time required for 95% of the phosphine to decompose. If we initially have 100% of the compound and 95% has reacted, then what is left must be (100% – 95%), or 5%. Thus, the ratio of the percentages will be equal to the ratio of the actual concentrations; that is,

$$[A]_t/[A]_0 = (5\%/100\%), \text{ or } 0.05/1.00 = 0.050$$

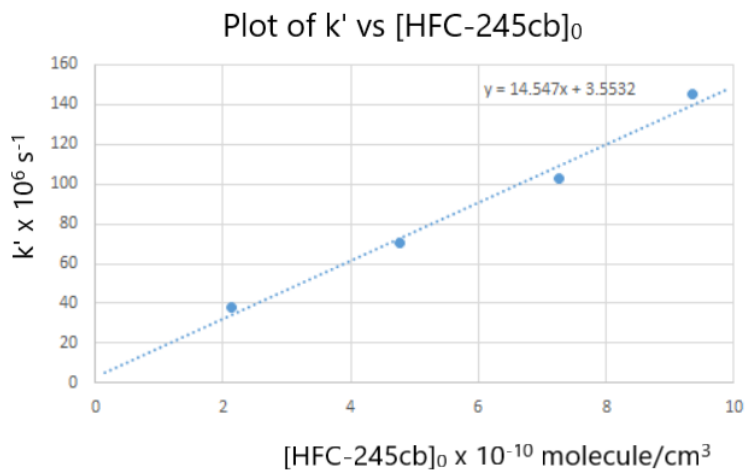
The time required for 95% of the phosphine to decompose can be found using

$$\ln\{[A]_t/[A]_0\} = -kt$$

$$t = -(1/k) \ln\{[A]_t/[A]_0\} = -(1/0.0198 \text{ s}^{-1}) \ln(0.05) = 151. \text{ s}$$

4) There are different ways to do this problem. One way is to plot k' vs $[\text{HFC-245cb}]_0$. Since $k' = k [\text{HFC-245cb}]_0$, the slope in such a plot is equal to k , the bimolecular rate constant.

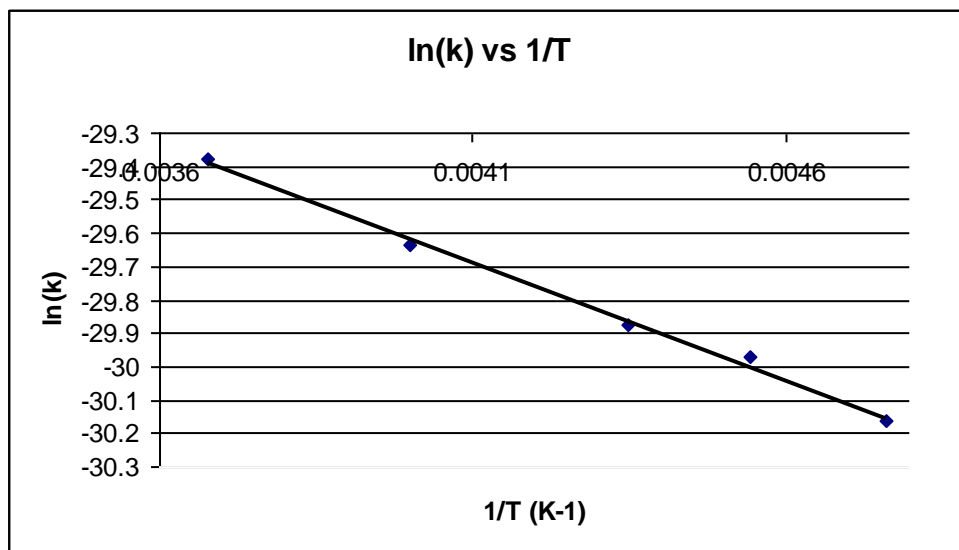
The data are plotted below.



Based on the plot, the value for k is equal to the slope, and so $k = 14.5 \times 10^{-16} \text{ cm}^3/\text{molecule}\cdot\text{s}$.

5) a) To fit the data to the Arrhenius equation we need to plot $\ln(k)$ vs $1/T$. The data are presented below along with the plot (given on the next page)

T (K)	$k \text{ (cm}^3/\text{molecule}\cdot\text{s)}$	$1/T \text{ (K}^{-1}\text{)}$	$\ln(k)$
210.	7.94×10^{-14}	0.004762	- 30.164
220.	9.62×10^{-14}	0.004545	- 29.972
230.	10.58×10^{-14}	0.004348	- 29.877
250.	13.48×10^{-14}	0.004000	- 29.635
272.	17.47×10^{-14}	0.003676	- 29.376



Based on the plot, I get slope = - 705.7 K
intercept = - 26.794

And so $E_a = -mR = -(-705.7 \text{ K})(8.3145 \text{ J/mol}\cdot\text{K}) = 5870. \text{ J/mol}$

$\ln A = -26.794$, and so $A = e^{-26.794} = 2.3 \times 10^{-12} \text{ cm}^3/\text{molecule}\cdot\text{s}$

b) At $T = 300. \text{ K}$

$$k = (2.3 \times 10^{-12} \text{ cm}^3/\text{molecule}\cdot\text{s}) \exp\left[-\frac{(5870. \text{ J/mol})}{(8.3145 \text{ J/mol}\cdot\text{K})(300. \text{ K})}\right]$$

$$= 21.8 \times 10^{-14} \text{ cm}^3/\text{molecule}\cdot\text{s}$$