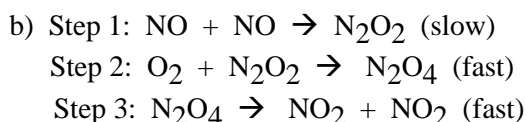
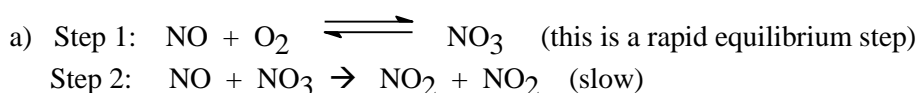
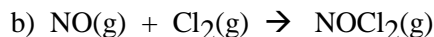
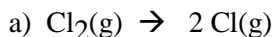


**Chem 152**  
**8-30 Homework**

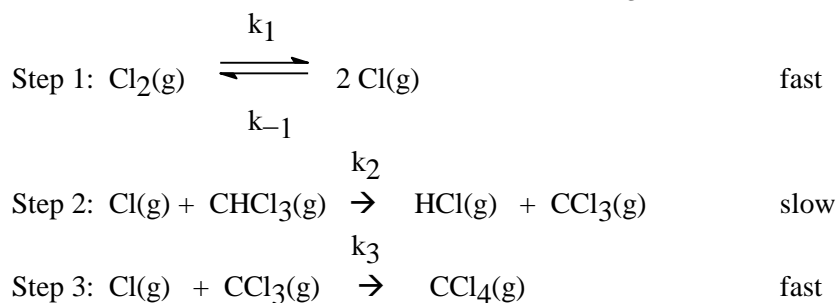
- 1) Under what experimental condition do we obtain a pseudo-rate constant, not the actual rate constant?
- 2) NOBr undergoes 2<sup>nd</sup> order decomposition to form nitrogen monoxide and elemental bromine. At 250°C, the rate constant is  $1.00 \times 10^{-5} \text{ M}^{-1}\text{s}^{-1}$ . Suppose that 0.100 moles of NOBr are placed in a 500.0 mL vessel at 250°C. What is the [NOBr] and how many bromine molecules are present after 24.0 hours have elapsed?
- 3) When the rate of the reaction  $2 \text{ NO(g)} + \text{ O}_2\text{(g)} \rightarrow 2 \text{ NO}_2\text{(g)}$  was studied, it was found experimentally that the rate doubled when the O<sub>2</sub> concentration alone was doubled, but quadrupled when the NO concentration alone was doubled. Do one, both, or none of the following mechanisms account for these rate observations? Justify your answers.



- 4) For each of the following elementary reactions, write the rate law and tell what the molecularity of the reaction is:



- 5) A valid mechanism for the reaction of chloroform (CHCl<sub>3</sub>) with Cl<sub>2</sub> in the gas phase is



Based on the mechanism, answer the following questions:

- a) What is the overall reaction?                      b) What are the intermediates in the reaction?
- c) What is the molecularity of each step?              d) What is the rate-determining step?
- e) What is the rate law predicted by this mechanism? (note: half-orders are possible!)

## Answers

#4 on previous HW

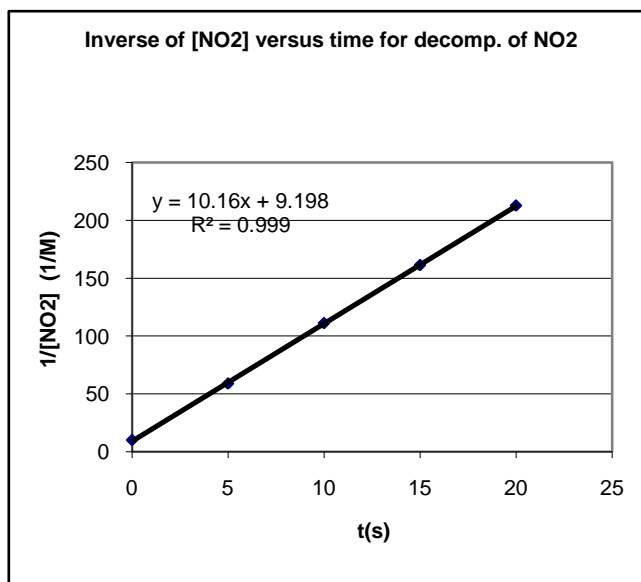
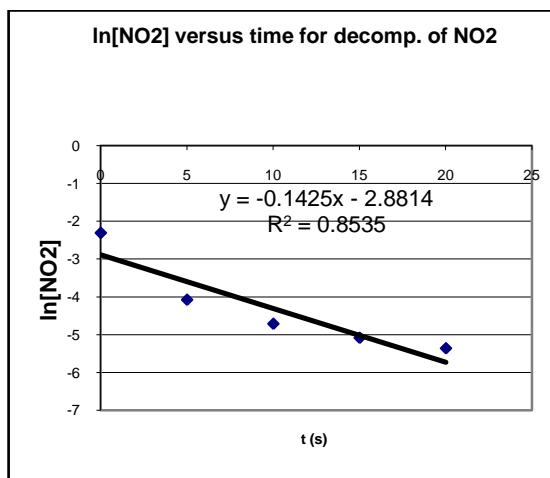
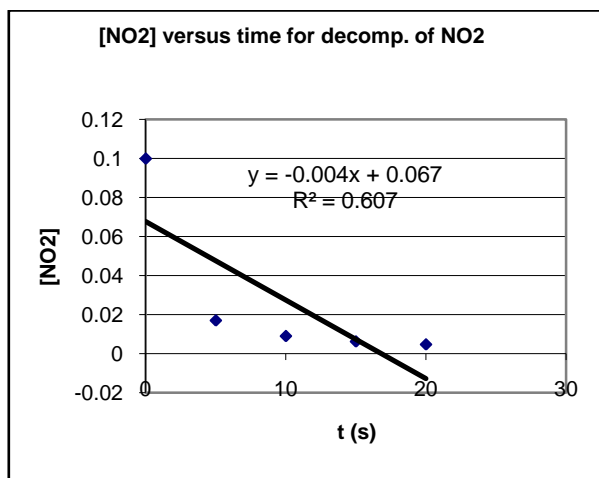
a) Based on rate plots, what is the order of the decomposition reaction? Show your graph.

b) What is the value of the rate constant, with proper units?

c) Calculate, using the appropriate equation, the time required for the  $[\text{NO}_2]$  to reach 0.00037 M.

d) Is half life a particularly useful quantity for this reaction? Briefly explain why or why not.

Since we're given concentration versus time data, we need to examine the rate plots for zeroeth, first, and second order and see which one gives the straightest line.



Since the plot of  $1/[\text{NO}_2]$  versus time is by far the straightest line, the decomposition reaction is 2<sup>nd</sup> order in  $\text{NO}_2$ .

The rate constant for the decomposition is  $10.16 \text{ M}^{-1}\text{s}^{-1}$  (the slope of the straight line). Note that the rate constant unit equals (y-axis unit/x-axis unit)

For 2<sup>nd</sup> order kinetics, the appropriate decay

$$\text{equation is } \frac{1}{[\text{NO}_2]} = kt + \frac{1}{[\text{NO}_2]_0}$$

To find the time required for  $[\text{NO}_2]$  to reach 0.00037 M, plug the data into the decay equation and solve for

$$t: \frac{1}{0.00037 \text{ M}} = (10.16 \frac{1}{\text{M s}}) t + \frac{1}{0.100 \text{ M}} \quad \rightarrow \text{ solve to get } t = 270 \text{ s (2 sig figs)}$$

Half-life is not a particularly useful quantity for a 2<sup>nd</sup> order reaction, because for 2<sup>nd</sup> order kinetics the half-life is constantly changing with concentration.

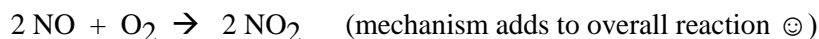
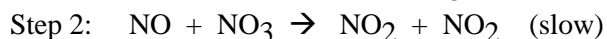
1)

In an experiment with more than one reactant, a pseudo-rate constant is obtained when the initial amounts of all reactants except one are very large. The amount of the reactants in large excess will change little compared to the lone limiting reactant. Because the amounts of reactants in large excess change little, these amounts (concentrations, partial pressures, etc.) remain approximately constant, and thus become part of the experimentally-determined rate constant, which is not “k” alone but rather the pseudo-rate constant k’.

2) Try this one for a couple of bonus points, if you get the correct answer. Due 9/1 at the start of class

3)

**First off, from the experimental info given in the problem, we know the experimental rate law is  $r = k[\text{NO}]^2[\text{O}_2]$ . If a mechanism is good, its rate law must match the experimental rate law.**

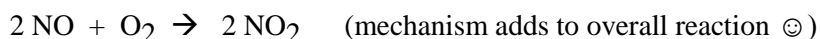
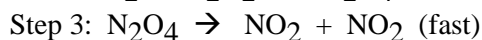
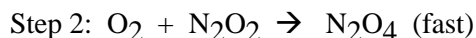


Rate law from mechanism is  $r = k_2[\text{NO}][\text{NO}_3]$  → we need to find  $[\text{NO}_3]$  from the rapid equilibrium step

From the rapid equilibrium step  $k_1[\text{NO}][\text{O}_2] = k_{-1}[\text{NO}_3] \rightarrow [\text{NO}_3] = k_1[\text{NO}][\text{O}_2]/k_{-1}$

Substituting for  $[\text{NO}_3]$  in rate law gives  $r = \left( \frac{k_2 k_1}{k_{-1}} \right) [\text{NO}]^2 [\text{O}_2] = k[\text{NO}]^2 [\text{O}_2] \rightarrow \mathbf{OK!}$

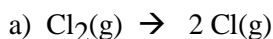
\*\*\* This is a good mechanism \*\*\*



Rate law from mechanism is  $r = k_1[\text{NO}]^2$ , which does not match experimental rate law because it shows no dependence on  $[\text{O}_2]$ , and the experimental rate law does.

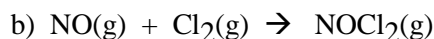
\*\*\* This is not a proper mechanism \*\*\*\*

4) For each of the following elementary reactions, write the rate law and tell what the molecularity of the reaction is:



$$r = k[\text{Cl}_2]$$

unimolecular



$$r = k[\text{NO}][\text{Cl}_2]$$

bimolecular

5) Please hand this one in on a single sheet of paper at the start of class on 9/1. See if you can tell what “molecularity” is by looking at question 4.