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 °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 verses time for the reaction

$$N_2O_5(g) \rightarrow NO_3(g) + NO_2(g) \quad (2.1)$$

time (s)	$[N_2O_5]$ (mol/L)	time (s)	$[N_2O_5]$ (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

$$\text{Rate} = - d[N_2O_5]/dt = k [N_2O_5]^p$$

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 s.

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

$$4\, PH_3(g) \rightarrow P_4(g) + 6\, H_2(g) \qquad d[PH_3]/dt = - k [PH_3] \qquad [PH_3]_t = [PH_3]_0\, e^{-kt} \quad (3.1)$$

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

a) The first order rate constant for the reaction.
b) 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on ozone in the stratosphere, chlorofluorocarbons (CFCs), commonly used in air conditioners and refrigerators, have been replaced by compounds such as hydrofluorocarbons (HFCs) that are more reactive in the troposphere and therefore less likely to migrate to the stratosphere and cause damage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 $CH_3CF_2CF_3$ (HFC-245cb).

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

$$CH_3CF_2CF_3(g) + OH(g) \rightarrow \text{“products”} \qquad \frac{d\,[CH_3CF_2CF_3]}{dt} = -\,k\,[CH_3CF_2CF_3]\,[OH] \qquad (4.1)$$

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 $[\text{HFC-245cb}]_0 >> [OH]_0$, and the following results were found (note $k' = k\,[\text{HFC-245cb}]_0$).

$[\text{HFC-245cb}]_0$ (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 cm^3/molecule•s.

5) Another hydrofluorocarbon used as a CFC substitute is CH_3CH_2F. In a 2003 research paper, Kozlov and coworkers obtained the following data for the temperature dependence of the bimolecular rate constant for the reaction

$$CH_3CH_2F(g) + OH(g) \rightarrow \text{"products"} \qquad (5.1)$$

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.