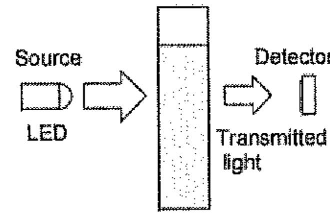
<u>Colorimetry</u>: An Experimental Method to Measure Reaction Rate

<u>Colorimetry</u>: an experimental method to measure reaction rate by using a Colorimeter (or spectrophotometer) to determine the Concentration of solution by analyzing its color intensity.

- Light from an LED light source passes through a Cuvette (tiny container) filled with a solution sample, as shown in the figure to the right.
- Some of the incoming light is absorbed by the solution. As a result, light of a lower intensity strikes a photodiode.



- The colorimeter is set to a wavelength the solution being studied absorbs the most, based on the color of the solution: of course, colorimetry only works if one of your reactants or products is Colored. ☺

Beer's Law

$$A = abc$$

A: absorbance

a: molar absorptivity (a proportionality constant that's different for every solution)

b: path length (usually 1.00 cm)

c: concentration (measured in molarity)

- Beer's Law is important because it demonstrates that absorbance is directly proportional to concentration (providing the absorbing substance, wavelength, and path length are fixed).
- By measuring the change in absorbance over time, you can use Beer's law to convert absorbance to Concentration.
- Graphing [reactant] vs. time, ln[reactant] vs. time, and 1/[reactant] vs time will allow you to determine if the reaction being studied is zero, first, or second order with respect to that reactant:
  - If **[reactant] vs. time** is most linear, the reaction is 0th order with respect to that reactant.
  - If **ln[reactant] vs. time** is most linear, the reaction is 1st order with respect to that reactant.
  - If **1/[reactant] vs. time** is most linear, the reaction is 2nd order with respect to that reactant.

Swamping

In order to focus on the order of a reaction with respect to a single reactant, a technique called Swamping is used.

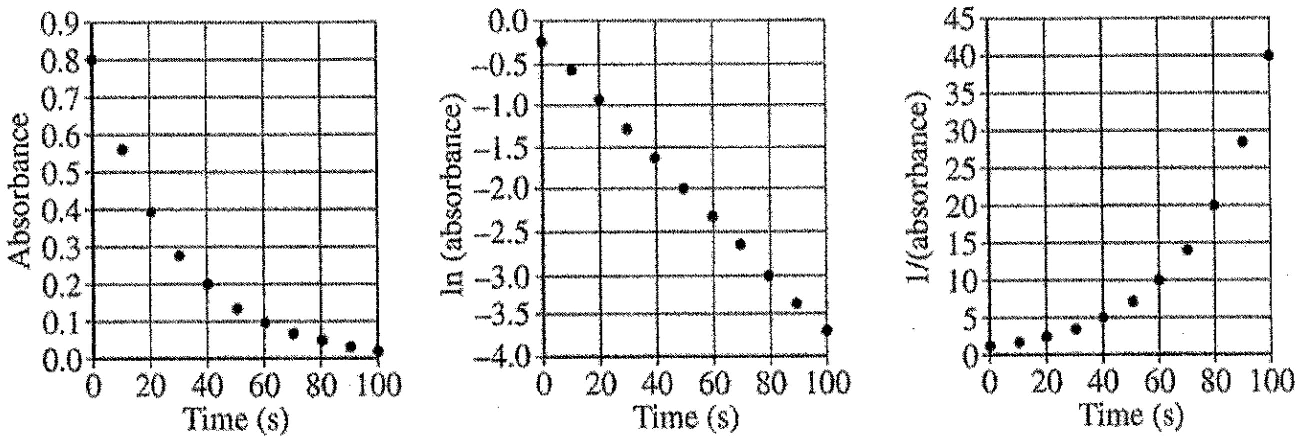
- All but one of the reactants will start at extremely high concentrations (1000X or more in excess)
- The reactants that are in excess won't change significantly during the experiment, so their concentrations can be considered effectively Constant; thus, any change in the measured rate of the reaction must be due to the limiting reactant being studied.
- A rate constant determined using the swamping technique is called a psuedo rate constant (since you will only know the order with respect to a single reactant).

AP Free Response Practice, yum! (2015 FR, modified)

$$Na_2C_{37}H_{34}N_2S_3O_9 + OCl^- \rightarrow \text{products}$$

blue *colorless*

1. Blue food coloring can be oxidized by household bleach (which contains OCl^-) to form colorless products, as represented by the equation above. A student used a spectrophotometer set at a wavelength of 635 nm to study the absorbance of the food coloring over time during the bleaching process. In the study, bleach is present in large excess so that the concentration of OCl^- is essentially constant throughout the reaction. The student used data from the study to generate the graphs below.



Graph I Graph II Graph III

a. Based on the graphs above, what is the order of the reaction with respect to the blue food coloring? Justify your answer.

b. What would the units be for the rate constant, *k*?

c. In a second experiment, the student prepares solutions of food coloring and bleach with concentrations that differ from those used in the first experiment. When the solutions are combined, the student observes that the reaction mixture reaches an absorbance near zero too rapidly. In order to correct the problem, the student proposes the following three possible modifications to the experiment.

- Increasing the temperature X increase rate!
- Increasing the concentration of the food coloring
- Increasing the concentration of the bleach X (in large excess already)

Circle the one proposed modification above that could correct the problem and explain how that modification increases the time for the reaction mixture to reach an absorbance near zero.

d. In another experiment, a student wishes to study the oxidation of red food coloring with bleach. How would the student need to modify the original experimental procedure to determine the order of the reaction with respect to the red food coloring?

a.) The rxn is 1st order w/ respect to blue food coloring, b/c the graph of ln(absorbance) vs. time is a straight line.

b.) 1/sec or sec^{-1}

c.) ↑ [food coloring] will increase the amount of time it takes for the reactants to completely convert into products (regardless of the rxn order!)

d.) The spectrophotometer should be set to a different wavelength (so the absorption of red light is measured optimally, rather than the absorption of blue.)