Chem 105 b
Exam 1
Thursday, February 11, 1999
Professor Hanna Reisler

<table>
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<tr>
<th>Questions</th>
<th>Points</th>
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Please Sign Below:
I certify that I have observed all the rules of Academic Integrity while taking this examination.
Signature: ____________________________

INSTRUCTIONS
1. You must show your work to receive credit.
2. If necessary, please continue your solutions on the back of the preceding page (facing you).
3. YOU MUST Use black ink.
4. There are 8 problems on 9 pages. Please count them before you begin.
1. **(12 points)** The initial rate of a reaction \( A + B \rightarrow C \) was measured for several different starting concentrations of \( A \) and \( B \), with the results given below:

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>([A]_0) (mol/L)</th>
<th>([B]_0) (mol/L)</th>
<th>Initial Rate (mol L(^{-1}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(2.0 \times 10^{-2})</td>
<td>(1.0 \times 10^{-2})</td>
<td>(1.0 \times 10^{-2})</td>
</tr>
<tr>
<td>2</td>
<td>(4.0 \times 10^{-2})</td>
<td>(2.0 \times 10^{-2})</td>
<td>(8.0 \times 10^{-2})</td>
</tr>
<tr>
<td>3</td>
<td>(4.0 \times 10^{-2})</td>
<td>(1.0 \times 10^{-2})</td>
<td>(4.0 \times 10^{-2})</td>
</tr>
</tbody>
</table>

Using these data, determine:

a. the rate law for the reaction.

\[
\text{Rate} = k [A]^m [B]^n
\]

From experiments 3 and 1: \( m = 2 \)

From experiments 3 and 2: \( n = 1 \)

10 pt.

\[
\text{Rate} = k [A]^2 [B]^1
\]

b. the order of the reaction.

2 pt.

2. **(8 points)** A general reaction \( 2A \rightarrow C + D \) is studied and gives the following data:

<table>
<thead>
<tr>
<th>([A]_0) (mol/L)</th>
<th>Initial Rate (mol/L s)</th>
</tr>
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<tbody>
<tr>
<td>0.100</td>
<td>0.000040</td>
</tr>
<tr>
<td>0.200</td>
<td>0.000160 mol/L s</td>
</tr>
</tbody>
</table>

from which it is concluded that the reaction is second order. Calculate the the rate constant, \( k \), for this reaction.

\[
\text{Rate} = k [A]^2
\]

\[
k = \frac{\text{Rate}}{[A]^2} = \frac{4 \times 10^{-5} \text{ mol/L s}}{0.01 \text{ mol/L}^2} = 0.004 \text{ mol}^{-1} \text{ L s}^{-1}
\]
3. (11 points) Write the equilibrium expression for the following reactions.

a. \( K_P \) for \( 2O_3(g) \rightleftharpoons 3O_2(g) \)

\[ k_P = \frac{P_{O_2}^3}{P_{O_3}^2} \]

b. (i) \( K_P \) for \( O_3(g) \rightleftharpoons \frac{3}{2} O_2(g) \)

\[ k_P = \frac{P_{O_2}^{3/2}}{P_{O_3}} \]

(ii) The relationship between \( K_P \) of part (b) and part (a).

\[ k_P^{b} = \sqrt{k_P^{a}} \]

c. \( K_P \) for \( 4Pb(s) + 5O_2(g) \rightleftharpoons P_4O_{10}(s) \)

\[ k_P = \frac{1}{P_{O_2}^5} \]

4. (11 points) The decomposition of \( N_2O \) is thought to proceed by the following mechanism:

(1) \( 2NO(g) + 2N_2O(g) \rightarrow 2N_2(g) + 2NO_2(g) \) slow

(2) \( 2NO_2(g) \rightarrow 2NO(g) + O_2(g) \) fast

a. Write the overall reaction that shows the final products of the decomposition reaction.

\[ 2N_2O \rightarrow 2N_2 + O_2 \]

b. What is the intermediate? \( N_2O_2 \)

c. What is the catalyst? \( N \)

d. What is the rate determining step? Step (1)
5. **(10 points)** For the elementary reaction

\[ 2\text{N}_2\text{O}_5(g) \rightarrow 4\text{NO}_2(g) + \text{O}_2(g) \]

the activation energy, \( E_a \) is 100 kJ/mole, and \( \Delta E \) is -23 kJ/mol.

**a.** Sketch the potential energy curve for this reaction (the change of potential energy as a function of reaction progress), indicating \( E_a \) and \( \Delta E \).

![Potential Energy Curve](image)

**b.** Calculate the activation energy for the reverse reaction.

\[ 100 + \Delta E = 123 \text{ kJ} \]
6. (16 points) A first-order reaction has a rate constant of 1.00x10^{-3} s^{-1}. 
   a. What is the value of the half-life?

   \[ t_{1/2} = \frac{0.693}{K} = \frac{0.693}{1.00 \times 10^{-3}} = 693 \text{ s} \]

   b. How long will it take for the reaction to go to 75% completion (75% of the reactant has been consumed)?

   This can be done in 2 ways:

   1) 25% of the reactants remain after 1 half-life:
      i.e. \[ t = 693 \times 2 = 1386 \text{ s} \]

   2) from the 1st order reaction
      \[ \ln \left( \frac{[A]_0}{[A]} \right) = -Kt \]
      \[ \ln \left( \frac{[A]_0}{[A]} \right)/K = t \]
      \[ t = \ln \left( \frac{1}{2} \right)/1.00 \times 10^{-3} = \frac{\ln 4}{1.00 \times 10^{-3}} = 1386 \text{ s} \]
7. (12 points) The activation energy, $E_a$, of a certain reaction is 76.7 kJ/mol. How many times faster will the reaction occur at 50°C (323 K) than at 0°C (273 K)?

\[
\ln \left( \frac{k_2}{k_1} \right) = -\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

\[T_2 = 323 \text{ K} \quad T_1 = 273 \text{ K}\]

\[
\ln \left( \frac{k_2}{k_1} \right) = \frac{-76700 \text{ J/mol}}{8.314 \text{ J/K mol}} \left( \frac{1}{273} - \frac{1}{323} \right)
\]

\[
\ln \left( \frac{k_2}{k_1} \right) = \frac{5.67 \times 10^{-4} \times 76700}{8.314} = 5.23
\]

\[e^{5.23} = 187\]

\[\therefore \text{At 50°C the reaction occurs 187 times faster than at 0°C.}\]
8. (20 points) Consider the reaction:

$$I_2(g) + Br_2(g) \rightleftharpoons 2IBr(g)$$

for which the equilibrium constant is found to be: $K = 10$. In an experiment, 2.00 mol $I_2$, 2.00 mole $Br_2$, and 2.00 mol IBr were put into a 1.00 L container.

a. Calculate in which direction will the reaction proceed to reach equilibrium.

$$K = 10 = \frac{[IBr]^2}{[I_2][Br_2]}$$

$$Q = \frac{a^2 \text{(mol/L)}^2}{2 \times a \text{(mol/L)}^2} = 1 < 10$$

Reaction will proceed forward (to the right)

b. Calculate the concentrations of $I_2$, $Br_2$ and IBr at equilibrium. (Note: you don't need to solve a quadratic equation to get the solution.)

<table>
<thead>
<tr>
<th></th>
<th>$[I_2]$</th>
<th>$[Br_2]$</th>
<th>$[IBr]$</th>
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<tbody>
<tr>
<td>initial</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>change</td>
<td>$-x$</td>
<td>$-x$</td>
<td>$2x$</td>
</tr>
<tr>
<td>final</td>
<td>$2-x$</td>
<td>$8-x$</td>
<td>$2+2x$</td>
</tr>
</tbody>
</table>

$$10 = \left(\frac{8+2x}{2-x}\right)^2 \Rightarrow \sqrt{10} = \frac{8+2x}{2-x} \Rightarrow x = 3.16$$

$$6.32 - 3.16x = 2 + 2x$$

$$4.32 = 5.16x \Rightarrow x = \frac{4.32}{5.16} = 0.84$$

$$[I_2]_{eq} = 2 - 0.84 = 1.16 \text{ mol/L} = [Br_2]_{eq}$$

$$[IBr]_{eq} = 2 + 0.84 \times 2 = 3.68 \text{ mol/L}$$