

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·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

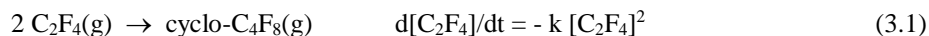
$$\frac{d[\text{CH}_3\text{CH}_2\text{Cl}]}{dt} = -k [\text{CH}_3\text{CH}_2\text{Cl}] \quad (2.2)$$

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 $d \ln(k)/d(1/T) = -13100. \text{ K}$.

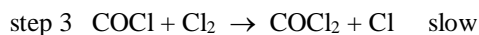
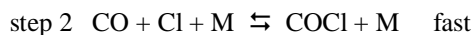
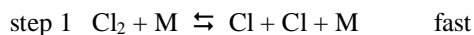
a) The initial concentration of C_2F_4 in a system at $T = 600. \text{ K}$ is $[C_2F_4]_0 = 3.50 \times 10^{-3} \text{ mol/L}$. What will the concentration of C_2F_4 be at $t = 1.00 \text{ hour}$?

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).

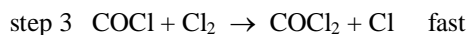
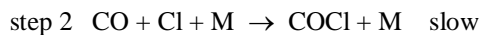
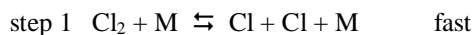
4. (16 points) Consider the following three mechanisms for the formation of $COCl_2$ from CO and Cl_2 in a gas mixture of $CO/Cl_2/\text{air}$. Note that $M = \text{air}$, and $[M] \gg [CO], [Cl_2]$



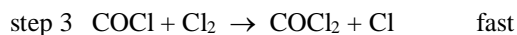
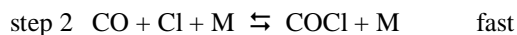
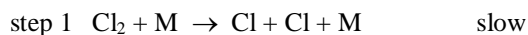
mechanism 1



mechanism 3

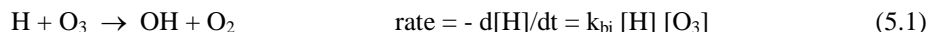


mechanism 2



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

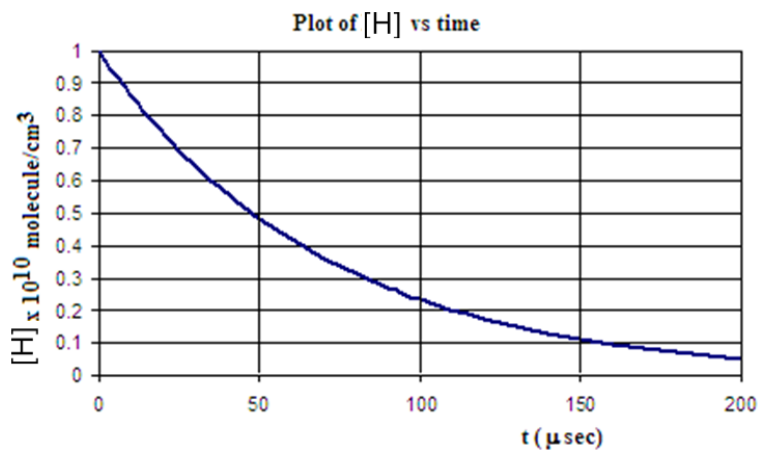


where [H] and [O₃] are the concentrations of H atoms and O₃ molecules in units of molecule/cm³, and k_{bi} is the bimolecular rate constant for the reaction.

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.



Solutions.

1) To find the reaction order for A we can compare trials 2 and 1

$$\frac{\text{rate 2}}{\text{rate 1}} = \frac{14.6 \times 10^{-5} \text{ mol/L}\cdot\text{s}}{3.6 \times 10^{-5} \text{ L/mol}\cdot\text{s}} = \frac{k[A_2]^p[B_2]^q}{k[A_1]^p[B_1]^q} = \frac{k(0.0200 \text{ M})^p(0.0100 \text{ M})^q}{k(0.0100 \text{ M})^p(0.0100 \text{ M})^q}$$

The term $k(0.0100 \text{ M})^q$ appears in both the numerator and denominator, and so cancels, leaving

$$(14.6 \times 10^{-5} / 3.6 \times 10^{-5}) = (0.0200 / 0.0100)^p$$

$$4.06 = 2^p \quad p = 2$$

To find the reaction order for B we can compare trials 3 and 1

$$\frac{\text{rate 3}}{\text{rate 1}} = \frac{7.0 \times 10^{-5} \text{ mol/L}\cdot\text{s}}{3.6 \times 10^{-5} \text{ L/mol}\cdot\text{s}} = \frac{k[A_3]^p[B_3]^q}{k[A_1]^p[B_1]^q} = \frac{k(0.0100 \text{ M})^p(0.0200 \text{ M})^q}{k(0.0100 \text{ M})^p(0.0100 \text{ M})^q}$$

The term $k(0.0100 \text{ M})^p$ appears in both the numerator and denominator, and so cancels, leaving

$$(7.0 \times 10^{-5} / 3.6 \times 10^{-5}) = (0.0200 / 0.0100)^q$$

$$1.94 = 2^q \quad q = 1$$

Notice that we have picked p and q as the integer values that give the best agreement with the experimental results.

Our rate law, therefore, is $\text{rate} = k[A]^2[B]$ (second order in A, first order in B, third order overall).

b) If we solve our rate law for k, we get

$$k = \frac{\text{rate}}{[A]^2[B]}$$

Using the data from the first trial, we get

$$k = \frac{(3.6 \times 10^{-5} \text{ mol/L}\cdot\text{s})}{(0.0100 \text{ M})^2(0.0100 \text{ M})} = 36.0 \text{ L}^2/\text{mol}^2\cdot\text{min}$$

Note that if we calculated k from one of the other trials we would get a slightly different value (36.5 $\text{L}^2/\text{mol}^2\cdot\text{min}$ for trial 2, 35.0 $\text{L}^2/\text{mol}^2\cdot\text{min}$ for trial 3). If this was a real experiment we would average the three experimental values. On an exam, however, you can just pick one data set to calculate k.

$$\begin{aligned} \text{c) rate} &= k[A]^2[B] = (36.0 \text{ L}^2/\text{mol}^2\cdot\text{min})(0.0150 \text{ M})^2(0.0300 \text{ M}) \\ &= 20.2 \times 10^{-5} \text{ mol/L}\cdot\text{min} \end{aligned}$$

$$2) \quad \text{a) } k = A \exp(-E_a/RT) = (4.0 \times 10^{-14} \text{ s}^{-1}) \exp[(-254000. \text{ J/mol})/(8.314 \text{ J/mol}\cdot\text{K})(300. \text{ K})]$$

$$= (4.0 \times 10^{-14} \text{ s}^{-1})(5.93 \times 10^{-49}) = 2.37 \times 10^{-30} \text{ s}^{-1}$$

b) We first need to find the value for k. For a first order homogeneous reaction

$$t_{1/2} = \ln(2)/k \quad k = \ln(2)/t_{1/2} = \ln(2)/(3600. \text{ s}) = 1.93 \times 10^{-4} \text{ s}^{-1}$$

$$k = A \exp(-E_a/RT)$$

$$(k/A) = \exp(-E_a/RT)$$

Taking the ln of both sides gives

$$\ln(k/A) = - (E_a/RT)$$

$$T = - \frac{E_a}{\ln(k/A)R} = - \frac{(254000. \text{ J/mol})}{\ln[1.93 \times 10^{-4}/4.0 \times 10^{-4}]} (8.314 \text{ J/mol}\cdot\text{K}) = 724. \text{ K}$$

3) a) For a second order homogeneous irreversible reaction, we may say

$$\begin{aligned} (1/[A]_t) &= (1/[A]_0) + kt = (1/3.50 \times 10^{-3} \text{ mol/L}) + (0.0262 \text{ L/mol}\cdot\text{s})(3600. \text{ s}) \\ &= 285.7 \text{ L/mol} + 94.32 \text{ L/mol} = 380.0 \text{ L/mol} \end{aligned}$$

$$[A]_t = 1/(380.0 \text{ L/mol}) = 2.63 \times 10^{-3} \text{ mol/L}$$

$$b) E_a = -R (d \ln k/d(1/T)) = - (8.3145 \text{ J/mol}\cdot\text{K})(- 13100. \text{ K}) = 108.9 \text{ kJ/mol}$$

$$k = A \exp(-E_a/RT)$$

so
$$A = k \exp(E_a/RT) = (0.0262 \text{ L/mol}\cdot\text{s}) \exp[(108900 \text{ J/mol})/(8.3145 \text{ J/mol}\cdot\text{K})(600. \text{ K})]$$

$$= 7.95 \times 10^7 \text{ L/mol}\cdot\text{s}$$

4) a) The overall rate is the rate of the slow step, and so

rate = $k_3 [\text{COCl}][\text{Cl}_2]$ This is in terms of a reaction intermediate, which must be eliminated.

The second step is fast and reversible, and so

$$k_2 [\text{CO}][\text{Cl}][\text{M}] = k_{-2} [\text{COCl}][\text{M}] \quad [\text{COCl}] = \frac{k_2 [\text{CO}][\text{Cl}][\text{M}]}{k_{-2} [\text{M}]} = \frac{k_2 [\text{CO}][\text{Cl}]}{k_{-2}}$$

The first step is also fast and reversible, and so

$$k_1 [\text{Cl}_2][\text{M}] = k_{-1} [\text{Cl}]^2[\text{M}] \quad [\text{Cl}]^2 = \frac{k_1 [\text{Cl}_2][\text{M}]}{k_{-1} [\text{M}]} = \frac{k_1 [\text{Cl}_2]}{k_{-1}}$$

and so $[\text{Cl}] = (k_1/k_{-1})^{1/2} [\text{Cl}_2]^{1/2}$

Substituting for [Cl] in the expression for [COCl] gives

$$[\text{COCl}] = \frac{k_2 [\text{CO}]}{k_{-2}} (k_1/k_{-1})^{1/2} [\text{Cl}_2]^{1/2} = (k_1/k_{-1})^{1/2} (k_2/k_{-2}) [\text{CO}][\text{Cl}_2]^{1/2}$$

Substituting into our expression for the rate of reaction we get our final result

$$\text{rate} = k_3 [\text{Cl}_2] \{ (k_1/k_{-1})^{1/2} (k_2/k_{-2}) [\text{CO}][\text{Cl}_2]^{1/2} \} = (k_1/k_{-1})^{1/2} (k_2/k_{-2}) k_3 [\text{CO}][\text{Cl}_2]^{3/2} = k [\text{CO}][\text{Cl}_2]^{3/2}$$

where $k = (k_1/k_{-1})^{1/2} (k_2/k_{-2}) k_3$

b) The overall rate is the rate of the slow step, and so

$$\text{rate} = k_1 [\text{Cl}_2][\text{M}]$$

c) The overall rate is the rate of the slow step, and so

rate = $k_2 [\text{CO}][\text{Cl}][\text{M}]$ This is in terms of a reaction intermediate, which must be eliminated.

The first step is fast and reversible, and so

$$k_1 [\text{Cl}_2][\text{M}] = k_{-1} [\text{Cl}]^2[\text{M}] \qquad [\text{Cl}]^2 = \frac{k_1 [\text{Cl}_2][\text{M}]}{k_{-1} [\text{M}]} = \frac{k_1 [\text{Cl}_2]}{k_{-1}}$$

and so $[\text{Cl}] = (k_1/k_{-1})^{1/2} [\text{Cl}_2]^{1/2}$

Substituting into the expression for the rate of reaction gives the final result

$$\text{rate} = k_2 [\text{CO}] [\text{M}] \{ (k_1/k_{-1})^{1/2} [\text{Cl}_2]^{1/2} \} = (k_1/k_{-1})^{1/2} k_2 [\text{CO}][\text{M}][\text{Cl}_2]^{1/2} = k [\text{CO}][\text{M}][\text{Cl}_2]^{1/2}$$

where $k = (k_1/k_{-1})^{1/2} k_2$

Notice that each of these rate mechanisms leads to a different rate law, and so experimental data could eliminate at least two of these mechanisms from consideration.

5) a) Since $[\text{O}_3]_0 \gg [\text{H}]_0$, we have pseudo-first order conditions, and so the pseudo-first order rate constant is related to the half life by the expression

$$t_{1/2} = \ln(2)/k' \qquad k' = k_{bi}[\text{O}_3]_0$$

$$k' = \ln(2)/t_{1/2} = \ln(2)/48. \times 10^{-6} \text{ s} = 1.44 \times 10^4 \text{ s}^{-1}$$

$$k_{bi} = (1.44 \times 10^4 \text{ s}^{-1}) / (5.0 \times 10^{14} \text{ molecule/cm}^3) = 2.88 \times 10^{-11} \text{ cm}^3/\text{molecule}\cdot\text{s}$$

b) Since $[\text{O}_3]_0$ is the same, and $[\text{O}_3]_0 \gg [\text{H}]_0$ is still true, the half life is the same, $t_{1/2} = 48. \mu\text{sec}$

c) Both experiments occur under pseudo-first order conditions and with the same initial concentration of O_3 , and so

$$\begin{aligned} \ln(k'_2/k'_1) &= - (E_a/R) \{ (1/T_2) - (1/T_1) \} \\ &= - [(3900. \text{ J/mol}) / (8.3145 \text{ J/mol}\cdot\text{K})] \{ (1/250. \text{ K}) - (1/300. \text{ K}) \} \\ &= - 0.3127 \end{aligned}$$

so $k'_2 = k'_1 e^{-0.3127} = (1.44 \times 10^4 \text{ s}^{-1})(0.7315) = 1.053 \times 10^4 \text{ s}^{-1}$

$$t_{1/2} = \ln(2)/(1.053 \times 10^4 \text{ s}^{-1}) = 6.58 \times 10^{-5} \text{ s} = 65.8 \mu\text{sec}$$