

Chemistry 2740 Spring 2009 Test 3 Solutions

1. (a) Compare experiments 1 and 2: The rate goes up by a factor of $1.24/0.31 = 4$ when the concentration of A doubles, so the reaction is of the second order with respect to A.
- (b) The only difference between experiments 1 and 3 is that the concentration of B has been increased by a factor of $2.1/1.4 = 1.5$, so since the reaction is $\frac{1}{2}$ -order with respect to B, the reaction rate should increase by a factor of $1.5^{1/2}$. The rate in experiment 3 should therefore be

$$v = (1.5^{1/2})(0.31 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}) = 3.8 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}.$$

(c)

$$\begin{aligned} v &= ka^2b^{1/2}. \\ \therefore k &= \frac{v}{a^2b^{1/2}} \\ &= \frac{0.31 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}}{(0.10 \text{ mol/L})^2(1.4 \times 10^{-3} \text{ mol/L})^{1/2}} = 0.83 \text{ L}^{3/2}\text{mol}^{-3/2}\text{s}^{-1}, \end{aligned}$$

using the data from experiment 1.

- (d) This reaction is certainly not elementary. An elementary reaction with this stoichiometry would have a rate law $v = kab$, by the law of mass-action.
2. (a) If it's a second-order reaction,

$$\frac{1}{[\text{HBrO}_2]} = \frac{1}{[\text{HBrO}_2]_0} + kt,$$

so a plot of $[\text{HBrO}_2]$ vs t should give a straight line of slope k . My graph is shown in figure 1. The fit is certainly very reasonable. The deviations around the line can be explained as random scatter. We can conclude that the reaction obeys second-order kinetics. The rate constant is found (by linear regression) to be

$$k = 6187 \text{ L mol}^{-1}\text{s}^{-1}.$$

To get k_4 , we have to be a little careful. The rate is

$$v = k_4[\text{HBrO}_2]^2.$$

Since

$$v = -\frac{1}{2} \frac{d[\text{HBrO}_2]}{dt},$$

we get

$$\frac{d[\text{HBrO}_2]}{dt} = -2k_4[\text{HBrO}_2]^2.$$

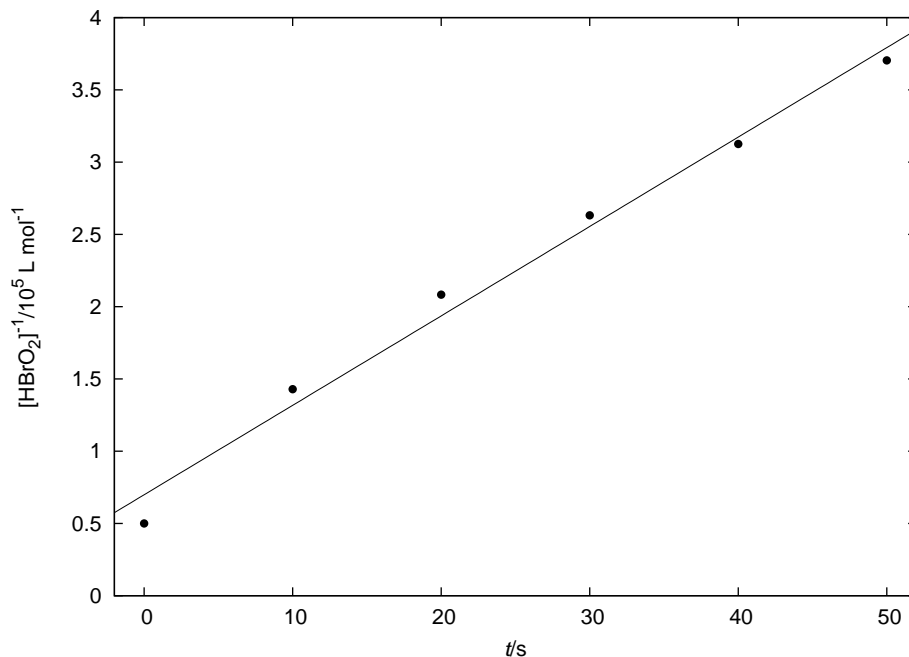


Figure 1: Second-order plot for question 2a

This means that the measured rate constant is related to k_4 by $k = 2k_4$. Therefore

$$k_4 = \frac{1}{2} (6187 \text{ L mol}^{-1}\text{s}^{-1}) = 3094 \text{ L mol}^{-1}\text{s}^{-1}.$$

(b) $K_4 = \frac{k_4}{k_{-4}} = \frac{3094 \text{ L mol}^{-1}\text{s}^{-1}}{1 \times 10^{-8} \text{ L}^2\text{mol}^{-2}\text{s}^{-1}} = 3 \times 10^{11} \text{ mol/L}$

(c) The rate of reaction is (for example)

$$v = \frac{d[\text{HOBr}]}{dt} = k_{4b}[\text{HBrO}_2][\text{H}_2\text{BrO}_2^+].$$

Apply the equilibrium approximation to step 4a to eliminate the concentration of the intermediate $[\text{H}_2\text{BrO}_2^+]$ from the rate law:

$$\begin{aligned} k_{4a}[\text{HBrO}_2][\text{H}^+] &\approx k_{-4a}[\text{H}_2\text{BrO}_2^+]. \\ \therefore [\text{H}_2\text{BrO}_2^+] &\approx \frac{k_{4a}}{k_{-4a}}[\text{HBrO}_2][\text{H}^+]. \\ \therefore v &= \frac{k_{4a}k_{4b}}{k_{-4a}}[\text{HBrO}_2]^2[\text{H}^+]. \end{aligned} \quad (1)$$

(d) The reaction was carried out in a large excess of sulfuric acid, so the hydrogen ion concentration varies little during the experiment.

Bonus: We substitute the equilibrium relationship 1 into the equation defining the total amount of HBrO_2 :

$$\begin{aligned} [\text{HBrO}_2]_{\text{tot}} &= [\text{HBrO}_2] + [\text{H}_2\text{BrO}_2^+] \\ &= [\text{HBrO}_2] + \frac{k_{4a}}{k_{-4a}} [\text{HBrO}_2][\text{H}^+] \\ &= [\text{HBrO}_2] \left(1 + \frac{k_{4a}}{k_{-4a}} [\text{H}^+] \right). \\ \therefore [\text{HBrO}_2] &= \frac{[\text{HBrO}_2]_{\text{tot}}}{1 + \frac{k_{4a}}{k_{-4a}} [\text{H}^+]} \end{aligned}$$

or, if we define $K_{4a} = k_{4a}/k_{-4a}$,

$$\begin{aligned} [\text{HBrO}_2] &= \frac{[\text{HBrO}_2]_{\text{tot}}}{1 + K_{4a}[\text{H}^+]}. \\ \therefore v &= \frac{k_{4a}k_{4b}}{k_{-4a}} [\text{H}^+] \left(\frac{[\text{HBrO}_2]_{\text{tot}}}{1 + K_{4a}[\text{H}^+]} \right)^2 \\ &= \frac{k_{4b}K_{4a}[\text{H}^+]}{(1 + K_{4a}[\text{H}^+])^2} [\text{HBrO}_2]_{\text{tot}}^2. \end{aligned}$$

The observed second-order rate constant is therefore

$$k_4 = \frac{k_{4b}K_{4a}[\text{H}^+]}{(1 + K_{4a}[\text{H}^+])^2}.$$

This relationship between k_4 and the hydrogen ion concentration has been confirmed by Försterling and Varga.

3. The apparatus is illustrated in figure 2. The reactants are shot into the mixing chamber by the motor-driven syringes. Mixing is rapid, and the reactive mixture moves into the flow tube. The mixing chamber represents $t = 0$, i.e. the initiation of the reaction. The mixture moves through the flow tube at constant speed, so a particular distance L from the mixing chamber represents a particular moment in time since mixing: $t = L/v$. The main disadvantage of this method is that it tends to use large volumes of reactants, which can be a problem if the reactants are either difficult or expensive to make.

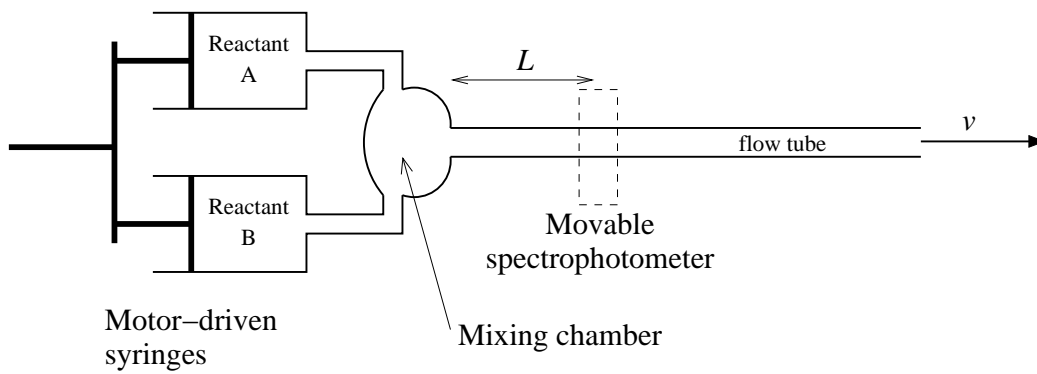


Figure 2: Diagram of a continuous-flow apparatus.