Chemistry 4A F'00, Exam III
November 17, 2000
Professors Cohen/Sauer/Boering

Problems
1. (15) 15
2. (10) 10
3. (25) 17
4. (25) 9
5. (25) 14

Total Exam Score (100)

Rules:
- No lecture notes or books permitted
- No word processing calculators
- Time: 50 minutes
- Show all work to get partial credit
- \( R = 8.3 J \text{ mol}^{-1} \text{K}^{-1} \)
1. (5+5+5 points)

The rate law for the reaction:

\[ 3 \text{VO}^{2+} + \text{HCrO}_4^- + \text{H}^+ \rightarrow 3\text{VO}_2^- + \text{Cr}^{2+} + \text{H}_2\text{O} \]

has been shown to be:

\[ \frac{d[\text{HCrO}_4^-]}{dt} = k \frac{[\text{VO}^{2+}]^2[\text{HCrO}_4^-]}{[\text{VO}_2^-]} \]

a) If the rate of disappearance of \( \text{HCrO}_4^- \) is \( 8.3 \times 10^{-2} \) moles liter\(^{-1}\) sec\(^{-1}\); the rate of disappearance of \( \text{VO}^{2+} \) is?

\[ 8.3 \times 10^{-2} \text{ moles/}l \times 3 \text{ moles/mol} = 0.249 \text{ moles/}l \text{ s} \]

b) If the concentrations of all the solutes present in the reaction are doubled, how does the rate of disappearance of \( \text{HCrO}_4^- \) change? Circle your answer:

- no change
- doubled
- quadrupled
- halved
- 8 times

(c) The rate law described in this problem is an example of product inhibition. Write the rate law for the initial disappearance of \( \text{HCrO}_4^- \) in the absence of products.

\[ \frac{d[\text{HCrO}_4^-]}{dt} = k \frac{[\text{VO}^{2+}]^2[\text{HCrO}_4^-]}{[\text{VO}_2^-]} \]

\[ -k \]
2. (10 points) For the reaction \( A + 2B \rightarrow \text{products} \), the following data were observed:

<table>
<thead>
<tr>
<th>Initial Rate (mole liter(^{-1}) sec(^{-1}))</th>
<th>Initial Concentration (mole liter(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.3 \times 10^{-4}</td>
<td>([A]) \quad 2.0 \times 10^{-3}\quad 4.0 \times 10^{-3}</td>
</tr>
<tr>
<td>12.6 \times 10^{-4}</td>
<td>([B]) \quad 2.0 \times 10^{-3}\quad 8.0 \times 10^{-3}</td>
</tr>
<tr>
<td>25.2 \times 10^{-4}</td>
<td>\quad 4.0 \times 10^{-3}\quad 4.0 \times 10^{-3}</td>
</tr>
</tbody>
</table>

The rate law for this reaction is (circle your answer)

\[ \text{rate} = k \]

\[ \text{rate} = k[A][B] \]

\[ \boxed{\text{rate} = k[A]^2[B]} \]  

\[ \text{rate} = k[A][B]^3 \]

\[ \text{rate} = k[A]^{1/2}[B] \]
3. (10 + 10 + 5 points)

The detailed mechanism for the association reaction

\[ \text{NO}_2 + \text{NO}_3 \rightarrow \text{N}_2\text{O}_5 \]

consists of two elementary reactions

\[ \text{NO}_2 + \text{NO}_3 \xleftrightarrow{k_1 \text{ and } k_2} \text{N}_2\text{O}_5^* \]

\[ \text{N}_2\text{O}_5^* + \text{M} \xrightarrow{k_1} \text{N}_2\text{O}_5 + \text{M} \]

a) Write a rate law for disappearance of \( \text{N}_2\text{O}_5 \) based on your mechanism.

\[ \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{k_1 [\text{NO}_2][\text{NO}_3]}{k_1 + k_2 [\text{M}]} + 2 \]

use and assume \[ [\text{N}_2\text{O}_5^*] = \frac{k_1 [\text{NO}_2][\text{NO}_3]}{k_1 + k_2 [\text{M}]} \]

use steady state and substitute in →

\[ \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{k_1 k_2 [\text{NO}_2][\text{NO}_3][\text{M}]}{k_1 + k_2 [\text{M}]} + 2 \]

b) Write the rate law at low pressure and at high pressure. Sketch the dependence of the rate of appearance of \( \text{N}_2\text{O}_5 \) on pressure.

(assume gas reaction where + pressure = + products)

\[ \text{rate} = \text{high reaction} = \text{low reaction} = \text{low pressure rate too} \]

\[ \frac{d[\text{M}]}{dt} = \text{high reaction} = \text{low reaction} = \text{low pressure rate too} \]

\[ \frac{d[\text{M}]}{dt} = \frac{k_1 k_2 [\text{NO}_2][\text{NO}_3]}{k_1 + k_2 [\text{M}]} + 2 \]

Sketch the dependence of the rate of appearance of \( \text{N}_2\text{O}_5 \) on pressure.

The overall reaction proceeds faster at low temperature. Why?

The first process, the second one, is exothermic, and thus the reaction's rate principle predicts a shift toward products when a product (heat) is removed.
4 (10 + 9 + 6 points)
(a) Write a catalytic cycle for the net reaction

$$2O_3 \rightarrow 3O_2$$

that involves CIOOC1. Label the rate determining step.

$$\text{ClOOC1} + O_3 \rightarrow \text{ClOOC1} + 2O_2$$
$$\text{ClOOC1} + M \rightarrow \text{ClOOC1} + \text{M}$$

(b) Use your mechanism to write a rate equation for ozone disappearance that shows the rate of ozone disappearance is proportional to $[\text{ClO}]^2$.

\[ \frac{dr}{dt} = k_2 [\text{ClOOC1}] [O_3] + k_3 [\text{ClO}]^2 [O_3] \] (consistent with above)

(c) List 2 reasons the Antarctic ozone hole forms in October and not in June.

The Antarctic summer is beginning in the October winter period thus this is the time after which the first light has reached the region (beginning the catalysis of O_3). Also, the reactions that produce the catalysts are encouraged by (PS1) clouds that form around +3195 K, temperatures reached only during the winter dark period... thus there is an excess of catalyst present at the beginning of the winter.
5. (5+15+5 points)

For the reaction of HOCl with an organic dye, assume it is first order in each reactant with a rate constant of $10^3$ liter-mole$^{-1}$s$^{-1}$. The dye concentration is $10^4$ mole-liter$^{-1}$.

a) What is the lifetime of the bleach? (circle your answer)

- 10,000 sec
- 1000 sec
- 100 sec
- 10 sec
- 1 sec

\[
\frac{1}{k} \cdot t \text{ half time } = \frac{1}{k} 
\]

b) The reaction rate doubles when the temperature is raised from 280K to 320K. Estimate the activation energy for this reaction.

\[
\ln \left( \frac{k_2}{k_1} \right) = \frac{E_a}{R} \left( \frac{1}{320} - \frac{1}{280} \right)
\]

\[
\ln 2 = \frac{E_a}{R} \left( \frac{1}{320} - \frac{1}{280} \right)
\]

\[
E_a \approx 1.3407 \text{ kJ/mol}
\]

5G FIGS

\( \text{1} \)

c) The following observations of transmission vs. time were made after mixing bleach and dye:

![Kinetics of a Bleached Dye Measured by Spectrophotometer](chart)

\[
\text{curve here dye is not zeroth order, even at pseudo 1st order for dye.}
\]

\[
\text{NO} \]

Mark the first and last data point you would include in an analysis to determine the reaction rate constant.