1. Three runs were used to study the reaction:

$$A + B \rightarrow 3\ C + D$$

The following data were obtained (initial concentrations of C and D = 0):

<table>
<thead>
<tr>
<th>Run</th>
<th>[A]</th>
<th>[B]</th>
<th>[A]</th>
<th>[B]</th>
<th>[C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.000</td>
<td>2.000</td>
<td>2.970</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>6.000</td>
<td>2.000</td>
<td>5.940</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3.000</td>
<td>4.000</td>
<td>2.880</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Fill in the missing concentrations in the table above.
(b) Calculate the rate of the reaction in M/s for each of the three runs.

(c) Determine the order with respect to A and B.

(d) Calculate the rate constant for the reaction, including units.
EXPERIMENT 14: Chemical Kinetics

THE RATE LAW FOR THE REACTION OF IODIDE WITH BROMATE

INTRODUCTION

The rate (speed) of a chemical reaction is measured by finding out how long it takes to consume a definite amount of a reactant or to form a definite amount of a product. Since we want the rate to be the same regardless of which reactant or product is chosen, the stoichiometry of the reaction must be taken into account. For example, if the reaction is

\[ a \text{ A} + b \text{ B} \rightarrow c \text{ C} + d \text{ D} \]

the rate is given by

\[
rate = \frac{\Delta[A]}{a\Delta t} = \frac{\Delta[B]}{b\Delta t} = \frac{\Delta[C]}{c\Delta t} = \frac{\Delta[D]}{d\Delta t}
\]

where \( \Delta[A] \) is the change in concentration of reactant A in the time interval \( \Delta t \), etc. Note that since A and B are being consumed (i.e., \( \Delta[A] \) and \( \Delta[B] \) are negative), a minus sign is placed in front of their rates of change, so that the rate of the reaction is always a positive number.

The objective of this experiment is to determine the rate law of a chemical reaction. The rate law is a mathematical relationship between the rate of the reaction and the concentrations of the species involved in the reaction. Rate laws are sometimes very complicated, but if we start out using a mixture containing only reactants and no products, the rate law generally takes the following form:

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

where x and y are usually small integers and k is a constant at constant temperature. The value of x is called the “order” of the reaction with respect to [A] and y is the order with respect to [B]. Note that x and y have no relationship to the stoichiometric coefficients a and b, and that each must be determined experimentally.

The value of x can be determined by changing [A] while holding [B] constant. For example, suppose the rate increases by a factor of four when [A] is doubled.

\[
\frac{\text{rate}(2)}{\text{rate}(1)} = 4 = \frac{k[A]^x[B]^y}{k[A]^x[B]^y} = \frac{(2[A])^x}{[A]^x} = 2^x
\]

Obviously the only way that \( 2^x \) can equal 4 is for x to be 2; that is, we now know that the rate law is

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

where y still needs to be determined.

Once x and y have been found, we can calculate k, the “rate constant,” as follows:

\[ k = \frac{\text{rate}}{[A]^x[B]^y} \]

If our values of x and y are correct, we should obtain the same number for the rate constant using the data from any of the runs we used to determine the orders. In practice, experimental error causes k to vary somewhat from one run to another, so the rate constant is usually reported as the average for all the runs.
The Iodine Clock Reaction

The reaction between iodide and bromate, often called the “iodine clock reaction,” occurs as follows:

\[
6 \text{I}^- + \text{BrO}_3^- + 6 \text{H}^+ \rightarrow 3 \text{I}_2 + \text{Br}^- + 3 \text{H}_2\text{O} \quad (1)
\]

In this experiment a chemical method is used to determine the amount of \( \text{I}_2 \) produced per unit time. A second reaction is used to assist in establishing the time required to produce a constant amount of iodine:

\[
\text{I}_2 + 2 \text{S}_2\text{O}_3^{2-} \rightarrow 2 \text{I}^- + \text{S}_4\text{O}_6^{2-} \quad (2)
\]

Reaction (2) is much faster than (1). If in each run a constant small amount of thiosulfate is present with the reactants, then as the iodine is produced in reaction (1), it is immediately used up in reaction (2). When the thiosulfate is exhausted, the first trace of iodine produced in (1) causes a blue color to appear due to its reaction with starch indicator also in the solution.

The stoichiometries of reactions (1) and (2) indicate that for every three moles of \( \text{I}_2 \) produced, six moles of thiosulfate are consumed. In other words,

\[
rate = \frac{\Delta [\text{I}_2]}{3 \Delta t} = \frac{-\Delta [\text{S}_2\text{O}_3^{2-}]}{6 \Delta t}
\]

where \( \Delta t \) is the time required to consume the thiosulfate originally present. (If the stopwatch is set to zero when the reactants are mixed, we can replace \( \Delta t \) simply with \( t \), the number of seconds required for the blue color to appear.) The concentration of thiosulfate added in each run is the same, namely,

\[
(10.0 \times 10^{-3} \text{ L})(2.50 \times 10^{-4} \text{ mol/L})/(50.0 \times 10^{-3} \text{ L}) = 5.00 \times 10^{-5} \text{ mol/L}
\]

Thus the rate of the reaction is

\[
rate = \frac{(-5.00 \times 10^{-5} M)}{6t} = \frac{8.33 \times 10^{-6} M}{t} \quad (3)
\]

in units of \( \text{M/s} \). In other words, the smaller the time before the color appears, the faster the rate. Note that equation (3) can be used to calculate the rate of all ten runs in the experiment.
EXPERIMENTAL (Please work in pairs.)

You will need a 5 mL pipet and 10 mL pipet for each solution (except the Na₂S₂O₃ solution, for which you only need one 10 mL pipet) and a stopwatch from the lab instructor.

The following are the solutions used in the experiment:

0.010 M KI ; 0.000250 M Na₂S₂O₃ ; 0.10 M HCl ; 0.040 M KBrO₃ ; 3% starch indicator

In order to start the reaction at a well-defined time, aliquots of the first two solutions are pipetted into one 250 mL Erlenmeyer flask (flask A), aliquots of HCl and water are added to a second 250 mL flask (flask B), and an aliquot of KBrO₃ plus 4 drops of starch indicator are added to a third 250 mL flask (flask C). You will be performing ten runs, as indicated in Table 1.

### Table 1: Reactant Volumes (mL)

<table>
<thead>
<tr>
<th>Run</th>
<th>Flasks A</th>
<th>Flasks B</th>
<th>Flasks C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KI</td>
<td>Na₂S₂O₃</td>
<td>HCl</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>10</td>
<td>10</td>
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<tr>
<td>4</td>
<td>20</td>
<td>10</td>
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<td>6</td>
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<td>9</td>
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<td>15</td>
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<tr>
<td>10</td>
<td>10</td>
<td>10</td>
<td>20</td>
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</tbody>
</table>

(1) To begin a run, zero the stopwatch, pour the contents of flask B into flask C, quickly add A to C and immediately swirl (the flask, of course) enthusiastically to insure thorough mixing. Your partner should start the stopwatch as soon as you add A to C. When the blue color first appears, stop the stopwatch and record the time and temperature. (If the flask is resting on a piece of white paper, the appearance of the blue color is easier to see.) Since the first run is used in all three of the plots to determine the orders in the rate law (see below), it is advisable to do this run in triplicate (3 times). Record the three times (in seconds) you obtain below, and show them to your lab instructor before proceeding to the other runs:

(2) Perform runs 2-10, and record the results for all the runs in the table below. (Use the averages of the three times and temperatures above for run 1.) Please take note of the temperature for each run; large variations in temperature will affect the accuracy of your results.
CALCULATIONS

The first step in determining the order for each reactant is to calculate the initial concentrations for each run. Note that in calculating the concentration of thiosulfate for equation (3), we divided by the total volume of the final mixture (0.0500 L). Use the same procedure to calculate the initial [I\(^-\)], [BrO\(_3\)-], and [H\(^+\)]. Fill your results into Table 2.

For example, in run 1 initial [I\(^-\)] is

\[
[I^-] = \frac{(0.010 \text{ M KI}) \times \frac{(1 \text{ mol I^-})}{(1 \text{ mol KI})} \times \frac{(0.0100 \text{ L})}{(0.0500 \text{ L})}}{(0.010 \text{ M KI})} = 0.0020
\]

Show another sample calculation below.
(3) Using equation (3) calculate the rate for each run, and record the results in Table 3. Show a sample calculation below.

Note that the data in Table 2 have been cleverly sorted so that runs 1-4 have the same [BrO₃⁻] and [H⁺] as run 1, but differing values for [I⁻]. The rate law for the clock reaction is

\[ \text{Rate} = k[I^-]^x[\text{BrO}_3^-]^y[H^+]^z \]  

(4)

where x, y and z are the orders in iodide, bromate, and hydrogen ion, respectively. Taking the logarithm of equation (4) gives the following result:

\[ \log(\text{rate}) = \log(k) + x(\log[I^-]) + y(\log[\text{BrO}_3^-]) + z(\log[H^+]) \]  

(5)

For runs 1-4 all terms on the right side of equation (5) are constant except the one involving [I⁻]. Thus equation (5) simplifies to

\[ \log(\text{rate}) = x(\log[I^-]) + \text{constant} \]

and a plot of log(rate) on the y-axis versus log[I⁻] on the x-axis should be linear with slope equal to x, the order in I⁻. Similar plots can be constructed to obtain y using runs 1 and 5-7, and z using runs 1 and 8-10. Before drawing your graphs, use the data in Table 2 to complete Table 3.

**Table 3. Data for Log – Log Plots**

<table>
<thead>
<tr>
<th>Run</th>
<th>Rate (M/s)</th>
<th>Log(rate)</th>
<th>Log[I⁻]</th>
<th>Log[BrO₃⁻]</th>
<th>Log [H⁺]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
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<td></td>
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</tbody>
</table>

Prepare your graphs using EXCEL or other graphing software. Determine the slope using the trend-line (EXCEL) or other linear regression option (other software). Include the graphs with your report. Note you must have three graphs for this experiment!!!
Determination of the reactant orders:
What is the order with respect to each reactant (from your slopes), rounded to the nearest integer?
x (I⁻ order) ________  y (BrO₃⁻ order) ________  z (H⁺ order) ________

Sample Calculation of the rate constant, k:

For each run, use the data in Tables 2 and 3 with the following equation:

\[ k = \frac{rate}{[I^-]^x[BrO_3^-]^y[H^+]^z} \]  \hspace{1cm} (6)

List the values you obtain below.

<table>
<thead>
<tr>
<th>Run</th>
<th>k</th>
<th>Run</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Average k for all runs

Units of k (from equation 6)

Show a sample calculation:
1. Suppose the temperature for your second try of run 1 was significantly higher than in the first try. Would your rate in the second try be faster or slower than in the first try? Explain.

2. Write the full equation for the rate law of the iodine clock reaction, including the orders and the rate constant you determined.

3. How well do you think the reaction follows your rate law? Discuss as fully as possible.

4. Suggest a way to improve the precision of this experiment.

5. Describe one more experiment that would enable you to determine the Arrhenius activation energy of the reaction. (See your text.)