INTRODUCTION

FACTORS INFLUENCING REACTION RATE:

The study of chemical reactions is not complete without a consideration of the rates at which these reactions proceed. We know that some reactions such as those between ions in solution frequently proceed very rapidly, while others proceed so slowly that the rate is not even detectable. The practical importance of these rate considerations is difficult to exaggerate. For example, a metal which is exposed to weather will undergo reactions with oxygen and water which result in corrosion.

Among the most important factors influencing the rate of a reaction are: temperature, concentration and catalysis. In addition, for solids the condition of the surface is of great importance.

There are two main theories involved in explaining reaction rates. These are the Activated Complex (Transition State) Theory and the Collision Theory. However, in the lecture part of the course, you will also look at the Activated Complex (Transition State) Theory.

COLLISION THEORY

Consider the simple reaction: \[ A + B \rightarrow \text{Products} \]

A and B are atoms, ions, or molecules, in order for A and B to react with each other, they must “collide” together. Since molecules are in rapid and continual motion, molecules of A and Be will collide with one another at frequent intervals. However, not every collision of A and B will result in the formation of products. Before a reaction can occur, the reactants collide with a certain amount of energy, this energy is called “activation energy” or “energy of activation”. This energy comes from the kinetic energy that A and B possess, so that only those collision which occur with sufficient force will be effective in causing reaction. If the concentration of either A or B is doubled, the number of collisions between A and B per time is doubled. If the temperature is raised, the kinetic energies of both A and B are increased so that there are more collisions per second, and a greater fraction of these will lead to chemical reaction. The rate, therefore, generally increases with increasing temperature.

The activation energy can be determined by using the Arrhenius Equation: \[ k = Ae^{-Ea/RT} \]

The Arrhenius equation can be re-written as: \[ \ln k = -\frac{Ea}{RT} + \ln A \]

Where:

- \( k \) = rate constant
- \( A \) = frequency factor
- \( Ea \) = activation energy
- \( R \) = gas constant as: 8.3145 J/mol K
- \( T \) = absolute temperature, K

When \( \ln k \) is plotted against \( 1/T \) the slope = \(-Ea/R\) and the slope intercept is \( \ln A \)

CATALYSIS

A catalyst can be thought of as an agent, which alters the speed of a chemical reaction. This results from a decrease in the amount of activation energy necessary for the reaction. When less activation energy is needed, a larger fraction of the collisions will possess the required energy, and the rate will increase. The manner in which the catalyst lowers the activation energy depends upon the type of catalyst. A catalyst which decreases the speed of a reaction is called an inhibitor.
CLOCK REACTION
In this experiment, the effect of temperature and concentration on the rate of a chemical reaction will be studied. The reaction chosen, frequently termed the "clock reaction", is actually a series of consecutive reactions represented by the following equations:

\[
\begin{align*}
\text{BrO}_3^{-} + 6 \text{I}^{-} + 6\text{H}^{+} & \rightarrow \text{Br}^{-} + 3\text{I}_2 + 3\text{H}_2\text{O} \\
\text{I}_2 + 2 \text{S}_2\text{O}_3^{2-} & \rightarrow 2 \text{I}^{-} + \text{S}_4\text{O}_6^{2-} \\
\text{I}_2 + \text{Starch} & \rightarrow \text{Blue color}
\end{align*}
\]

The iodine that is produced in reaction (1) is immediately used up in reaction (2), so that no appreciable concentration of iodine can build up until all of the Na$_2$S$_2$O$_3$ has been used up. When this occurs, the iodine concentration becomes great enough to change the color of a starch indicator to blue. The appearance of the blue color is thus an indication that all of the Na$_2$S$_2$O$_3$ has been used up.

RATE LAW
In this experiment, the rate law of the above reaction with be determined.

The rate law is:

\[\text{Rate} = k [A]^{x} [B]^{y} [C]^{z}\]

The numerical values of \(x\), \(y\), and \(z\) will be determined experimentally. \(x\), \(y\), and \(z\) are also the order of the reaction with respect to \(A\), \(B\), and \(C\). The sum of the individual orders of the reactant gives the overall order of the reaction. Once, \(x\),\(y\), and \(z\) are calculated, the rate constant, \(k\) can be calculated.

Experiment

EQUIPMENT
You will be working on this experiment in pairs. Each pair will fill out a slip (names of both students on slip) to check out the following four items form the stockroom:

- 1 2 mL volumetric pipet
- 3 5 mL volumetric pipets
- 1 pipet helper
- 1 timer

- During the Summer, students should keep all items, storing them in their drawers, until they have finished the experiment.
- During the Fall and Spring semesters, students must return all items to the stockroom at the end of the lab period, unless advised otherwise.
A. The Effect of Concentration on Reaction Rate

Lab Notebook: Set up a table in your lab notebook for the data for this portion of the experiment. (Make this table at least 1/2 page!)

**CAUTION**

**POTASSIUM IODIDE:** CAUSES IRRITATION. HARMFUL IF SWALLOWED******.  
**SODIUM THIOSULFITE:** HARMFUL IF SWALLOWED. MAY CAUSE ALLERGIC REACTION AND BREATHING DIFFICULTIES. MAY CAUSE IRRITATION TO SKIN, EYES, AND RESPIRATORY TRACT.********

**POTASSIUM BROMATE:** HARMFUL IF SWALLOWED. MAY CAUSE ALLERGIC REACTION AND BREATHING DIFFICULTIES. MAY CAUSE IRRITATION TO SKIN, EYES, AND RESPIRATORY TRACT.********

Table A: Concentration vs. Rate Data

<table>
<thead>
<tr>
<th>Run #</th>
<th>Test Tube #1</th>
<th>Test Tube #2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volume (mL)</td>
<td>Volume (mL)</td>
</tr>
<tr>
<td></td>
<td>0.010 M KI</td>
<td>0.0010 M Na₂S₂O₃</td>
</tr>
<tr>
<td>1</td>
<td>10.00</td>
<td>10.00</td>
</tr>
<tr>
<td>2</td>
<td>20.00</td>
<td>10.00</td>
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<tr>
<td>3</td>
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<tr>
<td>5</td>
<td>8.00</td>
<td>10.00</td>
</tr>
</tbody>
</table>

DO NOT RECORD YOUR DATA ON THIS PAGE. COPY TABLE INTO NOTEBOOK!

Note: In this part of the experiment, under some conditions, it may take as long as three minutes for the color change to occur. Part B reactions will be at ~ RT (Room Temperature)

1. Pipet 10 mL of 0.010 M KI, 10 mL of 0.0010 M Na₂S₂O₃ solution, and 10 mL of H₂O into each of two 8" test tubes. Label each Test Tube #1

2. Pipet 10 mL of 0.040 M KBrO₃ and 10 mL of 0.10 M HCl into each of two 8" test tubes. Add 5 drops of fresh starch solution to each test tube. Label each Test Tube #2.

3. Add Test Tube #1 it into a clean, dry 125 mL Erlenmeyer flask. Immediately add Test Tube #2 and swirl to mix immediately. Begin timing when you add Test Tube #2 to the Erlenmeyer flask. Stop timing, when the blue color appears and record the time of the reaction. (The color change should be very abrupt. If the change does not occur all at once throughout the solution, you did not mix the two reagents well enough.)

4. Repeat Step 5 with another set of samples, and time the reaction as before. If the time for this second run is significantly different than the time of the first run, repeat the procedure for a third run. Continue until two consistent values for time are obtained.
Answer the following questions in your notebook in the form of conclusions:

1. Using your data, calculate the rate orders with respect to KI, KBrO₃, and H⁺ as well as the overall rate order of the reaction. Note: use the average times.

2. Calculate the rate constant for the reaction at RT.

B. THE EFFECT OF TEMPERATURE ON REACTION RATE

Lab Notebook: Set up a table in your lab notebook for the data for this part of the experiment.

<table>
<thead>
<tr>
<th>Approximate Temperature</th>
<th>Run #</th>
<th>Measured Temperature (°C)</th>
<th>Average Temperature (°C)</th>
<th>Run Time (seconds)</th>
<th>Average Run Time (seconds)</th>
<th>Average Rate 1/Time (1/seconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>~40°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>~ RT* = ____</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</table>

*Room Temperature

**DO NOT RECORD YOUR DATA ON THIS PAGE. COPY TABLE INTO NOTEBOOK!**

**Note:** You need only do two good runs at each temperature, ~10°C, ~RT°C, and ~40°C. Do more than two runs at the same temperature only if the times for the two runs differ greatly. That is -- repeat the measurements at a particular temperature until two consistent values for time are obtained.

1. Set up a water bath in your 250 mL beaker. Heat the water bath to approximately 40°C.

2. Pipet 10 mL of 0.010 M KI, 10 mL of 0.0010 M NaS₂O₃ solution into each of two 8” test tubes. Add 5 drops of fresh starch solution to each test tube. Label each Test Tube #1.

3. Pipet 10 mL of 0.040 M KBrO₃ and 10 mL of 0.10 M HCl into each of two 8” test tubes. Label each Test Tube #2.

4. Place the test tubes in the water bath that has been heated to the desired temperature. Read and record the temperature of the water bath. Leave the samples in the water bath for at least 4 minutes.

5. Add Test Tube #1 into a clean, dry 125 mL Erlenmeyer flask. Immediately add Test Tube #2 and swirl to mix immediately. Begin timing when you add Test Tube #2 to the Erlenmeyer flask. Stop timing, when the blue color appears and record the time of the reaction. (The color change should be very abrupt. If the change does not occur all at once throughout the solution, you did not mix the two reagents well enough.)

6. Repeat Step 5 with another set of samples, and time the reaction as before. If the time for this second run is significantly different than the time of the first run, repeat the procedure for a third run. Continue until two consistent values for time are obtained.

7. Reduce the temperature of the water bath to approximately RT = _____ and repeat steps 2 through 6 at that temperature.

8. Reduce the temperature of the water bath, using ice, to approximately 10°C and repeat steps 2 through 6 at that temperature.
Answer the following question:

1. Make a plot of Time vs. Temperature (use the average time at each temperature); draw a smooth line through the points. Does the reaction rate increase or decrease with decrease in temperature? Explain, giving two reasons in terms of Collision Theory

Calculations/Graph:

1. Using your data and the reaction orders determined in part A, calculate the rate constant, $k$ at for the three temperatures.
2. Graph $\ln k$ vs $1/T$ and then using your graph determine the activation energy. (Hint: The slope = $-E_a/R$)

**Tape both graphs to blank pages following Table B.**
THE EFFECT OF TEMPERATURE AND CONCENTRATION ON REACTION RATE

PURPOSE:

EQUATIONS:

MATERIALS TABLE:

SAFETY:

PART A - The Effect of Concentration on Reaction Rate:

Procedure:

Data:

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Calculations:

1. a. Summary Table for the Molarity of I⁻, BrO₃⁻, and H⁺ after mixing:

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>I⁻</th>
<th>BrO₃⁻</th>
<th>H⁺</th>
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<tbody>
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b. Setups for the calculation of the Molarity of I⁻, BrO₃⁻, and H⁺ after mixing.

(Show a sample calculation for each of the required calculations)

Questions:

1. Using your data, calculate the rate orders with respect to KI, KBrO₃, and H⁺ as well as the overall rate order of the reaction. Note: Use the average times.

2. Calculate the rate constant for the reaction at RT.
PART B- The Effect of Temperature on Reaction Rate:

Procedure:

Data:
TABLE B: Temperature vs. Rate Data

<table>
<thead>
<tr>
<th>Approximate Temperature</th>
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Graphs:

Question:
1. Make a plot of Time vs. Temperature (use the average time at each temperature); draw a smooth line through the points. Does the reaction rate increase or decrease with decrease in temperature? Explain, giving two reasons in terms of Collision Theory

Calculations/Graph:
1. Using your data and the reaction orders determined in part A, calculate the rate constant, k at for the three temperatures.
2. Graph ln k vs 1/T and then using your graph determine the activation energy (Hint: The slope = -Ea/R)

SUMMARY: