Unit 5 Review for Midterms

Kinetics

You should be able to:

- Show how the rates of change of reactant and product concentrations are determined by stoichiometry
- Understand the factors that affect the rate of a reaction and why the rate is affected
- Determine a rate law using experimental initial rates and concentration data
- Infer the order of a reaction based on graphs of concentration vs time
- Calculate k of a rate law using graphs
- Perform calculations for zero, first, and second order reactions (equations on equation sheet)
- Understand half-life
- Understand elementary reactions
- Relate collision energy and orientation to reaction rates
- Use Maxwell-Boltzmann distribution curves to compare particle energies and reaction rates
- Represent the activation energy and overall energy change on a diagram/reaction energy profile
- Predict the rate law based on a reaction mechanism
- Use the terms intermediates, catalysts, activation energy accurately
- Represent the activation energy and overall energy change in a multistep reaction with a reaction energy profile

1. For the following equation, $C_6H_{12}0_{6(s)} + 6\ O_{2(g)} \rightarrow 6\ CO_{2(g)} + 6\ H_2O_{(g)}$.
    a. Discuss the relationship between rates of change of each of the species.
    b. Write a mathematical expression for part a.
2. $2N_2O_5 \rightarrow 4NO_2 + O_2$ The rate law is first order in N_2O_5. At 64 degrees, the rate constant is 4.82 x 10^{-3} s^{-1}.
    a. Write the rate law for the reaction.
    b. What is the rate of the reaction when $[N_2O_5]$ = 0.200 M?
    c. What happens to the rate when the concentration of N_2O_5 is tripled?
3. Initial rate data were collected for the following reaction in which iodide ion is oxidized to triiodide by peroxydisulfate ion:

    $S_2O_8^{2-}{}_{(aq)} + 3I^-{}_{(aq)} \rightarrow 2SO_4^{2-}{}_{(aq)} + I_3^-{}_{(aq)}$

Experiment	$[S_2O_8^{2-}]$ (M)	$[I^-]$ (M)	Initial rate (M/sec)
1	0.080	0.034	$2.2x10^{-4}$
2	0.080	0.017	$1.1x10^{-4}$

3	0.160	0.017	$2.2x10^{-4}$
4	0.280	???	$5.7x10^{-4}$

a. Write the rate law for the overall reaction.
b. Determine the value of the rate constant, *k*, for the reaction. Include units with your answer.
c. Calculate the initial concentration of I^- for experiment 4.
d. What is the overall order of this reaction?
e. What does the overall order indicate about the slow step of the reaction mechanism?

4. Consider the proposed mechanism for the reaction between nitrogen monoxide and hydrogen gas. Assume the mechanism is correct.

Step 1: $2NO \rightarrow N_2O_2$
Step 2: $N_2O_2 + H_2 \rightarrow N_2O + H_2O$
Step 3: $N_2O + H_2 \rightarrow N_2 + H_2O$

a. Use the steps in the mechanism to determine the overall balanced equation for the reaction. Clearly show your method
b. If step 2 is the rate-determining step, write the rate law for the reaction, explain your answer.
c. If the first step is the rate-determining step, what is the order of reaction with respect to each reactant?

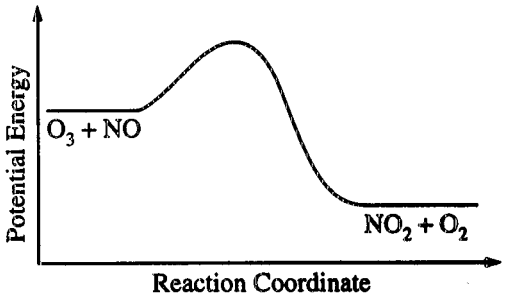
5. The first-order decomposition of a colored chemical species, X, into colorless products is monitored with a spectrophotometer by measuring changes in absorbance over time. Species X has a molar absorptivity constant of $5.00 \times 10^3\ cm^{-1}\ M^{-1}$ and the path length of the cuvette containing the reaction mixture is 1.00 cm. The data from the experiment are given in the table below.

[X] (M)	Absorbance	Time (min)
?	0.600	0.0
4.0×10^{-5}	0.200	35.00
3.0×10^{-5}	0.150	44.2
1.50×10^{-5}	0.075	?

a. Calculate the initial concentration of the colored species.
b. Calculate the rate constant for the first-order reaction using the values given for concentration and time. Include units with your answer.
c. Calculate the number of minutes it takes for the absorbance to drop from 0.600 to 0.075.
d. Calculate the half-life of the reaction. Include units with your answer.

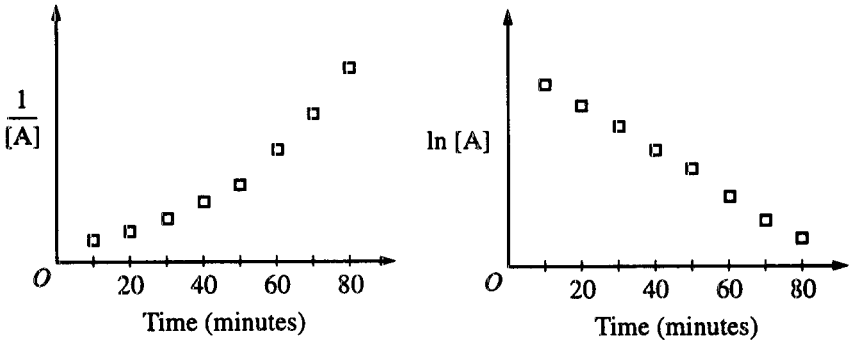
6. Answer the following questions regarding the kinetics of chemical reactions.
   a. The diagram below shows the energy pathway for the reaction: $O_3 + NO \rightarrow NO_2 + O_2$. Clearly label the following directly on the diagram:

      i. The activation energy *(E_a)* for the forward reaction
      ii. The enthalpy change (ΔH) for the reaction



b. Use the information in the graphs below to answer the following regarding A → B.

i. Write the rate-law expression for the reaction. Justify your answer.



ii. Describe how to determine the value of the rate constant for the reaction.

7. A reaction has a constant half-life. What does this tell you about the order of the reaction?
8. At elevated temperatures, nitrogen dioxide decomposes to nitrogen oxide and oxygen:

$$NO_2\,(g) \rightarrow NO\,(g) + \frac{1}{2}O_2\,(g)$$

The reaction is second order in NO_2 with a rate constant of 0.543 $M^{-1}s^{-1}$ at 300˚C. If the initial $[NO_2]$ is 1.260 M, how long will it take for the concentration to drop to 0.500 M?

9. The reaction below is first order in $[H_2O_2]$:

$$2\,H_2O_2 \rightarrow 2\,H_2O + O_2$$

A solution originally at 0.800 M H_2O_2 is found to be 0.175 M after 54 min. What is the half-life of this reaction?

10. Based on the below two-step mechanism, write the overall equation and predict the rate for the reaction. Note that an intermediate CANNOT be in the rate law. Substitute.

$NO + Br_2 \leftrightarrow NOBr_2$ (fast equilibrium)
$NoBr_2 + NO \rightarrow 2\,NOBr$ (slow)

11. For the following reaction,
    a. Write the overall equation
    b. Identify any intermediates
    c. Identify any catalysts

Step 1: $NO\,(g) + O_3\,(g) \rightarrow NO_2\,(g) + O_2\,(g)$

Step 2: $NO_2\,(g) + O\,(g) \rightarrow NO\,(g) + O_2\,(g)$