Determination of a Rate Law

INTRODUCTION: The rate of a chemical reaction may depend upon reactant concentrations, temperature, and the presence of catalysts. At a fixed temperature, the rate of a reaction may be mathematically described by a **rate law**. Consider the following hypothetical reaction:

$$A + 2\,B + 3\,C \rightarrow \text{Products} \qquad (1)$$

The **differential rate law** for this reaction represents the rate of change in concentration of a reactant and has the following form:

$$\text{rate} = \frac{-d[A]}{dt} = k[A]^x[B]^y[C]^z \quad (\text{mol L}^{-1}\ \text{s}^{-1}) \qquad (2)$$

where k is the **rate constant** and x, y, and z are the **orders** with respect to each reactant. The overall order of the reaction is the sum of x+y+z. Since A is disappearing, the derivative has a negative sign in order to make the rate a positive quantity.

The following reaction is to be investigated in this experiment:

$$H_2O_2(aq) + 2\,I^-(aq) + 2\,H^+(aq) \rightarrow 2\,H_2O(l) + I_2(aq) \quad (\text{slow}) \qquad (3)$$

Under the conditions of the experiment, the iodide and hydrogen ions are present in large excess. Consequently, their concentrations remain effectively constant during the reaction and do not appear on the right-hand side of the rate law (they are included in the rate constant). The rate law will thus depend only upon the concentration of hydrogen peroxide:

$$\frac{-d[H_2O_2]}{dt} = k\,[H_2O_2]^n \qquad (4)$$

We will determine the order ***n*** and the value of the rate constant ***k***. Although some reactions have quite complicated rate laws with fractional orders, we will test only for the relatively simple cases of n = 0, 1, or 2. In order to do this, it is necessary to integrate the rate law.

$$\frac{-d[H_2O_2]}{[H_2O_2]^n} = k\ dt \qquad (5)$$

The exact form of the integrated rate law depends upon the value of n. When n = 0 (zero order), the integrated rate law is as follows:

$$[H_2O_2] = [H_2O_2]_0 - kt \qquad (6)$$

When n = 1 (first order), the integrated rate law is as follows:

$$\ln[H_2O_2] = \ln[H_2O_2]_0 - kt \qquad (7)$$

When n = 2 (second order), the integrated rate law is as follows:

$$\frac{1}{[H_2O_2]} = \frac{1}{[H_2O_2]_0} + kt \qquad (8)$$

Note that each integrated rate law has the form of the equation of a straight line, $y = b + mx$. Only one of the three equations 6-8 will actually fit the concentration data for the reaction (i.e., only one of the three possible orders can be correct). If one can measure the concentration of hydrogen peroxide remaining at various times during the reaction, the data may be plotted in the form of each of the three integrated rate laws; only one graph will actually be a straight line, thus indicating the correct order. The value of the rate constant k will then be related to the slope of the graph (note that k is always a positive number, and has units which depend upon the order).

Since it is not possible to directly analyze for the hydrogen peroxide concentration while the reaction is taking place, we will instead analyze for the amount of iodine formed and use the stoichiometric relationships to determine how much hydrogen peroxide remains. After initiating the reaction, aliquots of standard sodium thiosulfate solution are added to the reaction mixture at intervals. The thiosulfate ion reacts with the iodine formed by the principal reaction as follows:

$$I_2(aq) + 2\ S_2O_3^{2-}(aq) \rightarrow 2\ I^-(aq) + S_4O_6^{2-}(aq) \quad \text{(fast)} \qquad (9)$$

Since this reaction is much faster than the main reaction, any iodine formed by reaction (3) is immediately consumed by the thiosulfate ion. In addition, starch is added to the mixture to indicate the presence of molecular iodine:

$$I_2(aq) + \text{starch} \rightarrow \text{blue complex} \quad \text{(fast)} \qquad (10)$$

The method of analysis is as follows. The principal reaction (equation 3) is initiated in the presence of a starch solution and a timer is started. The mixture immediately turns blue as iodine is formed (see the rising line beginning at zero time in Figure 1; the rising lines indicate the formation of I_2, and the vertical lines indicate the consumption of I_2 by thiosulfate). An aliquot of standard sodium thiosulfate solution is quickly added from a burette (first vertical part of the trace on the graph). This amount of thiosulfate is deliberately in excess and will immediately consume all of the iodine formed by the principal reaction; the mixture thus becomes colorless. There is now an excess of thiosulfate ion present in the flask. As more and more iodine is produced (second rising portion of the graph), the fixed amount of thiosulfate is eventually consumed. At this point, the blue color reappears and the time is noted; the appearance of the blue color signifies that the exact stoichiometry of equation 9 has been attained (2 mmol thiosulfate:1 mmol I_2).

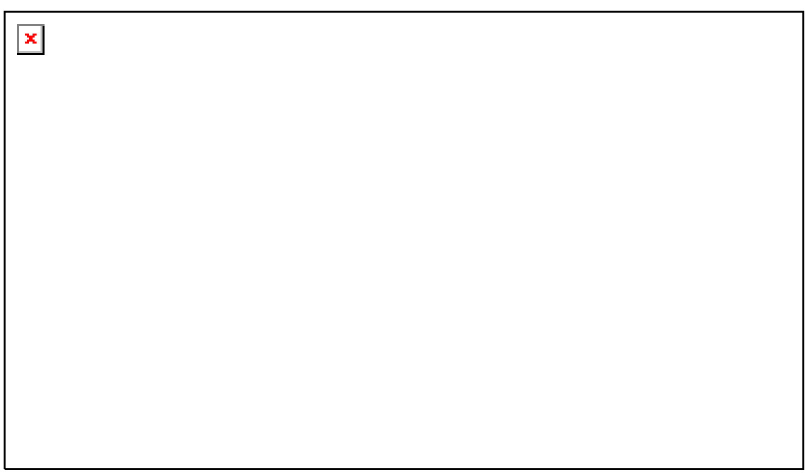

Figure 1. Relative Amounts of I_2 and $S_2O_3^{2-}$ During the Experiment

The **total** amount (in millimoles) of iodine **produced** at time **t** can then be calculated from the **total** amount of thiosulfate used up to that point (the total amount added **prior** to the color change, since the beginning of the reaction). The **total** number of moles of iodine produced is then used to calculate the **total** number of moles of hydrogen peroxide **consumed** up to that time (see stoichiometry of equation 3); this number is then subtracted from the initial number of moles of hydrogen peroxide, since the number of moles of hydrogen peroxide **remaining** is needed. Another excess of thiosulfate is added (second vertical portion of the graph) and the time is again noted when the blue color reappears (second rising portion of the graph); this process is repeated several times to obtain sets of concentration-time data for fitting to the three assumed rate laws. The initial amount of hydrogen peroxide is determined by allowing the reaction to proceed to completion and determining the total amount of iodine produced, then relating this to the total amount of hydrogen peroxide which was initially present.

Example: The third appearance of the blue color (fourth data point, counting zero time as the first) was at 141 seconds, **after** 1.73 mL total (since the beginning of the experiment) of 0.1283 M sodium thiosulfate had been added. There were initially 0.543 mmol of hydrogen peroxide present in the flask. The total amount of thiosulfate added is (1.73 mL)(0.1283 mmol/mL) = 0.222 mmol. The amount of hydrogen peroxide **consumed** is one-half of this amount, or 0.111 mmol. The amount of hydrogen peroxide **remaining** is (0.543 - 0.111) = 0.432 mmol. The total volume in the flask is now 206.73 mL, so the molarity of hydrogen peroxide remaining is 0.432 mmol / 206.73 mL = 0.00209 M.

EQUIPMENT: 50-mL burette, 20-mL pipet, 100-mL and 10-mL graduated cylinders, 500-mL Erlenmeyer flask, timer, burette funnel, pipet bulb

EXPERIMENTAL: Fill a clean burette with about 20 mL of the standard sodium thiosulfate solution, making sure that the tip is filled. Record the molarity of the solution and the initial burette reading (to the nearest 0.01 mL).

Place 150.0 mL of deionized water, 10.0 mL of 1.0 M sulfuric acid solution, and 5.0 mL of starch solution in a clean, dry Erlenmeyer flask. Pipet in exactly 20.00 mL of hydrogen peroxide solution and mix well.

Add 20.0 mL of 1.00 M potassium iodide solution from a graduated cylinder as quickly as possible, starting the timer **at the same time as the addition.** The timer must run continuously throughout the experiment.

Immediately add about 1.2 mL of sodium thiosulfate solution from the burette and record the burette reading. The blue color will disappear. When the solution turns blue again, record the timer reading **while the timer continues to run.**

Add another increment of sodium thiosulfate and again record the volume and the time at which the color reappears. Continue to repeat this process until ten data points have been recorded. The size of the added increments of sodium thiosulfate should be steadily decreased in order to have the time intervals remain roughly constant.

Stop the timer and let the mixture stand for one hour. This will be sufficient time for the reaction to reach completion. **Carefully** titrate the solution with the remaining sodium thiosulfate in your burette until the blue color just disappears (it should not return). Record the final burette reading, then clean up all of your equipment.

CALCULATIONS: Perform calculations in millimoles. Note that molarity is the same value either in mol/L or number of **millimoles** of solute per **milliliter** of solution, so number of millimoles = (Molarity)(Volume in mL).

1. First calculate the initial (total) number of millimoles of hydrogen peroxide present from the **total** volume of thiosulfate used in the experiment. Take note of the stoichiometries of equations (3) and (9).

2. Set up a data table with columns for total elapsed time (include a point for zero time), the total volume of thiosulfate used up to that point, the total volume of the solution in the flask, the number of mmol of thiosulfate used, the number of mmol of hydrogen peroxide **consumed**, the number of mmol of hydrogen peroxide, the molarity of hydrogen peroxide remaining (using the total solution volume), the natural logarithm of the molarity, and the reciprocal of the molarity; be sure to include units. Show one complete set of calculations in detail with explanations. The calculations should be done with a spreadsheet, in which case the formulas used in each column should be explained in the report (remember that the method of calculation is always explained in a lab report). If you print the table in landscape format (sideways on the paper) it should all fit on one page.

3. Prepare graphs of [H_2O_2] vs. time, the natural logarithm of peroxide concentration vs. time, and the reciprocal of peroxide concentration vs. time. Do not plot the data point corresponding to completion of the reaction. Carry out a linear regression on the graph which most closely shows a linear relationship. Plot the **data points** and **best-fit line** on this graph; do a marker-plus-line plot for the other two (i.e., connect the points). Include the point for zero time on the graphs. Be sure to put a descriptive title (**not** in Y vs. X form) on each graph. Explain in your report the correct order and how you determined it, give the value of the rate constant with correct units and uncertainty, and give the complete integrated rate law.

4. Calculate the time required for the reaction to reach 99% completion, i.e., when the number of mmol of peroxide has fallen to 1% of its initial value. Comment upon the significance of this result with respect to the waiting period in the experiment.

Remember that the goal of the experiment is to determine the rate law for the reaction, with an order and a rate constant with proper units. You should give both the differential and integrated forms of the rate law in your discussion

REPORT: In addition to reporting your data, calculations, and the necessary graphs, you will write a conclusion for today's experiment. In a conclusion, you briefly outline the results and conclusions of the experiment.