INTENT

To introduce you to the fundamental methods by which one studies the kinetics of a reaction. To show that by varying the concentrations of the species involved in a reaction one at a time, one can begin to speculate on the steps by which the reaction occurs.

DISCUSSION

Kinetics is the branch of chemistry concerned with determining how fast chemical reactions occur under different conditions and, if possible from that information inferring the detailed steps by which the reactants are converted to products, i.e., the reaction mechanism. A reaction may involve one step or many steps. Each of the steps must involve the reaction particles (atoms, molecules, or ions) colliding, leading to the formation of a new substance(s). Therefore how often they collide will be important. The greater the concentrations of reactants, the greater the probability that they will collide, and therefore, the greater the probability that they will react, i.e., the faster the reaction.

The rate at which a chemical reaction occurs can be expressed in different ways, one related to this idea of the probability of collisions based on concentrations, and the other more empirical, based on the simple rate of disappearance of the reactants or the rate of production of the products. Therefore, for a typical reaction of ...

\[ A + B \longrightarrow C + D \]

the rate law of a chemical reaction can be expressed as ...

\[ \text{Rate} = k [A]^m [B]^n \]

where \( k \) is a proportionality constant, called the \textit{rate constant}; the exponent \( m \) is "the order of the reaction with respect to \( A \)"; and \( n \) is "the order of the reaction with respect to \( B \)." The sum of \( m \) and \( n \), each of which are usually whole numbers, is "the overall order of the reaction."

Alternatively, it can be expressed as the change in the molar concentration of a reactant or product per unit time. Since \( A \) is a reactant, then the rate an be expressed as ...

\[ \text{Rate} = -\frac{\Delta [A]}{\Delta T} \]

where the "-" means that the molar concentration of \( A \), \([A] \), is decreasing with time. We will use whichever expression for the reaction rate is more appropriate for our purpose at the time.
The concentration of the reactants is not the only factor which goes into determining the rate of a chemical reaction. A list of the factors includes:

1. the concentrations of the reactants,
2. the nature of the reactants,
3. the temperature of the reactants, and
4. the presence/absence of a catalyst. (where the amount of catalyst is often rate determining)

As stated above, Factor 1 is related to the number of collisions. The second factor includes the fact that the reactants may likely need to come together in a specific orientation. That is, when reacting molecules collide there may only be one relative orientation of the molecules that leads to a reaction. Consider the reaction of IBr to Br₂ and I₂:

\[ 2\text{IBr} \rightarrow \text{Br}_2 + \text{I}_2 \]

\[ \begin{array}{c}
\text{Br} \\
\text{I}
\end{array} + \begin{array}{c}
\text{Br} \\
\text{I}
\end{array} \rightarrow \begin{array}{c}
\text{Br} \\
\text{Br}
\end{array} \begin{array}{c}
\text{I}
\end{array} \rightarrow \begin{array}{c}
\text{Br} \\
\text{Br}
\end{array} \begin{array}{c}
\text{I}
\end{array} + \begin{array}{c}
\text{Br} \\
\text{I}
\end{array}
\]

If the molecules did not collide in the proper orientation shown, they would not be able to react.

\[ \begin{array}{c}
\text{Br} \\
\text{I}
\end{array} + \begin{array}{c}
\text{Br} \\
\text{I}
\end{array} \rightarrow \begin{array}{c}
\text{Br}
\end{array} \begin{array}{c}
\text{I}
\end{array} + \begin{array}{c}
\text{Br}
\end{array} \begin{array}{c}
\text{I}
\end{array}
\]

Factor 3 takes into account the energy that may be required to initiate a reaction (an activation energy) even if the overall reaction is exothermic. Since this energy comes from the kinetic energy of the reacting particles, the greater the average kinetic energy (i.e., the higher the temperature), the more high energy particles there are, and the more likely the reaction is to proceed.

The fourth Factor, a catalyst, changes the mechanism (or the steps) of the reaction to one with a lower activation energy, and therefore without increasing the temperature, a greater fraction of the molecules will be able to react, because a greater fraction of the collision will have enough energy to exceed the activation energy.
In the rate law the effect of Factors 2-4 are incorporated into $k$, the rate constant. For a given reaction the rate constant can vary, but only if the temperature is varied.

In order to investigate the details of a reaction, kinetic studies which measure the rate of a reaction under different conditions are undertaken. Concentrations of the reactants, temperature of the reaction, and the addition of a catalyst can be used to gain insight into the individual steps of the reaction mechanism.
**Single-Step Reactions**

If the entire reaction consists of one molecule of A colliding with one molecule of B, over and over again to form the product(s), then the one and only step of the reaction is ...

\[ 1 \text{A} + 1 \text{B} ----> \text{products} \]

One factor that determines how fast this reaction occurs would be the frequency of collision between a molecule of A and a molecule of B, i.e., the greater the likelihood of these collisions, the faster the reaction, all other things being equal. Since the probability of collision between A and B goes up (is directly proportional to) the concentration of each of the species, the rate of the reaction will depend on the \([\text{A}]\) and \([\text{B}]\) as in...

\[
\text{Rate} = k \ [\text{A}]^1[\text{B}]^1
\]

where the *exponents* in the rate law are the same as the *coefficients in the single step* of the reaction (which is also the overall reaction).

If the rate of the reaction is known for specific concentrations of A and B and at a specific temperature, then keeping everything the same except doubling the \([\text{A}]\), results in doubling the number of collision between molecules of A and molecules of B; and therefore, the rate of the reaction would double. The same could be said for doubling \([\text{B}]\).

**Multiple-Step Reactions**

Although the rate depends on the concentration of one or more reactants, it is not possible, in general, to tell from the overall stoichiometry of the reaction how a change in a given concentration will affect the rate. We saw that the rate can be determined from the stoichiometry, but only IF the reaction occurred in a single step. When a reaction occurs in more than one step there is often a slow step, the rate determining step, that will control the rate of the overall reaction. If the first step is the slow step then it will be straightforward to determine the rate law and the order of the reaction from the stoichiometry of that slow step. If however, the slow step is other than the first step, fitting the rate law to the steps is more complicated.

For example, suppose that the second step of a multiple-step reaction is the slow step. Then the product, \(P_1\), of the first step (a fast reaction) will accumulate because it is being produced quickly, but only used slowly. As a result, some of \(P_1\), while its waiting to be used in the second step, can react to go back to the reactants of the first step.

\[
\text{A} + \text{B} \underset{\text{rapid}}{\overset{\text{slow}}{\longrightarrow}} \text{P}_1 \rightarrow \text{P}_2 \rightarrow \text{P}_{\text{final}}
\]

Hence, because the second step is slow there will be time for the first reaction to reverse and for that first step to reach a state of equilibrium. That is, the product of the first reaction will more quickly revert back to starting materials than it will react further to form the products of the second step. We will see such an example in this experiment.
In this experiment you will look at the rates of reaction of bleach with food coloring (dye) as a function of: (1) different food colorings, (2) changes in the concentrations of either the bleach or the dye, (3) changes in the temperature, and (4) changes in the bleaching reactant. You will study the bleaching of one food coloring in some detail, by varying one factor at a time—either one of the reactant concentrations or the temperature. Varying the concentration of a single reactant will allow you to determine the exponent on the concentration of that reactant in the rate law; and varying the temperature will allow you to determine the activation energy.

In this experiment we will study:

\[ \text{dye} + \text{bleach} \to \text{products} \]

So, with respect to each reactant, the rate can be expressed as either the change in \([\text{dye}]\) with time or the change in \([\text{bleach}]\) with time, i.e., \(\Delta[\text{dye}] / \Delta\text{time}\) or \(\Delta[\text{bleach}] / \Delta\text{time}\), respectively. We will always follow the progress of the reaction by observing the loss of color as the dye is bleached (oxidized) to form a light yellow product. Therefore, we will use....

\[
\text{Rate} = -\frac{\Delta[\text{dye}]}{\Delta(\text{time})}
\]

Since the overall reaction that we will examine is essentially irreversible, the initial reactants will not reform over the course of the reaction. We will measure the time for the "complete" reaction, as determined by eye from the loss of the dye color and convert it into an average rate over the course of the entire reaction. Since the overall reaction is not an equilibrium (i.e., it goes to completion), the average rate will be proportional to the initial rate.

Even in those experiments where you are varying the concentration of the bleach, you will still be following the reaction by monitoring the change in the concentration of the dye, not the bleach. That is, we can use this expression whether we are varying the concentration of either the dye or the bleach or varying anything else for that matter.

In this experiment the general form of the rate law becomes...

\[
\text{Rate} = k [\text{bleach}]^m [\text{dye}]^n
\]

where \(m\) and/or \(n\) will turn out to be either 0, 1, or 2.

When you add drops of dye, the volume of each drop will not be identical. However, the variation in the drop volume from the same dropper will not affect the accuracy of your calculations. Since you are commonly working with two (2) significant figures and each drop will vary by less than 5%, the volume of "1 drop" can be considered accurate to 2 sig figs and treated as 1.0 drop, 2 drops can be treated as 2.0 drops, etc., in all of your calculations.
Techniques of Studying Kinetics

Determining the Order with Respect to a Reactant. Starting with Rate = k[A]^m [B]^n and one at a time, varying the concentration of one reactant, while keeping the concentration of the other reactant constant, will allow you to determine, one at a time, m and n, the order of the reaction with respect to [A] or [B]. For example, by running two experiments with different initial concentrations of A (while keeping the temperature and the concentration of B constant) you obtain two different rates, R_1 and R_2.

\[ \text{Rate}_1 = k[A_1]^m [B]^n \quad \text{Rate}_2 = k[A_2]^m [B]^n \]

You can determine m by first taking the ratio of the two rates, which gives...

\[ \frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k[A_1]^m [B]^n}{k[A_2]^m [B]^n} \]

Since neither the temperature nor [B] changed from one experiment to the other, both k and [B]^n will be the same in the numerator and the denominator:

\[ \frac{R_1}{R_2} = \left( \frac{[A_1]^m}{[A_2]^m} \right) = \left( \frac{[A_1]}{[A_2]} \right)^m \]

Taking the logarithm of both sides will allow you to determine m:

\[ \log(R_1/R_2) = \log \left( \left( \frac{[A_1]}{[A_2]} \right)^m \right) = m \cdot \log \left( \frac{[A_1]}{[A_2]} \right) \]

Solving for m gives ...

\[ m = \frac{\log (R_1/R_2)}{\log \left( \frac{[A_1]}{[A_2]} \right)} \]
As shown here, we will sometimes use "R" (usually subscripted) for a rate. Do not confuse this with the gas constant, R, which is found in the Arrhenius equation. It should be clear form the context which R is meant.

**Determining the Value of n, the Order of the Reaction in Dye.**

We could vary the dye concentration to determine the value of n, just as we will for the value of m, by maintaining a constant bleach concentration and varying the dye concentration. Instead we will use graphical analysis of the drop in dye concentration with time during the bleaching reaction to determine n.

Analyzing the diminishing of the dye concentration during the reaction, while keeping the bleach concentration constant, will generate different types of linear graphs depending on the value of n. Specifically, if

1. If the drop in dye concentration is linear with time, then the value of n is 0.
2. If the drop in natural log (ln) of dye concentration is linear with time, then the value of n is 1.
3. If the drop in the recipricol of the dye concentration is linear with time, then the value of n is 2.

See these graphs:
**Determining the Activation Energy.** The Arrhenius equation relates the rate constant with temperature and the activation energy. One form of the Arrhenius equation is...

\[ k = A \cdot e^{-\frac{E_a}{RT}} \]

where \( k \) is the rate constant; \( A \), the frequency factor; \( E_a \) is the activation energy; \( R \) is the gas constant; and \( T \) is the kelvin temperature. The frequency factor, \( A \), is a combination of a steric factor and a collision frequency so its value is approximately constant for a given reaction over small ranges in temperature. Since molecules move faster as the temperature increases, the collision frequency will also very slightly increase, but since it is already very high, the increase is insignificant.

The activation energy can be obtained by a method similar to the one used before to find the order of the reaction. Run two reactions – this time varying only temperature, take a ratio of the rates (or a ratio of k’s), take the log, and rearrange to obtain the desired quantity. Taking the rate ratio assuming that the two A’s are equal gives...

\[ \frac{k_1}{k_2} = \frac{e^{-\frac{E_a}{RT_1}}}{e^{-\frac{E_a}{RT_2}}} = e^{-\frac{E_a}{RT_1}} \cdot e^{+\frac{E_a}{RT_2}} = e^{\left(-\frac{E_a}{RT_1} + \frac{E_a}{RT_2}\right)} \]

Taking the natural logarithm (ln) of each side gives...

\[
\ln \left(\frac{k_1}{k_2}\right) = -\left(\frac{E_a}{RT_1}\right) + \left(\frac{E_a}{RT_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)
\]

Since the Rate = \( k[A]^m[B]^n \), and changing only the temperature changes only \( k \). Therefore, \( R_1/R_2 \) (the two rates) can be substituted for \( k_1/k_2 \).

\[
\ln \left(\frac{R_1}{R_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)
\]
Then separating the ln term and converting ln to log gives...

\[
\log\left(\frac{R_1}{R_2}\right) = \frac{E_a}{R \cdot 2.303} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

or

\[
\left( \log R_1 - \log R_2 \right) = \frac{E_a}{R \cdot 2.303} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

**HALF-LIFE OF A REACTION**

**Use of Spectrophotometer.** Since one of the reactants is a dye we will be able to follow its reaction (disappearance) by spectrophotometer. You will measure the absorbency of 625 nm light (the wavelength for maximum absorption by the blue dye in the visible region) after it passes through a solution of the dye and bleach. Since 625 nm is in the orange portion of the spectrum, for the dye color you see it as white light minus orange; and the color appears blue.

The measured absorbency will be directly proportional to the dye concentration. The proportionality constant between the two quantities incorporates two factors: how much solution the light passes through and how strongly the complex absorbs light at the single wavelength used. Both factors are constant in this spectrophotometer experiment. The amount of bleach available in this reaction compared to the small amount of dye reacted, also guarantees that the amount of bleach during the reaction is essentially constant, and only the dye changes significantly in concentration. In these measurements the bleach will be pseudo zero order. By measuring absorbency you are obtaining relative concentrations of the dye, where a decreasing absorbency corresponds to a decreasing concentration of the dye.

You will use these values (each of which is proportional to an instantaneous concentration) that you have collected here to graphically determine the dye concentration dependency (n) and the rate constant of the reaction and its half-life* (a constant for the reaction and also independent of the actual concentration of dye if the reaction is first order or pseudo-first order) in questions 1 and 2 at the end of the lab.

* Half-life = the time required for ½ of any sample to be consumed during a reaction, i.e., the time required for any sample to reduced to ½ of its original amount or concentration.
**First Order Reactions.** First order reactions are unique in that the half-life of the reaction remains constant over the course of the reaction. We can determine a relationship between the half-life and the rate constant by equating the two different expressions for the rate which were given on the first page of this experiment. If a reaction is first order in only reactant, then ...

\[ \frac{\Delta [A]}{\Delta T} = k[A] \]  which rearranges to \[ \frac{\Delta [A]}{A} = -k \Delta t \]

If you consider the "\( \Delta \)'s" to be infinitesimally small changes, then you can use calculus to "integrate" this expression to give...

\[ \ln [A] = -kt + \ln[A]_o \]

where \([A]_o\) is the concentration at time = 0. Plotting \(\ln [A]\) vs time gives a line with an intercept of \(\ln [A]_o\) and a slope of \(-k\).” This equation can be rearranged to give ...

\[ \ln [A] - \ln [A]_o = -kt \]
\[ \ln \{ [A] / [A]_o \} = -kt \]

So that at the half life, when \([A]/[A]_o = \frac{1}{2} \); \(\ln (\frac{1}{2}) = -\ln 2 = -kt\), or \(t_{1/2} = (\ln 2)/k\)

\[ t_{1/2} = \frac{0.693}{k} \]

for a first order reaction.

**PROCEDURE**

You will prepare various mixtures of the dye and bleach. By varying the concentrations of first the bleach and then the dye you will be able to determine the order of the reaction with respect to each of these reactants. You will also follow the course of one bleaching process spectrophotometrically. Then you will run a series of identical reactions, but at different temperatures to see that affect of the activation energy. You will also see how the addition of a catalyst, hydronium ion, speeds up the reaction. In all of your experiments Erlenmeyer flasks, with their slanted sides, will be used to prevent any loss of your reaction mixture when you swirl your solutions to insure good mixing.
CHM 1041
EXPERIMENT 4

PRELIMINARY QUESTIONS  (To be answered BEFORE coming to lab.)

Examine a jug of chlorine bleach.  What is the active ingredient?

____________________________________________________________

Based on your answer, what ions are present in large amounts in this aqueous solution?

____________________________________________________________

Are either of these two ions an aqueous acid?... a base??  ________________

Explain:____________________________________________________________

EXPERIMENTAL

Nature of the Dye

Since different chemicals react with oxidizing agents to varying degrees and at different rates, we will illustrate this be bleaching two different dyes.

To each of two 50 mL Erlenmeyer flask add 15.0 mL of 0.10M NaOH (aq) and 5.0 mL of concentrated (stock) bleach solution.  We use 0.10M NaOH (aq) to maintain a near constant pH of the system.  The pH which would change from run to run if deionized water alone was used to prepare different bleaching solutions.  Swirl the flasks to mix the liquids.  Once the solutions have been mixed, it is unnecessary to keep swirling when the reaction is at room temperature.  Determine the temperature of one of these solutions.  (Assume the other one has the same temperature.)

\[ T = \text{__________________________} ^\circ \text{C} \]

To one of these flasks add one drop of the red dye solution while swirling it.  (Swirling insures complete mixing.)  Determine the time in seconds from the moment the drop hits the solution until the red color disappears (the pale yellow color of the bleach will still remain).  Record the time.

\[ \text{Time for red food coloring to react} = \text{__________________________} \text{ s} \]

Take the other bleach solution and perform the same operation, only this time use one drop of the blue dye solution.  Record the time and retain this solution.

\[ \text{Time for blue food coloring to react} = \text{__________________________} \text{ s} \]

This solution now contains the "completely bleached" blue dye.  The remainder of this experiment will involve experiments that will allow you to determine the rate law for the

Bieber/PC/Chm2/chm2labs.rx_rate.wpd  9/02
reaction of this blue dye with the bleach. The solution was kept to provide a color comparison to help you minimize inconsistencies in determining the end of each of the remaining reactions with the blue dye.
**Varying the Bleach Concentration-Determining m**

Varying the concentration of the bleach while holding all other conditions constant will allow you to determine the value of m in the rate law:

\[ \text{Rate} = k [\text{bleach}]^m [\text{dye}]^n \]

Prepare five (5) 0.10M NaOH (aq) diluted bleach solutions (exactly 20.0 mL each) in 50 mL Erlenmeyer flasks using the same concentrated bleach solution and 0.10M NaOH (aq) in the amounts listed in the table below and label each solution. Determine the temperature of the solution in Flask 5. (Assume all solutions are at the same temperature.) Read the next set of directions to get ready to use the Spectronic 20 spectrophotometer to measure the times needed to bleach your blue dye in 0.10M NaOH (aq) solutions.

\[ T = \text{________________________} \pm 0.1^\circ \text{C} \]

You will start measuring the bleach time as soon as you add your drop of blue dye to your bleach in 0.10M NaOH (aq) solutions, and time until the color is bleached out equal to your standard.

To one solution at a time, add one drop of blue dye while swirling the flask and immediately begin measuring the time, to the nearest second, required to bleach the blue dye. Record the reaction time in the table below.
Run | Volume of Bleach Sol’n | Volume of 0.10M NaOH (aq) | Relative Bleach Conc. | Reaction Time (Δt) | Relative Rate \(-\Delta[dye]/\Delta t\)^** or (1/time) **x 10^{-2}**
---|---|---|---|---|---
1 | 2.0 mL | 18.0 mL | 1.0 | | **
2 | 4.0 mL | 16.0 mL | 2.0 | | **
3 | 5.0 mL | 15.0 mL | 2.5 | | **
4 | 8.0 mL | 12.0 mL | 4.0 | | **
5 | 10.0 mL | 10.0 mL | 5.0 | | **

** To calculate a rate for each run you must know how the [dye] changes. Since change is always FINAL state minus INITIAL state, the negative of the change, \(-\Delta[dye]\), is \([dye]_{initial} - [dye]_{final}\). Therefore, with the final concentration of dye being essentially zero, \(-\Delta[dye]\), is \([dye]_{initial}\). The initial concentration of dye is the same for Runs 1-5. However, its actual values is unknown. Without this knowledge we will not be able to get absolute rates from this experiment, only “relative rates.”

Since we will take ratios, relative rates will be sufficient. (That is, a ratio of relative rates is the same as a ratio of exact rates.) We can assume any value for the initial concentration of the dye that is convenient. We will assume a value equal to the number of drops of dye. Calculate and record that “relative rates,” not as a fraction, but as some number “x 10^{-2}”

Because of inconsistencies in determining the end of each reaction it will be necessary to determine an average value of m using all of these relative rates, rather than just comparing two relative rates. However, you can get an approximate value of m by comparing just two relative rates.

The only difference between Run 1 and Run 2 was that the concentration of the bleach was double in Run 2. As a result of this doubled concentration, the rate of Run 2 is approximately (the same as, double, or quadruple) the rate of Run 1 and a tentative value of m = (0, 1, or 2) can be assigned. In the same way you could also compare Run 2 with Run 4 or Run 3 with Run 5.
As a way to average out any errors in determining the end of each reaction, we will make many, different comparisons between the rates of the reactions. Averaging will help eliminate errors in individual measurements. This is what you are doing when you calculate the ratios of relative rates and ratios of relative bleach concentrations for the Runs indicated in the table below. When you then calculate values of \( m \) and average your answers, small errors should average out.

<table>
<thead>
<tr>
<th>Run Ratio</th>
<th>Relative Rate Ratio (R*)</th>
<th>Relative Bleach Concentration Ratio (C*)</th>
<th>( \log R^* ) = m</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/3</td>
<td></td>
<td>1.0/2.5 = 0.40</td>
<td></td>
</tr>
<tr>
<td>2/4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3/5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4/1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5/2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Calculate an average value of m _______   Assuming that m is a whole number, the value (either 0, 1, or 2) of m = ____________________
Based on your experimental results, complete the rate law, thus far, for this reaction using $\text{OCl}^{-}$ for bleach:

$$\text{Rate} = k \quad \Box$$

**Determining the Order of the Dye Concentration in the Rate Law—Determining $n$**

Varying the concentration of the bleach, while holding all other conditions constant, should have led you to this conclusion for your rate law with respect to bleach:

$$\text{Rate} = k [\text{bleach}]^1$$

Now we will determine the value of $n$ in the rate law by graphical analysis.

$$\text{Rate} = k [\text{bleach}]^1 [\text{dye}]^n$$

Mix 2.0 mL of bleach solution and 18.0 mL of 0.10M NaOH (aq) in a 50 mL Erlenmeyer flask (as done in Run 1).

**Using Spectrophotometer to Follow the Extent of the Reaction**

By determining the concentration of the dye as a function of time we will be able to determine the half-life of the reaction with respect to the dye and the rate constant for the reaction. It will also give us an alternative method of determining the order of the reaction with respect to the dye.

Obtain one of the spectrophotometer tubes (cuvettes) from the stockroom to use in the spectrophotometer. Handle it carefully; cuvettes are expensive and easily damaged. Use them only in the spectrophotometer and return them to the stockroom at the end of the period. Clean and dry the cuvette with a soft tissue.

Now zero the spectrophotometer according to the following directions. (The spectrophotometer should have been warming up for at least 30 minutes before use.) The following four-step instructions apply specifically to the Spectronic 20. (Some of these steps may have already been done for you; consult your instructor.)

1. Check the wavelength selector for the correct setting (625 nm).
2. With the cell compartment empty, use the knob on the left front to adjust the meter to read 0% transmission (∞ absorbency).
3. Put a cuvette filled with 0.10M NaOH(aq) into the cell compartment, aligning the mark or label on the tube with the mark at the front of the cell compartment. This is a reference solution or “blank.” Use the knob on the right front to adjust the meter to read 100% transmission (zero absorbency).
4. Remove the reference tube. If the meter does not read 0% transmission go back to Step 2 and continue to repeat the steps until the meter does read 0% after removing the blank.
Prepare to use a clean, dry cuvette (or rinse a wet cuvette, previously used, with a small amount of 0.10M NaOH (aq), and drain the cuvette into a waste container. Add two (2) drops of blue dye, swirl the flask, and quickly transfer enough of this solution to nearly fill your waiting cuvette. Quickly dry the outside of the cuvette again, if necessary, handling it only by the rim to avoid getting fingerprints on the surface of the tube. Now insert the cuvette into the spectrophotometer’s sample holder. Start recording the absorbency when it has a value of 1.00. Record your readings of the absorbency (to as many sig figs as possible) every ten (10) seconds for a total of 150 seconds. This will give you a convenient starting value later for log of the absorbency, namely 0.000. The actual value of absorbency when you mix the solutions is not important-only how the value changes with time.
Later calculate the log₁₀ of the absorbency and 1/absorbency and record them in the table. Your graphs of these three functions should allow you to choose the exponent of the dye term, \( n \). You will use these values (each of which is proportional to an instantaneous concentration) that you have collected here to graphically determine the rate constant of the reaction and its half-life in Questions 1 and 2 at the end of the lab.

**Varying the Temperature–Determining \( E_a \)**

To test the effect of temperature upon the rate of reaction, prepare four identical solutions in 50 mL Erlenmeyer flasks, each with 10.0 mL of concentrated bleach solution and 10.0 mL of 0.10M NaOH (aq). Mix the solutions by swirling. Number them 10-13. Set up your own ice-water bath to pre-chill the diluted bleach solutions to approximately the temperatures indicated in the table below. As they become available, place each solutions, one at a time, in the appropriate water bath (adding ice to the baths, as necessary, to maintain the temperature of the bath–check with a thermometer in the bath). Place a thermometer in your reaction flask and swirl the flask to achieve good mixing. Do NOT stir the solution with the thermometer. When the temperature of each reaction mixture becomes constant at the desired value (when it’s thermostated), record the actual temperature in the flask. You will maintain this temperature during the reaction by holding your flask in the bath as the reaction occurs in each solution. Begin swirling your flask in the water bath and add one drop of blue food coloring to the solution. Continue to swirl the flask; and record the time that it takes to completely bleach the blue dye. Repeat the process with the remaining
flasks.

<table>
<thead>
<tr>
<th>Run</th>
<th>Approx. Temp</th>
<th>Actual Temp.</th>
<th>Rxn Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>RT</td>
<td>____________ °C</td>
<td>__________ s</td>
</tr>
<tr>
<td>10</td>
<td>20°C</td>
<td>____________ °C</td>
<td>__________ s</td>
</tr>
<tr>
<td>11</td>
<td>15°C</td>
<td>____________ °C</td>
<td>__________ s</td>
</tr>
<tr>
<td>12</td>
<td>10°C</td>
<td>____________ °C</td>
<td>__________ s</td>
</tr>
<tr>
<td>13</td>
<td>5°C</td>
<td>____________ °C</td>
<td>__________ s</td>
</tr>
</tbody>
</table>

Again, $-\Delta [\text{dye}] = + [\text{dye}]_{\text{initial}}$ and the same for all runs in this section. Take the value to be 1.0, the number of drops, in Runs 10-13, as you did in Run 5.

<table>
<thead>
<tr>
<th>Run</th>
<th>Actual Reaction Temp.</th>
<th>Reaction Time ($\Delta t$)</th>
<th>Relative Rate $-\Delta [\text{dye}]/\Delta t$</th>
<th>Log of the Relative Rate</th>
<th>Reciprocal of Temp. $1/K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>___ °C = ___ K</td>
<td>___ s</td>
<td>___ x 10^{-2}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>___ °C = ___ K</td>
<td>___ s</td>
<td>___ x 10^{-2}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>___ °C = ___ K</td>
<td>___ s</td>
<td>___ x 10^{-2}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>___ °C = ___ K</td>
<td>___ s</td>
<td>___ x 10^{-2}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>___ °C = ___ K</td>
<td>___ s</td>
<td>___ x 10^{-2}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

You will use the data that you have obtained here to graphically determine the activation energy in Question 3 at the end of the lab.
Adding Additional Catalyst

Just as you saw a different reaction rate when a different dye (red vs blue) was bleached, changing the bleach can also change the rate. Adding H₃O⁺ can change the bleach into a much stronger bleaching agent by converting OCl⁻ into HOCl. Adding H₃O⁺ can also change the dye into a substance which can be more easily attacked by the bleach. There is a small amount of H₃O⁺ present in the stock bleach solution to act as a catalyst—you will be adding more H₃O⁺. (Adding H₃O⁺ may also produce some Cl₂, which is also a stronger bleach than either OCl⁻ or HOCl.)

Use five 50 mL flasks to prepare identical solutions for Runs 14-18. Add 5.0 mL of bleach solution and 15.0 mL of deionized water to each. (Using 0.10M NaOH (aq) here would only consume the acid we will add and block its effects.) Then add the indicated number (see table below) or drops of 3 M HCl(aq) to each flask. Add 1 drop of dye to each solution, one solution at a time while swirling, and measure the time to decolorize (to yellow) the blue dye solution. Record each time of reaction.

<table>
<thead>
<tr>
<th>Run</th>
<th>Drops of 3 M HCl</th>
<th>Reaction Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>0</td>
<td>____________ s</td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>____________ s</td>
</tr>
<tr>
<td>16</td>
<td>2</td>
<td>____________ s</td>
</tr>
<tr>
<td>17</td>
<td>3</td>
<td>____________ s</td>
</tr>
<tr>
<td>18</td>
<td>5</td>
<td>____________ s</td>
</tr>
</tbody>
</table>

You earlier wrote an expression of the rate law which did not consider what you have just seen regarding the affect on the rate of added H₃O⁺.

In light of these observations, modify your previous rate law to include the affect of added acid. (Since you don’t know the order of the reaction with respect to H₃O⁺, use a variable as the exponent on [H₃O⁺].)
QUESTIONS AND PROBLEMS

The absorbance that you observed shows how the concentration of one of the reactants (the dye) decreased as a function of time. Plot the absorbency data on the first of three graphs. Plot the absorbency (in the y axis) vs time (on the x axis), then the log of the absorbency vs time, then the reciprocal of the absorbency vs time. **Plot each datum point and circle it.** Draw a single, smooth curve that closely matches all of the points. **However, for one of these plots you should be able to draw a straight line (use a ruler) from the data points.**

1. **Order of the Dye (n):** If the plot of absorbency vs time is linear, then the reaction is _______ order in dye. If the plot of log of the absorbency vs time is linear, then the reaction is _______ order dye. If the plot of the reciprocal of the absorbency vs time is linear, then the reaction is _______ order in dye.

2. **Half-life Time (T_{1/2}):** On the smooth curve of absorbency vs time...
   a. Select points **(write the coordinates next to each point)** which correspond to absorbency (concentration) halvings to determine several half-lives of this reaction. List the points used and the half-lives determined.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>From</td>
<td>To</td>
</tr>
<tr>
<td>________</td>
<td>________</td>
</tr>
<tr>
<td>________</td>
<td>________</td>
</tr>
<tr>
<td>________</td>
<td>________</td>
</tr>
<tr>
<td>________</td>
<td>________</td>
</tr>
</tbody>
</table>

   b. If this reaction is first order in dye you should have obtained half-lives that are **approximately** constant. Is this reaction first order in dye based on these absorbency halvings from the plot of absorbency vs time, yes or no?
c.  *Show* the calculation of the average half-life from your data above.
Calcs.:

Best value of half-life is ________________ s

d.  *Show* the calculation of the rate constant from the half-life.
Calcs.:

Rate constant calculated from your half-life is ________________ s\(^{-1}\)

3.  The plot which yields a straight line is the plot of __________ vs time.

a.  Therefore, this is a __________ order reaction in dye; and the slope is equal to __________.

b.  Determine the slope of this line from two selected points.  *Write the coordinates next those points on your graph* and below.

The slope is ________________

c.  Show the calculation of the rate constant (k) for this reaction from the slope.
Calcs.:

The slope gives a rate constant of ________________ s\(^{-1}\)
4. Use the final graph to plot the log of the relative rate (on the y axis) vs the reciprocal of the temperature, 1/K, (on the x axis)—an Arrhenius plot. **Plot each datum point and circle it. Use a ruler to draw one straight line which best fits all of the data points.**

*Pick two convenient points on your straight line (do not use actual data points—write the coordinates next to the points), and calculate the activation energy for this reaction from the equation:*

\[
\log R_1 - \log R_2 = \frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

where \( R \) is the gas constant (8.3145 J \( \cdot \) K\(^{-1} \) \cdot mol\(^{-1} \)); and \( R_1 \) and \( R_2 \) are the two relative rates that you selected; and as always, temperature is in kelvins.

\[ E_a = \text{__________________________ kJ} \cdot \text{mole}^{-1} \]

5. for the reaction that you have studied here, assume the net stoichiometric reaction can be represented by ...

\[
\text{Dye + OCl}^- \rightarrow \text{Cl}^+ + \text{O-dye}
\]

where O-dye represents the decolorized (oxidized) form of the dye (food coloring).

a. Given below are three mechanisms that you are to consider for this reaction. Determine whether one or more of them is/are consistent with all of your observations, including the rate enhancement seen with the addition of strong acid. Show your reasoning.

A. \[ \text{OCl}^- + \text{dye} \rightarrow \text{ClO-dye}^+ \text{ (slow)} \]
   \[ \text{ClO-dye}^+ \rightarrow \text{Cl}^+ + \text{O-dye} \text{ (fast)} \]

B. \[ \text{OCl}^- + \text{H}_2\text{O}^+ \rightarrow \text{HOCl} + \text{H}_2\text{O} \text{ (fast)} \]
   \[ \text{HOCl} + \text{dye} \rightarrow \text{HO-dye}^{1+} + \text{Cl}^- \text{ (slow)} \]
   \[ \text{HO-dye}^{1+} + \text{H}_2\text{O} \rightarrow \text{O-dye} + \text{H}_3\text{O}^{1+} \text{ (fast)} \]

C. \[ \text{dye} + \text{H}_2\text{O}^{1+} \rightarrow \text{dye-H}^{1+} + \text{H}_2\text{O} \text{ (fast)} \]
   \[ \text{dye-H}^{1+} + \text{OCl}^- \rightarrow \text{O-dye-H}^{1+} + \text{Cl}^- \text{ (slow)} \]
   \[ \text{O-dye-H}^{1+} + \text{H}_2\text{O} \rightarrow \text{O-dye} + \text{H}_3\text{O}^{1+} \text{ (fast)} \]

b. If you have determined more than one consistent mechanism, suggest additional experiments that might support one mechanism over another.