CHEM 4363  
Test #1  
Spring 2010 (Buckley)

Short answer part. Answer the questions as indicated. For multiple choice questions, just circle the letter corresponding to the best answer.

1. 3 points) Consider the reaction:

\[ 2 \text{A} + 3 \text{B} + \text{C} \rightarrow 3 \text{D} + \text{X} \]

Write the expression for the rate of reaction in terms of derivatives for each of reactants and products in the reaction.

\[ \text{rate} = -\frac{1}{2} \frac{d[\text{A}]}{dt} = -\frac{1}{3} \frac{d[\text{B}]}{dt} = -\frac{d[\text{C}]}{dt} = \frac{1}{2} \frac{d[\text{D}]}{dt} \]

2. (2 points) The rate law for a particular reaction is one-half order in A, first order in B, and three-halves order in C. What are the units for the rate constant using M as the concentration unit and seconds as the time unit? Circle the letter corresponding to the best answer.

a. s⁻¹  
b. M¹s⁻¹  
c. M²s⁻¹  
d. M³s⁻¹  
e. M⁵s⁻¹

3. (2 points) In a particular reaction mechanism one of the elementary steps is given as:

\[ \text{NO}_2 + \text{NO}_3 \rightarrow \text{NO} + \text{O}_2 + \text{NO}_2 \]

Circle the letter corresponding to a true statement for this step.

a. The rate law for this step will depend on the other reactions occurring in this mechanism.

b. The rate law for this step may be written down directly as

\[ \text{Rate} = k[\text{NO}_2][\text{NO}_3] \]

c. The rate for this step will depend on the concentration of NO

d. The substance NO₃ is an intermediate.

e. The substance NO₂ is an intermediate.
4. (2 points) During an initiation step in a chain reaction which of the following occurs. Circle the letter corresponding to the best answer.
   a. Two radicals combine to form a molecule
   b. One radical undergoes a reaction to form another radical
   O One molecule breaks into radicals
   d. Two molecules combine to form a product
   e. A radical and a molecule combine to form another radical and another molecule.

Consider the following initial rate data for Questions 5 – 7 (2 points each).

<table>
<thead>
<tr>
<th>Run #</th>
<th>[A] (M)</th>
<th>[B] (M)</th>
<th>Rate (Ms⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.15</td>
<td>0.10</td>
<td>3.0 × 10⁻⁴</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.10</td>
<td>2.0 × 10⁻⁴</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.20</td>
<td>1.6 × 10⁻⁴</td>
</tr>
</tbody>
</table>

5. Which of the following is the rate law for the reaction?
   a. Rate = k [A] [B]
   b. Rate = k [A]²[B]
   O Rate = k [A] [B]²
   d. Rate = k [A]² [B]
   e. Rate = k [A]

6. What is the value of the rate constant for the reaction?
   a. 0.0200 M⁻¹s⁻¹
   b. 0.133 M²s⁻¹
   O 0.200 M²s⁻¹
   d. 1.33 M³s⁻¹
   e. 0.00200 s⁻¹

7. What is the rate of the reaction if the initial concentration of A is 0.18 M and that of B is 0.13 M?
   a. 4.68 × 10⁻⁴ Ms⁻¹
   b. 5.60 × 10⁻⁴ Ms⁻¹
   O 3.38 × 10⁻⁴ Ms⁻¹
   d. 7.28 × 10⁻⁴ Ms⁻¹
   e. 3.60 × 10⁻⁴ Ms⁻¹
8. The stoichiometric equation for the reaction between iodide ions and the cobalt complex Co(CN)_5OH^2- is:

\[ \text{Co(CN)}_5\text{OH}^2- + I^- \rightarrow \text{Co(CN)}_5I^3- + H_2O \]

The mechanism for this reaction is thought to be:

\[ \text{Co(CN)}_5\text{OH}^2- + I^- \xrightarrow{k_1} \text{Co(CN)}_5I^3- + H_2O \]

\[ \text{Co(CN)}_5I^3- \xrightarrow{k_2} \text{Co(CN)}_5I^2- \]

a. Apply the steady-state assumption to the intermediate and derive the rate law for this reaction based on the mechanism above.

\[ \frac{d}{dt} \left[ \text{Co(CN)}_5I^3- \right] = \frac{k_1 [\text{Co(CN)}_5\text{OH}^2-][I^-]}{k_1 + k_2 [I^-]} \]

\[ \frac{d}{dt} [\text{Co(CN)}_5\text{OH}^2-] = \frac{k_1 [\text{Co(CN)}_5I^3-][I^-]}{k_2 [I^-] + k_1} \]

\[ \frac{d}{dt} [I^-] = -k_1 [\text{Co(CN)}_5\text{OH}^2-] - k_2 [\text{Co(CN)}_5I^3-][I^-] \]

b. Based on your answer to part a, what is the expected rate law under conditions of high I^- conditions, what is the rate-limiting step in this case, and what is the overall order of the reaction?

1. At high [I^-], \( \frac{d}{dt} [\text{Co(CN)}_5\text{OH}^2-] = \frac{k_1 [\text{Co(CN)}_5I^3-][I^-]}{k_2 [I^-] + k_1} \)

2. \( k_1 \) is the rate-limiting step

3. First order overall

c. Based on your answer to part a, what is the expected rate law under conditions of low I^- conditions, what is the rate-limiting step in this case, and what is the overall order?

1. At low [I^-], \( \frac{d}{dt} [\text{Co(CN)}_5\text{OH}^2-] = \frac{k_1 [\text{Co(CN)}_5I^3-][I^-]}{k_2 [I^-] + k_1} \)

2. Rate limiting step: \( k_2 \)

3. Second order
9. A "rule-of-thumb" in organic chemistry is that a reaction rate typically doubles for every 10 °C rise in temperature. If a reaction rate doubles when the temperature is raised from 40 °C to 50 °C, what is the activation energy for the reaction?

\[
T_1 = 313 K, \\
T_2 = 323 K
\]

\[
\frac{k_2}{k_1} = \frac{Ae^{-E_A/R_T_1}}{Ae^{-E_A/R_T_2}} = 2 \\
2 = e^{-E_A/R_T_1 (T_2/T_1 - 1)} \\
ln 2 = - \frac{E_A}{R} \left( \frac{T_2}{T_1} - 1 \right)
\]

\[
E_A = - \frac{RT_1 ln 2}{T_2/T_1 - 1} = \frac{8.314 J/kmol}{1} \left( \frac{313 K}{323 K} - \frac{1}{313 K} \right) = 58.3 kJ/mole
\]

10. The rate law for a particular reaction is given as:

\[
\frac{d[A]}{dt} = k[A]^{1/2}
\]

a. Find the integrated form of the rate law.

\[
\int \frac{2[A]^{1/2}}{[A]_0^{1/2}} = \int k dt \\
2[A]^{1/2} = k t + C
\]

b. Find an expression for the half-life based on the rate law.

\[
A = 0.5 [A]_0 \int \frac{2[A]^{1/2}}{[A]_0^{1/2}} = \frac{2}{k[A]^{1/2}_0} = \frac{2}{k(0.5)} = t_h
\]

\[
\frac{2[A]^{1/2}_0}{[A]^{1/2}_0} = k t_h
\]

c. If the value of the rate constant is \(3.24 \times 10^{-3} \text{ M}^{-1/2} \text{s}^{-1}\), how much A would remain after 25 minutes if its starting concentration was 0.100 M?

\[
\frac{2}{[A]^{1/2}_0} - \frac{2}{[A]^{1/2}} = (3.24 \times 10^{-3} \text{ M}^{-1/2} \text{s}^{-1})(25 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}})
\]

\[
[A] = 3.620 \times 10^{-2} \text{ M}
\]