Name ______________________________Chem 163 Section: ______ Team Number: ______

ALE 5. Reaction Mechanisms

(Reference: 16.7 *Silberberg 5th edition*)

How does a reaction occur step by step?

The Model: The Rate-Determining Step of a Reaction Mechanism

Suppose you are going from Tacoma to Auburn. A likely route may involve you using I-5 passing through Fife, Milton and Federal Way and then might hop onto Highway 18 and cruise on down the hill to Auburn. You might think of the route being a series of steps, which may be represented as chemical equations such as:

Step 1 $\quad \text{Tacoma} \xrightarrow{k_1} \text{Fife}$

Step 2 $\quad \text{Fife} \xrightarrow{k_2} \text{Milton}$

Step 3 $\quad \text{Milton} \xrightarrow{k_3} \text{Federal Way}$

Step 4 $\quad \text{Federal Way} \xrightarrow{k_4} \text{Auburn}$

Suppose you could drive at the 60 mph speed limit all the way from Tacoma to Auburn (*i.e.*, suppose $k_1 = k_2 = k_3 = k_4$ in the above "reaction mechanism"). If that were the case, you'd be able to complete the trip in about 15 to 20 minutes. But suppose there is an accident somewhere between Tacoma and Auburn and one or more lanes are closed off, thus creating a bottleneck in traffic. If there were an accident between Tacoma and Fife, then k_1 would be smaller (*e.g.*, perhaps an average of 30 mph) than the other "rate constants." How fast you'd get to Auburn wouldn't really depend on how fast you could get from Fife to Auburn—it would depend on how fast you could get from Tacoma to Fife, so that step is called the "**rate-determining step**." If there were an accident between Fife and Milton, then how fast you would get to Auburn would depend on how fast you could get from Fife to Milton: k_2 would be smaller than the other rate constants, and Step 2 would be the rate-determining step.

Key Questions

1. Consider the decomposition of ozone to become molecular oxygen. The chemical equation and rate law for the decomposition of ozone: $\mathbf{2\ O_3 \rightarrow 3\ O_2}$ $\quad$ **Rate =** $\boldsymbol{k}$ **[**$\mathbf{O_3}$**]**

   a. Explain why the rate law shows that the decomposition of ozone does <u>not</u> occur via a mechanism involving a bimolecular collision between two ozone molecules. <u>*Hint*</u>: consider the exponent for O_3 in the rate law.

b. Draw the Lewis structures of ozone (O_3), molecular oxygen (O_2), and atomic oxygen (O).

c. Explain how thermal energy (i.e. heat) can cause an ozone molecule to decompose yielding an oxygen molecule as shown in step 1 of part f, below. *Hint*: think about vibrational kinetic energy!

d. Looking at the Lewis structure of atomic oxygen, what can you infer about the chemical reactivity of atomic oxygen? *Explain.*

e. Which would you expect to occur at a faster rate: **a.)** the production of atomic oxygen from the decomposition of O_3 or **b.)** the reaction between atomic oxygen and another ozone molecule? Circle your choice and *explain your reasoning*:

f. How does the following ***reaction mechanism for the decomposition of ozone*** account for why the decomposition of ozone is first order with respect to ozone concentration? What assumption may you make about the relative values of k_1 and k_2?

Step 1 $$O_3 \xrightarrow{k_1} O_2 + O$$

Step 2 $$O + O_3 \xrightarrow{k_2} O_2 + O_2$$

g. *Step 1*, above, is a unimolecular elementary step, and Step 2 is a bimolecular elementary step. The terms "unimolecular" and "bimolecular" refer to the **molecularity** of an elementary step of a reaction mechanism. What does the molecularity of an elementary step inform a reader of?

2. The decomposition of hydrogen peroxide into water and oxygen gas occurs very slowly on its own. But the rate of decomposition is catalyzed by iodide. The reaction mechanism for the iodide-catalyzed decomposition of hydrogen peroxide is:

Step 1 $H_2O_2 + I^- \xrightarrow{k_1} H_2O + IO^-$

Step 2 $IO^- + H_2O_2 \xrightarrow{k_2} H_2O + O_2 + I^-$

a. Both hypoiodite (IO^-, in the above mechanism for the decomposition of hydrogen peroxide) and atomic oxygen (O, in the above mechanism for the decomposition of ozone) are called **intermediates**. As far as being produced and being consumed go, what do intermediates have in common with each other?

b. As far as being produced and being consumed go, how does a catalyst compare to an intermediate?

c. Are intermediates part of the overall chemical reaction? Are catalysts? (Note: It's customary to write the catalyst above the reaction arrow.)

d. Concerning the iodide-catalyzed decomposition of hydrogen peroxide, $k_1 << k_2$. Which step is the rate-determining step? What is the rate law of the iodide-catalyzed decomposition of hydrogen peroxide according to the rate-determining step approximation?

The Model: Mechanisms involving a Step with a Fast-Equilibrium

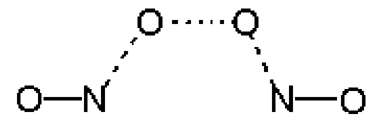
If there is a reversible step preceding the rate-determining step of a reaction mechanism, then the reactants and products of the reversible step are assumed to be in chemical equilibrium. At chemical equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction. It is assumed that both the reactants and the products of the fast-equilibrium step are present before the rate-determining step occurs.

Key Questions

3. Consider the reaction between nitrogen monoxide and oxygen in the atmosphere to form the air pollutant, nitrogen dioxide. The chemical equation and rate law this reaction:

$$\mathbf{2\,NO + O_2 \rightarrow 2\,NO_2} \qquad \mathbf{Rate} = \boldsymbol{k}\,\mathbf{[O_2]\,[NO]^2}$$

   a. It is *conceivable* that two molecules of nitrogen monoxide and one molecule of oxygen all come together with exactly the right energy and with exactly the right relative orientation in space to form the activated complex shown on the right. Explain why it is <u>*highly unlikely*</u> that the reaction occurs in one elementary step with a molecularity of 3.



A possible but highly unlikely transition state for a reaction between 2 NO molecules and one O_2 molecule

   b. The reaction between NO and O_2 is believed to occur via the following mechanism:

Step 1	$2\,NO \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} N_2O_2$	**Fast Equilibrium**
Step 2	$N_2O_2 + O_2 \xrightarrow{k_2} 2\,NO_2$	**Slow**

   Use the rate-determining step to write an approximation of the rate law.

   Rate =

   c. <u>*The concentration of an intermediate should never appear in a rate law*</u>—can you think of the reason? So we need to rewrite $[N_2O_2]$ in terms of the concentrations of one or more of the other reactants. If Step 1 is an equilibrium, then that means the rate at which the forward reaction is occurring is equal to the rate at which the reverse reaction is occurring.

      i. Use the fact that the forward reaction involves the bimolecular collision between two nitrogen monoxide molecules to write the rate law of the <u>*forward reaction of Step 1*</u>.

      $\mathbf{R_{fwd\ rxn}} =$

      ii. Use the fact that the reverse reaction is just a unimolecular decomposition of dinitrogen dioxide to write the rate law of the <u>*reverse reaction of Step 1*</u>.

      $\mathbf{R_{rev\ rxn}} =$

      iii. Below we've set the rate of the forward reaction of Step 1 equal to the rate of the reverse reaction of Step 1. Substitute the rate expressions from the rate laws (your answers to Questions 3ci and 3cii) and algebraically solve for $[N_2O_2]$ in terms of [NO] and the rate constants (k_1 and k_{-1}).

      Step 1 (at equilibrium): $\mathbf{R_{fwd\ rxn} = R_{rev\ rxn}}$

d. Substitute what you found to be true for [N_2O_2] based on the fast-equilibrium approximation (answer for Question 3ciii.) into the rate law you found for the rate-determining step approximation (answer for Question 3b.). Simplify (recall that the product or quotient of constants is a constant) *and confirm that reaction mechanism predicts the observed rate law*.

Exercises

4. A mechanism is proposed in the literature for the decomposition of hydrogen peroxide (w/o a catalyst):

Step 1: $H_2O_2 \rightarrow 2OH$
Step 2: $H_2O_2 + OH \rightarrow H_2O + HO_2$
Step 3: $HO_2 + OH \rightarrow H_2O + O_2$

In order to help determine which step may be rate limiting, you measure the rate at which hydrogen peroxide decomposes and obtain the following data.

Time (s)	0	100.	300.	600.	1200.	1800.	2400.	3600.
[H_2O_2] (mol/L)	1.27	1.23	1.15	1.04	0.85	0.70	0.58	0.39

a. From the elementary steps of the mechanism, write the balanced chemical equation for the decomposition of hydrogen peroxide.

b. Identify the reactants, products, and reaction intermediates in the above mechanism.

Reactants:

Products:

Intermediates:

c. Identify the molecularity of each of the three elementary steps in the mechanism.

Step 1:

Step 2:

Step 3:

d. Write the rate law for the first elementary step.

e. Write the rate law for the second elementary step.

f. Plotting the above data with *Excel* as Ln [H_2O_2] vs. time gives a straight line with negative slope with $R^2 = 0.9999$. What is the integrated rate law for the decomposition of hydrogen peroxide? What is the differential rate law for the decomposition of hydrogen peroxide?

g. In view of the analysis of the data and your answer to part f, above, which step in the mechanism is the rate determining step? *Explain why*.

h. The slope of the plot of Ln [H_2O_2] vs. time is -3.277×10^{-4}. Determine the rate constant from the data. *Show work with units and sig. figs.*

i. Calculate the half-life of this reaction. If the initial concentration is changed, does the half-life change? *Explain*.

j. Determine the number of half-lives it takes for the concentration of hydrogen peroxide to be reduced to 1/8 (12.5%) of its initial value? Identify two methods for obtaining an answer.

5. A researcher proposes the following 3-step mechanism for the reaction between the bleach, ClO^-, and the iodide ion, I^-.

(Step 1) $ClO^-\,(aq) + H_2O\,(l) \rightleftharpoons HClO\,(aq) + OH^-\,(aq)$ **[fast-equilibrium]**

(Step 2) $I^-\,(aq) + HClO\,(aq) \rightarrow HIO\,(aq) + Cl^-\,(aq)$ **[slow]**

(Step 3) $OH^-\,(aq) + HIO\,(aq) \rightarrow H_2O\,(l) + IO^-\,(aq)$ **[fast]**

a. What is the overall balanced chemical equation for the reaction between ClO^- and I^-?

b. Identify the intermediates, if any.

c. What is the molecularity and rate law for each step of the reaction mechanism?

Step	Molecularity	Rate Law
(1)		
(2)		
(3)		

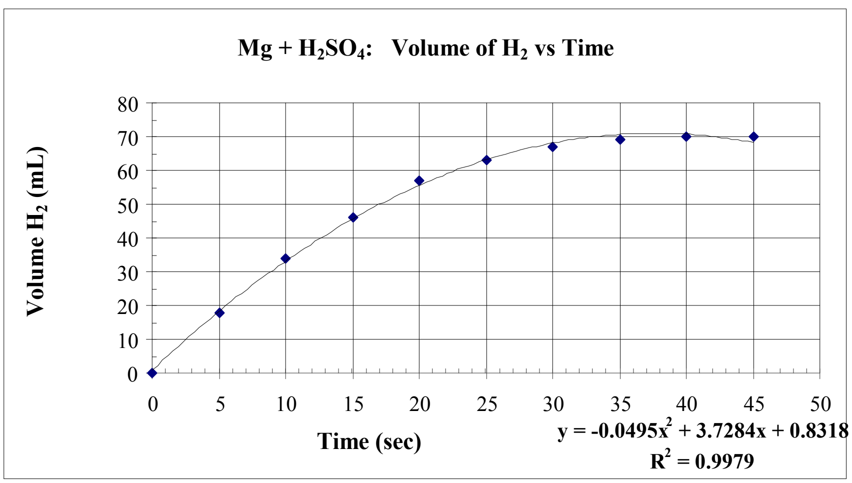
d. Use the proposed 3-step mechanism to derive the rate law for the reaction between ClO^- and I^-. *Hint*: You'll need to follow the procedure used in question 3.

e. If researchers in other labs experimentally determine the actual rate law to be Rate = k [ClO^-][I^-], what does this tell you about the proposed mechanism? *Explain*.

Comprehensive Exercises

6. An experiment was carried out at room conditions in order to investigate the rate of reaction between magnesium metal and dilute sulfuric acid, H_2SO_4. The following data was obtained when **0.070g of magnesium ribbon** was reacted with excess dilute sulfuric acid. The volume of hydrogen gas produced every 5 seconds was recorded.

Time (s)	Volume of gas (cm^3)
0	0
5.	18
10.	34
15.	47
20.	57
25	63
30.	67
35	69
40.	70.
45	70.



a. Using a pencil, sketch a curve on the graph that might have been obtained if **0.070g of magnesium powder** had been used instead of magnesium ribbon.

b. When is the reaction fastest? Explain and indicate on the graph when the reaction was fastest.

c. How could you use the graph to determine the initial rate of reaction?

d. Write the balanced chemical equation for the reaction between magnesium and sulfuric acid.

e. Use the graph to determine how long it takes for the 0.070g of magnesium to react completely. Show your work on the graph and record your answer below.

Time required for complete reaction of 0.070 g Mg: ____________

f. Use the *equation of the curve*, $y = -0.0495x^2 + 3.7284x + 0.8318$, to determine how long it would take for 0.050g Mg to react. Assume the molar volume of an ideal gas to be 24.4 L at room conditions. *Show your work using units and sig. figs*.

Hints: i.) First calculate the volume of H_2 produced.

ii.) For a quadratic equation, $\boldsymbol{ax^2 + bx + c = 0}$, the value of $\boldsymbol{x}$ is given by: $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

g. Other than surface area, suggest at least three other factors that would affect the rate of the reaction between magnesium and sulfuric acid.

7. Archeologists can determine the age of artifacts made of wood or bone by measuring the concentration of radioactive isotope ^{14}C present in the object. The amount of isotope decreases in a *first-order* process. If 15.5% of the original amount of ^{14}C is present in a wooden tool at the time of analysis, what is the age of the tool? The half-live of ^{14}C is 5730 years.