

Homework 4

Distributed: Sunday, February 15, 2004**Due: Friday, February 20, 2004****Name:** _____

Recitation Section (circle one):

Zach: 6:30 7:30**Student Number:** _____**Jen:** 6:30 7:30

Other members of your work group _____

How much time did you spend on this assignment? _____
(This is used only to monitor class work load.)

During the first kinetics lecture, we traced the efforts of atmospheric chemists to explain the depletion of ozone in the upper atmosphere. (The powerpoint slides have been posted on Blackboard for your review.) U2 spy planes gathered much of the initial data that linked ClO in the stratosphere to the ozone depletion. The data collected during these flights showed the concentrations of various chemical species in the stratosphere, but did not measure how fast the processes were occurring. To determine the kinetics (rates) of ozone depletion reactions, chemists perform controlled laboratory studies. In this homework, we will interpret data obtained from such laboratory experiments to study the ozone depletion reaction:



The data will allow us to:

- (1) determine the reaction rate of the uncatalyzed reaction
- (2) determine the effect of the presence of chlorine on the kinetics of the reaction
- (3) determine the effect of temperature on the reaction rate

Rate law of the uncatalyzed reaction

1. (1 pt) Use the data in Table 1 to calculate the initial rate of reaction (1), for the initial concentrations and temperature used in that experiment. Note that atmospheric chemists express concentrations in terms of molecules/cm³ instead of the (moles/liter) we have been using in class. Also, following the convention of atmospheric chemistry, we'll use units of molecules/cm³ for O (as opposed to atoms/cm³).

2. (2 pts) Use the data in Tables 1 through 4 to determine the rate law for the uncatalyzed reaction at 230K. The rate law should be of the form: $\text{rate} = k [\text{O}_3]^n [\text{O}]^m$, with concentrations in units of $(\text{molecules}/\text{cm}^3)$. Please determine both the powers and the rate constant. Check that your rate law can account for the initial rate of all 4 experiments (Tables 1-4).

Rate law of the catalyzed reaction

3. (3 pts) Molina and Rowland proposed that the presence of Cl atoms accelerates the destruction of ozone by acting as a catalyst. The catalyzed reaction can be written:



Use the data in Tables 5 through 9 to determine the rate law for the catalyzed reaction (2). Check that your rate law can account for the initial rate of all 5 experiments (Tables 5-9). [Note that since the rate of a reaction depends on the presence of a catalyst, it is appropriate to include the concentration of a catalyst in the rate law.]

4) (1 pt) Consider initial concentrations of $[O_3] = 1.350 \times 10^{15}$ molecules/cm³ and $[O] = 2.100 \times 10^{11}$ molecules/cm³. At what concentration of Cl atoms (in molecules/cm³) will the catalyzed depletion of ozone be 10 times faster than the uncatalyzed depletion reaction? This is an estimate for the amount of Cl atoms needed to have a large effect on ozone depletion. How does this concentration compare to that of ozone ($[O_3] = 1.350 \times 10^{15}$ molecules/cm³), i.e. how many ozone molecules are there for each Cl atom?

5) (3pts) The data in Tables 10-12 contain information on the dependence of the reaction rate on temperature. The Arrhenius equation (see page 682 of your text) can be used to model the temperature effect of many reactions,

$$k = Ae^{-E_a/RT}$$

Based on the data in Tables 10-12, determine the activation energy E_a (in J) and the pre-factor A for the uncatalyzed ozone depletion reaction. Please show your Arrhenius plot, along with the numerical values for A and E_a .

Uncatalyzed reaction**Table 1**

Initial $[O_3] = 1.530 \times 10^{15}$ molecules/cm³
 Initial $[O] = 1.471 \times 10^{11}$ molecules/cm³
 T = 230 K

Exp. 1

t (ms)*	$\Delta[O_3] / (\text{molec/cm}^3)**$
0.00	0.00
0.50	-1.159×10^8
1.00	-2.318×10^8
1.50	-3.475×10^8
2.00	-4.631×10^8
2.50	-5.787×10^8

Table 2

Initial $[O_3] = 2.780 \times 10^{15}$ molecules/cm³
 Initial $[O] = 1.471 \times 10^{11}$ molecules/cm³
 T = 230 K

Exp. 2

t (ms)	$\Delta[O_3] / (\text{molec/cm}^3)$
0.00	0.00
0.50	-2.106×10^8
1.00	-4.208×10^8
1.50	-6.308×10^8
2.00	-8.405×10^8
2.50	-1.050×10^9

Table 3

Initial $[O_3] = 1.530 \times 10^{15}$ molecules/cm³
 Initial $[O] = 1.150 \times 10^{11}$ molecules/cm³
 T = 230 K

Exp. 3

t (ms)	$\Delta[O_3] / (\text{molec/cm}^3)$
0.00	0.00
0.50	-9.069×10^7
1.00	-1.813×10^8
1.50	-2.718×10^8
2.00	-3.623×10^8
2.50	-4.527×10^8

Table 4

Initial $[O_3] = 2.250 \times 10^{15}$ molecules/cm³
 Initial $[O] = 2.100 \times 10^{11}$ molecules/cm³
 T = 230 K

Exp. 4

t (ms)	$\Delta[O_3] / (\text{molec/cm}^3)$
0.00	0.00
0.50	-2.435×10^8
1.00	-4.867×10^8
1.50	-7.296×10^8
2.00	-9.723×10^8
2.50	-1.215×10^9

* time in milliseconds

** this is the *change* in concentration of O_3 from the initial concentration

Catalyzed reaction

Table 5

Initial $[O_3] = 1.350 \times 10^{15}$ molecules/cm³
 Initial $[O] = 2.100 \times 10^{11}$ molecules/cm³
 Initial $[Cl] = 3.100 \times 10^{11}$ molecules/cm³
 T = 230 K

Exp. 5

t (ms)	$\Delta[O_3] / (\text{molec}/\text{cm}^3)$
0.00	0.00
0.50	-9.084×10^8
1.00	-2.365×10^9
1.50	-3.812×10^9
2.00	-5.249×10^9
2.50	-6.676×10^9

Table 6

Initial $[O_3] = 1.790 \times 10^{15}$ molecules/cm³
 Initial $[O] = 2.100 \times 10^{11}$ molecules/cm³
 Initial $[Cl] = 3.100 \times 10^{11}$ molecules/cm³
 T = 230 K

Exp. 6

t (ms)	$\Delta[O_3] / (\text{molec}/\text{cm}^3)$
0.00	0.00
0.50	-9.463×10^8
1.00	-2.450×10^9
1.50	-3.943×10^9
2.00	-5.425×10^9
2.50	-6.897×10^9

Table 7

Initial $[O_3] = 1.350 \times 10^{15}$ molecules/cm³
 Initial $[O] = 1.500 \times 10^{11}$ molecules/cm³
 Initial $[Cl] = 3.100 \times 10^{11}$ molecules/cm³
 T = 230 K

Exp. 7

t (ms)	$\Delta[O_3] / (\text{molec}/\text{cm}^3)$
0.00	0.00
0.50	-6.480×10^8
1.00	-1.690×10^9
1.50	-2.724×10^9
2.00	-3.750×10^9
2.50	-4.769×10^9

Table 8

Initial $[O_3] = 1.350 \times 10^{15}$ molecules/cm³
 Initial $[O] = 2.100 \times 10^{11}$ molecules/cm³
 Initial $[Cl] = 5.300 \times 10^{11}$ molecules/cm³
 T = 230 K

Exp. 8

t (ms)	$\Delta[O_3] / (\text{molec}/\text{cm}^3)$
0.00	0.00
0.50	-1.469×10^9
1.00	-3.846×10^9
1.50	-6.197×10^9
2.00	-8.520×10^9
2.50	-1.082×10^9

Table 9

Initial $[O_3] = 3.650 \times 10^{15}$ molecules/cm³
 Initial $[O] = 1.560 \times 10^{11}$ molecules/cm³
 Initial $[Cl] = 5.300 \times 10^{11}$ molecules/cm³
 T = 230 K

Exp. 9

t (ms)	$\Delta[O_3] / (\text{molec}/\text{cm}^3)$
0.00	0.00
0.50	-1.238×10^9
1.00	-3.184×10^9
1.50	-5.106×10^9
2.00	-7.003×10^9
2.50	-8.876×10^9

Temperature Dependence**Table 10:**

$[O_3] = 1.530 \times 10^{15} \text{ molecules/cm}^3$

$[O] = 1.471 \times 10^{11} \text{ molecules/cm}^3$

$[Cl] = 0.00$

$T = 230 \text{ K}$

Exp. 10	
t (ms)	$\Delta[O_3] / (\text{molec/cm}^3)$
0.00	0.00
0.50	-1.159×10^8
1.00	-2.318×10^8
1.50	-3.475×10^8
2.00	-4.631×10^8
2.50	-5.787×10^8

Table 11:

$[O_3] = 1.530 \times 10^{15} \text{ molecules/cm}^3$

$[O] = 1.471 \times 10^{11} \text{ molecules/cm}^3$

$[Cl] = 0.00$

$T = 298 \text{ K}$

Exp. 11	
t (ms)	$\Delta[O_3] / (\text{molec/cm}^3)$
0.00	0.00
0.50	-8.937×10^8
1.00	-1.782×10^9
1.50	-2.665×10^9
2.00	-3.542×10^9
2.50	-4.414×10^9

Table 12:

$[O_3] = 1.530 \times 10^{15} \text{ molecules/cm}^3$

$[O] = 1.471 \times 10^{11} \text{ molecules/cm}^3$

$[Cl] = 0.00$

$T = 270 \text{ K}$

Exp. 12	
t (ms)	$\Delta[O_3] / (\text{molec/cm}^3)$
0.00	0.00
0.50	-4.369×10^8
1.00	-8.725×10^8
1.50	-1.307×10^9
2.00	-1.740×10^9
2.50	-2.172×10^9