

## Homework 5

**Distributed: Friday, February 20, 2004**
**Due: Friday, February 27, 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.)

In Homework 4, we studied the phenomenology of the ozone depletion kinetics, both for the uncatalyzed reaction and for the chlorine catalyzed reaction.

In this homework assignment you will attempt to develop chemical mechanisms to explain the phenomenological results.

Remember that we are interested in the following overall reaction:



### Mechanism of the uncatalyzed reaction

What is the rate law from experiments on this reaction? (You may use your answer from last week's assignment or the proposed answer in the solutions)

1. In a discussion following your work on the phenomenological problems, you and your study partners suggested some different mechanisms for the reaction. For each of the following mechanisms, derive the rate law, and state where it agrees with the experimentally observed, phenomenological, rate law recorded above.

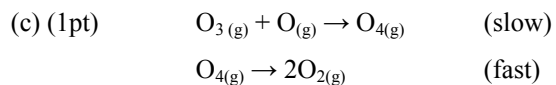
(a) (0.5 pt)       $\text{O}_3(\text{g}) + \text{O}(\text{g}) \rightarrow 2\text{O}_2(\text{g})$  (single step mechanism)

|  |
|--|
| Rate law: _____ Agrees with experimentally observed rate:    yes    no    (circle one) |
|--|

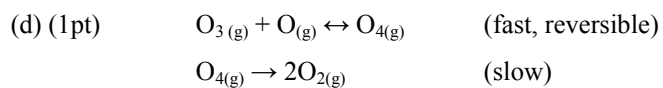
(b) (1 pt)       $\text{O}_3(\text{g}) \leftrightarrow \text{O}_2(\text{g}) + \text{O}(\text{g})$       (fast, reversible)

$\text{O}(\text{g}) + \text{O}(\text{g}) \rightarrow \text{O}_2(\text{g})$       (slow)

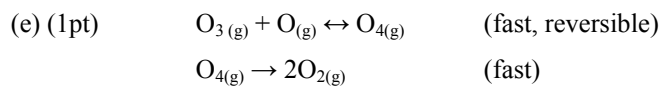
|  |
|--|
| Rate law: _____ Agrees with experimentally observed rate:    yes    no    (circle one) |
|--|



Rate law: \_\_\_\_\_ Agrees with experimentally observed rate:    yes    no    (circle one)



Rate law: \_\_\_\_\_ Agrees with experimentally observed rate:    yes    no    (circle one)



Rate law: \_\_\_\_\_ Agrees with experimentally observed rate:    yes    no    (circle one)

f) (1pt) In mechanisms (c), (d) and (e), the mechanistic steps are identical. The differences arise only from assumptions about which reactions are slow and fast. The rate laws for mechanisms (c) and (d) should correspond to limiting behaviors of the rate law in part (e). Please report the limiting behavior that would connect (e) to (c) and (e) to (d) [i.e.  $k_1 \gg k_2$  or  $k_2 \ll k_1$ , etc] and show that the rate law for (e) shows the correct limiting behavior:

(c) is the limiting behavior of (e) for \_\_\_\_\_ (i.e.  $k_1 \gg k_2$  or  $k_2 \ll k_1$ ). Your work above should show that the rate law for mechanism (e) does indeed become that of (c) under these assumptions.

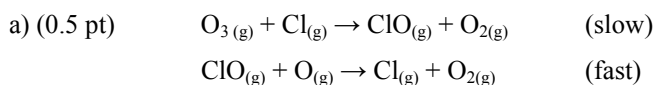
(d) is the limiting behavior of (e) for \_\_\_\_\_ (i.e.  $k_1 \gg k_2$  or  $k_2 \ll k_1$ ). Your work above should show that the rate law for mechanism (e) does indeed become that of (d) under these assumptions.

(g) (1pt) Two or more of the above mechanisms give rate laws that are in agreement with the experimentally observed rate law. Suggest one further experiment that would help you to identify the correct mechanism among the ones that leads to the experimental rate law.

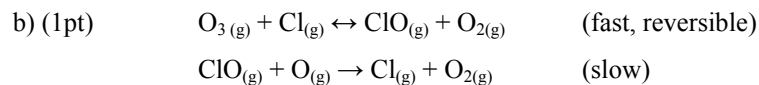
### Mechanism of the catalyzed reaction

What is the rate law for this experiment? (You may use your guess or the proposed answer in the solutions.)

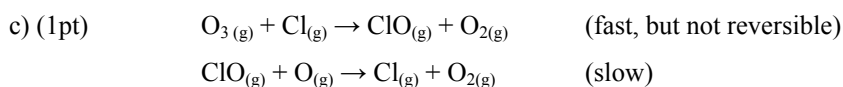
2. Consider the following proposed mechanism for the catalyzed reaction:



Rate law: \_\_\_\_\_ Agrees with experimentally observed rate:    yes    no    (circle one)



Rate law: \_\_\_\_\_ Agrees with experimentally observed rate: yes no (circle one)



Rate law: \_\_\_\_\_ Agrees with experimentally observed rate: yes no (circle one)

The mechanism in 2c is of a form that is not discussed directly in class or the text. To derive the expected rate law for the experiments in homework 4, take into consideration the relative concentrations of  $\text{O}_3$  and  $\text{Cl}$  in those experiments. For those relative concentrations, what do you expect to results from the fast reaction in mechanism (c)?

d) (1pt) In reviewing the data from the chlorine catalyzed reaction study; you realize that the amount of ozone extrapolated to time 0 is less than the amount of ozone added at the beginning of the experiment (see the figure below). Explain this observation in terms of the proposed mechanism (c) for the reaction.

