Chemistry 2740 Spring 2009 Test 3

Time: 50 minutes
Questions: 3
Marks: 40
Aids allowed: calculator, 8.5×11-inch formula sheet
Answer all questions in the booklets provided.

Attempt the bonus question only if you have done all you can on the other questions!

1. Consider the following table, which gives the results of a set of initial rate experiments for a reaction with the stoichiometry $A + B \rightarrow P$.

Experiment	$a/\mathrm{mol\,L^{-1}}$	$b/10^{-3}\mathrm{mol\,L^{-1}}$	$v/10^{-3}\mathrm{mol\,L^{-1}s^{-1}}$
1	0.10	1.4	0.31
2	0.20	1.4	1.24
3	0.10	2.1	

   (a) What is the order with respect to A? [2 marks]

   (b) In a separate set of experiments, it was determined that the order with respect to B is $\frac{1}{2}$. What reaction rate would you predict for experiment 3? [3 marks]

   (c) What is the value of the rate constant? [3 marks]

   (d) Could this reaction be elementary? Why or why not? [2 marks]

2. In strongly acidic solutions, $HBrO_2$ disproportionates according to the overall reaction[1]

$$2HBrO_{2(aq)} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} HOBr_{(aq)} + BrO^-_{3(aq)} + H^+(aq).$$

(a) The following data have been obtained by Försterling and Varga for this reaction in 1 M sulfuric acid at 20°C:[2]

t/s	0	10	20	30	40	50
$[HBrO_2]/10^{-5}\,\mathrm{mol\,L^{-1}}$	2.00	0.70	0.48	0.38	0.32	0.27

Under these conditions, the reaction is essentially irreversible. Confirm that this reaction obeys second-order kinetics, and calculate the rate constant k_4. [8 marks]

(b) The rate constant for the reverse reaction has been measured by others, and has been found to be $k_{-4} = 1 \times 10^{-8}\,\mathrm{L^2mol^{-2}s^{-1}}$. What is the equilibrium constant for this reaction under these experimental conditions? [2 marks]

(c) The mechanism for this reaction is thought to be

$$HBrO_2 + H^+ \underset{k_{-4a}}{\overset{k_{4a}}{\rightleftharpoons}} H_2BrO_2^+$$

$$HBrO_2 + H_2BrO_2^+ \xrightarrow{k_{4b}} HOBr + BrO_3^- + 2H^+$$

The protonation equilibrium is fast. Show that this mechanism predicts a second-order dependence of the rate on the $HBrO_2$ concentration. [8 marks]

(d) You should find that your rate law implies a dependence of the rate on the hydrogen ion concentration.[3] Why were Försterling and Varga able to observe a simple second-order dependence of the rate on $HBrO_2$ in the experiment described above? [2 marks]

Bonus: Under the conditions of this experiment, both $HBrO_2$ and $H_2BrO_2^+$ are present in significant amounts, but spectroscopically these two species are indistinguishable. Thus, the measured value of $[HBrO_2]$ is really the total amount, $[HBrO_2]_{tot} = [HBrO_2] + [H_2BrO_2^+]$. Rewrite your rate law in terms of $[HBrO_2]_{tot}$ (instead of $[HBrO_2]$).

Hint: You will need to reuse an equation you had already used in developing the rate law to eliminate $[H_2BrO_2^+]$.

3. Describe the continuous flow experiment and explain how it can be used to study fast reactions. What is the most important disadvantage of this technique? [10 marks]

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[1] This reaction is part of the mechanism of the Belousov-Zhabotinsky reaction. The number of these rate constants is a convention connected to the appearance of this reaction in that mechanism.

[2] *J. Phys. Chem.* **97**, 7932 (1993). In their experiments, the concentration of $HBrO_2$ was monitored continuously by a spectrophotometric method. The data presented here are just points chosen at regular intervals from their time series.

[3] The prediction isn't quite right, for reasons explored in the bonus question.