

# Chemistry 2740 Spring 2009 Test 3

**Time:** 50 minutes

**Questions:** 3

**Marks:** 40

**Aids allowed:** calculator,  $8.5 \times 11$ -inch formula sheet

**Answer all questions** in the booklets provided.

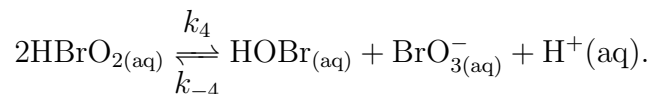
**Attempt the bonus question only if you have done all you can on the other questions!**

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	$a/\text{mol L}^{-1}$	$b/10^{-3}\text{mol L}^{-1}$	$v/10^{-3}\text{mol L}^{-1}\text{s}^{-1}$
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,  $\text{HBrO}_2$  disproportionates according to the overall reaction<sup>1</sup>

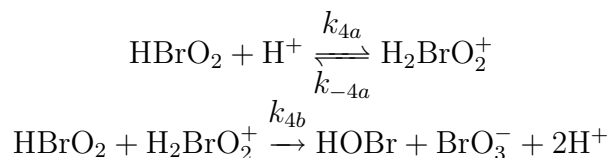


- (a) The following data have been obtained by Försterling and Varga for this reaction in 1 M sulfuric acid at 20°C:<sup>2</sup>

$t/\text{s}$	0	10	20	30	40	50
$[\text{HBrO}_2]/10^{-5} \text{ mol L}^{-1}$	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  $k_{-4} = 1 \times 10^{-8} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ . What is the equilibrium constant for this reaction under these experimental conditions? [2 marks]
- (c) The mechanism for this reaction is thought to be



The protonation equilibrium is fast. Show that this mechanism predicts a second-order dependence of the rate on the  $\text{HBrO}_2$  concentration. [8 marks]

- (d) You should find that your rate law implies a dependence of the rate on the hydrogen ion concentration.<sup>3</sup> Why were Försterling and Varga able to observe a simple second-order dependence of the rate on  $\text{HBrO}_2$  in the experiment described above? [2 marks]

**Bonus:** Under the conditions of this experiment, both  $\text{HBrO}_2$  and  $\text{H}_2\text{BrO}_2^+$  are present in significant amounts, but spectroscopically these two species are indistinguishable. Thus, the measured value of  $[\text{HBrO}_2]$  is really the total amount,  $[\text{HBrO}_2]_{\text{tot}} = [\text{HBrO}_2] + [\text{H}_2\text{BrO}_2^+]$ . Rewrite your rate law in terms of  $[\text{HBrO}_2]_{\text{tot}}$  (instead of  $[\text{HBrO}_2]$ ).

Hint: You will need to reuse an equation you had already used in developing the rate law to eliminate  $[\text{H}_2\text{BrO}_2^+]$ .

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]

<sup>1</sup>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.

<sup>2</sup>*J. Phys. Chem.* **97**, 7932 (1993). In their experiments, the concentration of  $\text{HBrO}_2$  was monitored continuously by a spectrophotometric method. The data presented here are just points chosen at regular intervals from their time series.

<sup>3</sup>The prediction isn't quite right, for reasons explored in the bonus question.