### 14.2 Effect of concentration on rate of reaction/reaction order

Subjects: Kinetics, reaction order
Description: Two samples of blue food dye in water, one with double the concentration of dye. Bleach is added to both samples and the time until the blue color disappears is recorded. From this, the reaction order for concentration of blue food dye is determined.

## Materials:

2400 mL beakers
Blue food coloring
2 magnetic stir bars
Stir rod
110 mL graduated cylinder
1100 mL graduated cylinder
Timer
10 mL household bleach, undiluted ${ }^{\ddagger}$
Stir plate (located in top drawer opposite the chemical storage cabinets or on the bench)
Transfer pipets
Optional: Vernier Spectrometer - requires Logger Pro software*
Cuvettes*
Computer with USB port
$\ddagger$ Bleach is located in the refrigerator
*Located in the drawers opposite the bin storage shelves

## Pre-class preparation:

Prepare the blue dye solutions:

1. Add three drops of food coloring to 300 mL water.
2. Take 100 mL of the above solution and dilute with 100 mL water to get a solution of half the concentration.

## Procedure:

1. Place one solution on the stir plate and add the magnetic stir bar. Add the bleach and visually measure the amount of time it takes for the color to disappear (takes about 5-6 minutes).
2. Repeat for the other solution.

Alternatively: keep the concentration of the dye constant (make one solution and split it in half) and add different amounts of bleach ( 10 mL and 20 mL ) to observe the affect of the bleach concentration.

Optional Procedure: Use the Spectrometer to determine the length of time it takes for the absorbance to reach zero.

1. Calibrate the spectrometer.
a. Prepare a blank by filling an empty cuvette $3 / 4$ full with distilled water.
b. Choose Calibrate from the Sensors menu of LabQuest or the Experiment menu of Logger Pro.
c. Place the blank in the spectrophotometer; make sure to align the cuvette so that the clear sides are facing the light source of the spectrophotometer. When the warmup period is complete, select Finish Calibration. Select OK.
2. Determine the maximum wavelength for the food colored solution and set up the mode of data collection.
d. Empty the blank cuvette and rinse it twice with small amounts of the food colored solution. Fill the cuvette $3 / 4$ full with the solution and place it in the spectrophotometer.
e. Start data collection. A full spectrum graph of the solution will be displayed. Note that one area of the graph contains a peak absorbance, and there may be other lesser peaks that characterize this substance. Stop the data collection.
f. Store the run by clicking the File Cabinet icon or choosing Store Latest Run from the Experiment menu.
g. To set up the data collection mode for the reaction of food coloring and bleach:

- Click the Configure Spectrometer button on the toolbar, M. Click Abs vs. Time as the Collection Mode. The wavelength of maximum absorbance ( $\lambda$ max) will be selected. The default settings are suitable for this experiment. Select OK.

3. Collect absorbance-time data for the reaction of food colored solution and bleach.
h. Remove the cuvette from your spectrophotometer and pour out the solution.
i. DO THIS QUICKLY: Add the 10 mL of bleach to the beaker of food coloring solution. Swirl the reaction mixture with a plastic transfer pipet and use the pipet to fill the cuvette $3 / 4$ full of the reaction mixture. Place the cuvette in the spectrophotometer. Start data collection.
j. Absorbance data will be plotted every second for 200 seconds. To continue collecting after 200 seconds, click the start collection button and select "Append".
k. Examine the graph of absorbance $v s$. time, showing a gradual decrease in absorbance. Store the run by clicking the File Cabinet icon or choosing Store Latest Run from the Experiment menu.
4. Repeat the procedure to conduct a second trial with a new food colored solution and another 10 mL sample of bleach.

## Discussion:

The purpose of this demo is to experimentally determine how the dye concentration affects the rate. Using the time it takes for the blue color to disappear, and knowing that the concentration of the second is double that of the first reaction, the reaction order with respect to the blue food coloring concentration can be determined.

Rate is proportional to concentration: $\quad \mathrm{R} \propto[\mathrm{A}]^{\mathrm{n}}$

Rate is also given by the following equation:
$\mathrm{R}=-\Delta[$ dye $] / \Delta \mathrm{t}=-\left([\text { dye }]_{\mathrm{f}}-\left[\right.\right.$ dye $\left._{\mathrm{i}}\right) /\left(\mathrm{t}_{\mathrm{f}}-\mathrm{t}_{\mathrm{i}}\right) \quad \mathrm{t}_{\mathrm{i}}=0$ and $\left[\mathrm{dye}_{\mathrm{f}}=0\right.$
Simplifying to $R=[\text { dye }]_{i} / t_{f}$
Rate $_{1}=\left[\right.$ dye $_{1} / \mathrm{t}_{1} \quad$ Rate $_{2}=\left[\right.$ dye $_{2} / \mathrm{t}_{2}$
Taking the ratio of the above rate equations:
Rate $_{1} /$ Rate $_{2}=\left\{[\text { dye }]_{1}\left(\mathrm{t}_{2}\right) /\left[\right.\right.$ dye $\left._{2}\left(\mathrm{t}_{1}\right)\right\} \quad$ We know that: $[\text { dye }]_{2}=1 / 2[\text { dye }]_{1}$
Therefore:
Rate $_{1} /$ Rate $_{2}=\left\{\left[\right.\right.$ dye $_{1}\left(\mathrm{t}_{2}\right) / 1 / 2\left[\right.$ dye $\left._{1}\left(\mathrm{t}_{1}\right)\right\}=2 \mathrm{t}_{2} / \mathrm{t}_{1}$
The rate equations for both reactions can also be written as:
Rate $_{1}=\mathrm{k}[\text { dye }]_{1}{ }^{\mathrm{x}}[\text { bleach }]_{1} \mathrm{y} \quad$ Rate $_{2}=\mathrm{k}[\text { dye }]_{2} \mathrm{x}[\text { bleach }]_{2} \mathrm{y}$
Taking the ratio of each and cancelling [bleach] and k gives
Rate $_{1} /$ Rate $_{2}=[\text { dye }]_{1}{ }^{x} /[\text { dye }]_{2}{ }^{x}=\left([\text { dye }]_{1} /[\text { dye }]_{2}\right)^{x}$
We know that: $[\text { dye }]_{2}=1 / 2[\text { dye }]_{1}$
Therefore:
Rate $_{1} /$ Rate $_{2}=\left(\left[\right.\right.$ dye $_{1} / 1 / 2\left[\text { dye }_{1}\right)^{\mathrm{x}}=2^{\mathrm{x}}$
Setting the results equal to each other gives:
$2 \mathrm{t}_{2} / \mathrm{t}_{1}=2^{\mathrm{x}}$

Once the reaction order is calculated, you can use the appropriate rate equation to solve for the rate constant, assuming the concentration is known.

For $1^{\text {st }}$ Order reactions: $\quad \ln \left([\mathrm{R}]_{\mathrm{t}} /[\mathrm{R}]_{0}\right)=-\mathrm{kt}$
For $2^{\text {nd }}$ Order reactions: $\quad 1 /[\mathrm{R}]_{\mathrm{t}}-1 /[\mathrm{r}]_{0}=\mathrm{kt}$ For $0^{\text {th }}$ Order reactions: $\quad[\mathrm{R}]_{0}-[\mathrm{R}]_{\mathrm{t}}=\mathrm{kt}$

Note: The following data was obtained using the spectrometer.

| Experiment 1 | [Dye] at $\mathrm{t}_{0}$ | [Bleach] at $\mathrm{t}_{0}$ | Time | Rate |
| :---: | :---: | :---: | :---: | :---: |
| 1 | $\begin{aligned} & 3 \text { drops/0.31L = } \\ & 9.67 \text { drop/L } \end{aligned}$ | $10 \mathrm{~mL} / 0.31 \mathrm{~L}$ | 400s (6.67m) | 0.024 drops/L.s |
| 2 | $\begin{aligned} & 1.5 \text { drops/0.31L } \\ & =4.84 \text { drops } / \mathrm{L} \end{aligned}$ | $10 \mathrm{~mL} / 0.31 \mathrm{~L}$ | 400 s(6.67m) | 0.012 drops/L.s |

Rate $1 /$ Rate $2=0.024 / 0.012=2.0$
The rate decreased by a factor of 2 , which means the rate is proportional to the dye concentration, thus $\mathrm{x}=1$.

Using the above equations: $2(400) / 400=2^{\wedge} \mathrm{x}$
Solving for x gives 1 .
The rate is first order with respect to dye.
Using $\ln \left([R]_{t} /[R]_{0}\right)=-k t$ and knowing that because $k$ is independent of concentration for a first order reaction, we can use any units of concentration for the calculation, including drops/L.

To calculate k, we can't use the final concentration as zero, so let's assume that at 400 sec the concentration is approaching zero at $0.001 \mathrm{drops} / \mathrm{L}$. This is $[\mathrm{R}]_{\mathrm{t}}$. Thus,
$\ln (0.001 / 9.67)=\ln \left(1.03 \times 10^{-4}\right)=-\mathrm{kt} \quad \mathrm{k}=9.18 / \mathrm{t} \quad=9.18 / 6.67 \mathrm{~m}=1.37 / \mathrm{min}$
Rate $=k\left[\right.$ dye $^{\mathrm{x}} \sim 1.37$ [dye]
Safety: Use caution when handling bleach solutions. Use gloves to prevent skin contact.

Disposal: Solutions can be flushed down the drain with water

## References:

1. Prof. Fermann
