

CHM 3400 – Fundamentals of Physical Chemistry
Third Hour Exam

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

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

1. (24 points) Consider the reaction



Initial rate data, obtained at $T = 360 \text{ K}$, are given below.

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

Find the following:

- The order of the reaction with respect to A and with respect to B.
- The rate constant for the reaction (including correct units).
- The initial rate of the reaction when $[A]_0 = 0.01500 \text{ M}$, $[B]_0 = 0.0300 \text{ M}$.

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



is an example of a first order chemical reaction, with

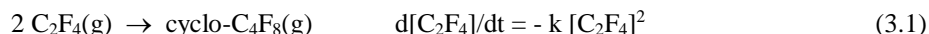
$$\frac{d[\text{CH}_3\text{CH}_2\text{Cl}]}{dt} = -k [\text{CH}_3\text{CH}_2\text{Cl}] \quad (2.2)$$

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

$$k = A e^{-E_a/RT} \quad A = 4.0 \times 10^{14} \text{ s}^{-1} \quad E_a = 254.0 \text{ kJ}/\text{mol}$$

- What is the numerical value for the rate constant, k , for the above reaction at $T = 300.0 \text{ K}$?
- 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



At $T = 600. \text{ K}$, $k = 0.0262 \text{ L/mol}\cdot\text{s}$, and $d \ln(k)/d(1/T) = -13100. \text{ K}$.

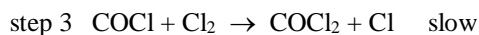
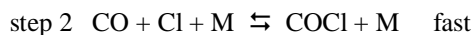
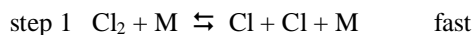
a) The initial concentration of C_2F_4 in a system at $T = 600. \text{ K}$ is $[C_2F_4]_0 = 3.50 \times 10^{-3} \text{ mol/L}$. What will the concentration of C_2F_4 be at $t = 1.00 \text{ hour}$?

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).

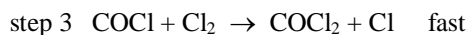
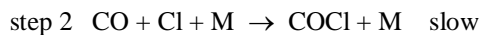
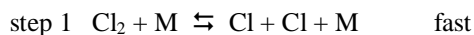
4. (16 points) Consider the following three mechanisms for the formation of $COCl_2$ from CO and Cl_2 in a gas mixture of $CO/Cl_2/\text{air}$. Note that $M = \text{air}$, and $[M] \gg [CO], [Cl_2]$



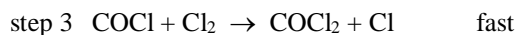
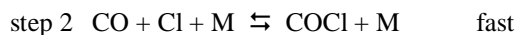
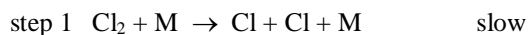
mechanism 1



mechanism 3

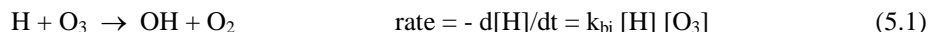


mechanism 2



Find the rate law predicted for each of the above three mechanisms. Show your work.

5. (24 points) In the gas phase hydrogen atoms (H) will react with ozone molecules (O₃) by an irreversible bimolecular reaction



where [H] and [O₃] are the concentrations of H atoms and O₃ molecules in units of molecule/cm³, 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 [O₃]₀ = 5.0 x 10¹⁴ molecule/cm³ and [H]₀ = 1.00 x 10¹⁰ molecule/cm³. 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 [O₃]₀ = 5.0 x 10¹⁴ molecule/cm³, but the initial concentration of hydrogen atoms is doubled, so [H]₀ = 2.00 x 10¹⁰ molecule/cm³. 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, [O₃]₀ = 5.0 x 10¹⁴ molecule/cm³, and [H]₀ = 1.00 x 10¹⁰ molecule/cm³. 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.

