CHM 3400 – Fundamentals of Physical Chemistry
Third Hour Exam

There are five problems on the exam. Do all of the problems. Show your work

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R = 0.08206 L•atm/mole•K	N_A = 6.022 x 10^{23}
R = 0.08314 L•bar/mole•K	1 L•atm = 101.3 J
R = 8.314 J/mole•K	1 atm = 1.013 bar = 1.013 x 10^5 N/m^2
F = 96485. C/mol	1 atm = 760 torr
(1 volt)•(1 Coulomb) = 1 Joule	

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1. (24 points) Consider the reaction

$$A + B \rightarrow \text{"products"} \qquad (1.1)$$

Initial rate data, obtained at T = 360. K, are given below.

Trial	$[A]_0$ (mol/L)	$[B]_0$ (mol/L)	Initial Rate (mol/L•min)
1	0.0100	0.0100	3.6 x 10^{-5}
2	0.0200	0.0100	14.6 x 10^{-5}
3	0.0100	0.0200	7.0 x 10^{-5}

Find the following:

a) The order of the reaction with respect to A and with respect to B.
b) The rate constant for the reaction (including correct units).
c) The initial rate of the reaction when $[A]_0$ = 0.01500 M, $[B]_0$ = 0.0300 M.

2. (16 points) The gas phase decomposition of chloroethane

$$CH_3CH_2Cl(g) \rightarrow C_2H_4(g) + HCl(g) \qquad (2.1)$$

is an example of a first order chemical reaction, with

$$\frac{d[CH_3CH_2Cl]}{dt} = -k\,[CH_3CH_2Cl] \qquad (2.2)$$

The value for the rate constant k for the reaction is given by the Arrhenius equation

$k = A\,e^{-Ea/RT}$ A = 4.0 x 10^{14} s^{-1} E_a = 254.0 kJ/mol

a) What is the numerical value for the rate constant, k, for the above reaction at T = 300.0 K?
b) At what value of temperature will the half-life for chloroethane be 1.00 hour?

3. (20 points) Tetrafluoroethene (C_2F_4) will, at high temperatures, form the cyclic compound cyclo-C_4F_8, by the second order irreversible process

$$2\ C_2F_4(g) \rightarrow \text{cyclo-}C_4F_8(g) \qquad d[C_2F_4]/dt = -\ k\ [C_2F_4]^2 \qquad (3.1)$$

At T = 600. K, k = 0.0262 L/mol•s, and d ln(k)/d(1/T) = - 13100. K.

a) The initial concentration of C_2F_4 in a system at T = 600. K is $[C_2F_4]_0 = 3.50 \times 10^{-3}$ mol/L. What will the concentration of C_2F_4 be at t = 1.00 hour?

b) Based on the information above, and assuming the reaction obeys the Arrhenius equation, find the values for A (pre-exponential factor) and E_a (activation energy) for the above reaction (including correct units).

4. (16 points) Consider the following three mechanisms for the formation of $COCl_2$ from CO and Cl_2 in a gas mixture of CO/Cl_2/air. Note that M = air, and [M] >> [CO], [Cl_2]

stoic. $CO + Cl_2 \rightarrow COCl_2$ (4.1)

mechanism 1

step 1	$Cl_2 + M \leftrightarrows Cl + Cl + M$	fast
step 2	$CO + Cl + M \leftrightarrows COCl + M$	fast
step 3	$COCl + Cl_2 \rightarrow COCl_2 + Cl$	slow

mechanism 2

step 1	$Cl_2 + M \rightarrow Cl + Cl + M$	slow
step 2	$CO + Cl + M \leftrightarrows COCl + M$	fast
step 3	$COCl + Cl_2 \rightarrow COCl_2 + Cl$	fast

mechanism 3

step 1	$Cl_2 + M \leftrightarrows Cl + Cl + M$	fast
step 2	$CO + Cl + M \rightarrow COCl + M$	slow
step 3	$COCl + Cl_2 \rightarrow COCl_2 + Cl$	fast

Find the rate law predicted for each of the above three mechanisms. <u>Show your work</u>.

5. (24 points) In the gas phase hydrogen atoms (H) will react with ozone molecules (O_3) by an irreversible bimolecular reaction

$$H + O_3 \rightarrow OH + O_2 \qquad \text{rate} = -d[H]/dt = k_{bi}\,[H]\,[O_3] \qquad (5.1)$$

where [H] and [O_3] are the concentrations of H atoms and O_3 molecules in units of molecule/cm^3, and k_{bi} is the bimolecular rate constant for the reaction.

a) In a particular experiment carried out at T = 300. K, the initial concentrations of ozone molecules and hydrogen atoms were $[O_3]_0 = 5.0 \times 10^{14}$ molecule/cm^3 and $[H]_0 = 1.00 \times 10^{10}$ molecule/cm^3. A plot of [H] vs time is given below. Based on the plot, the half-life for hydrogen atoms in the reaction is $t_{1/2}$ = 48. μsec. Using this information find the value for k_{bi}, the bimolecular rate constant for the reaction (including correct units).

b) In a second experiment, also carried out at T = 300. K, the initial concentration of ozone molecules is again $[O_3]_0 = 5.0 \times 10^{14}$ molecule/cm^3, but the initial concentration of hydrogen atoms is doubled, so $[H]_0 = 2.00 \times 10^{10}$ molecule/cm^3. What will be the value for $t_{1/2}$, the half-life for hydrogen atoms, for this set of initial conditions? Give your value for $t_{1/2}$ in units of μsec.

c) In a third experiment, carried out at T = 250. K, the initial concentrations of ozone molecules and hydrogen atoms is the same as in the first experiment, $[O_3]_0 = 5.0 \times 10^{14}$ molecule/cm^3, and $[H]_0 = 1.00 \times 10^{10}$ molecule/cm^3. Given that the rate constant for the experiment obeys the Arrhenius equation, and that E_a = 3.90 kJ/mol, what will be the value for $t_{1/2}$, the half-life for hydrogen atoms, for this set of initial conditions? Give your value for $t_{1/2}$ in units of μsec.