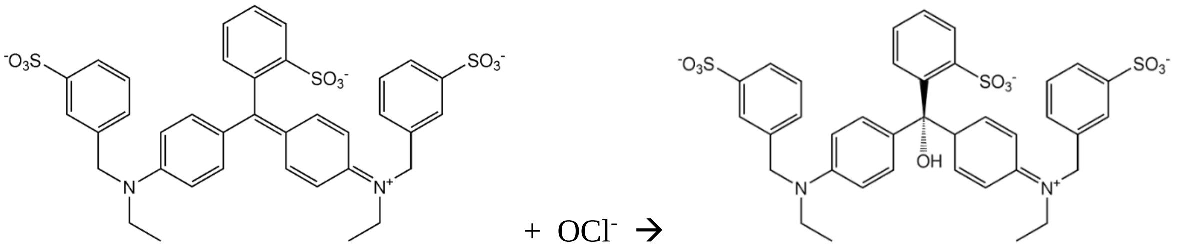
Chemical Kinetics: Determining Rate Laws for Chemical Reactions v010615

INTRODUCTION

It is thought that the birth of chemical kinetics occurred in 1850 when a German chemist, Ludwig Ferdinand Wilhelny, studied the rate of sucrose inversion. Modern chemical kinetics was solidified in 1864 when two Norwegian chemists, Peter Waage and Cato Guldberg, formulated the law of mass action, which states that rate of many chemical reactions are proportional to the amount of reacting substances. Chemical kinetics deals with how fast chemical reactions happen and with how these rates are dependent upon factors such as concentration, temperature, or the presence of a catalyst.

In this experiment we will examine the effect of the change of initial concentrations on the reaction rate of the food dye, FD&C Blue #1 (792.85 g/mol), and hypochlorite ion:



Equation 1

blue colorless colorless

We can determine the rate of the dye reaction with OCl^- by using a SPEC-20 to monitor the drop in absorbance of the dye in solution.

THE CHEMICAL RATE LAW

Consider the following reaction:

$$D + B \rightarrow C \qquad \text{Equation 2}$$

A **rate law** for this chemical reaction will be defined as:

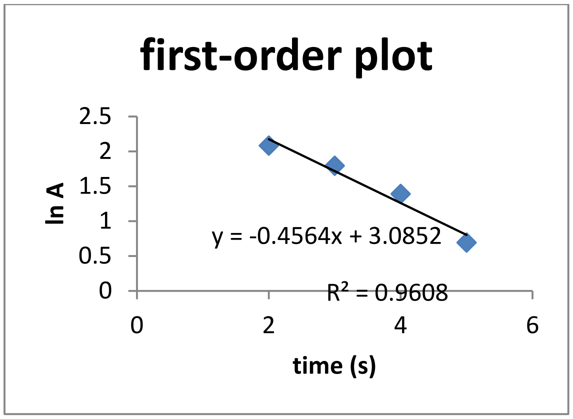
$$\text{rate} = k[D]^x[B]^y \qquad \text{Equation 3}$$

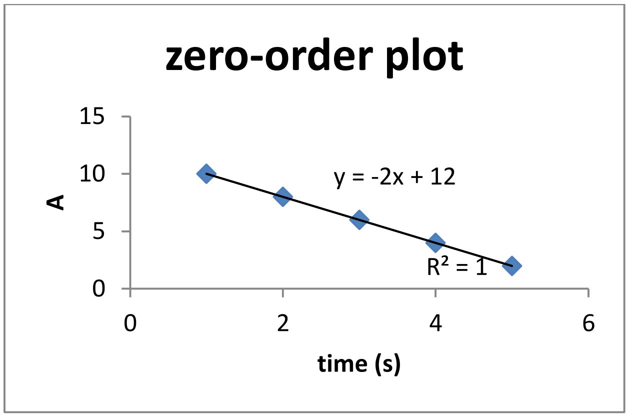
In Equation 3, k is called the **rate constant**. It is proportionality factor whereby the magnitude of k relates directly to how fast the reaction occurs. [D] is the molar concentration of reactant D, and [B] is the molar concentration of reactant B. The coefficient x is referred to as the **order** with respect to reactant D, and y is the **order** with respect to reactant B. The sum of all reactant orders in a chemical reaction, in this case x + y, is the **overall order of a chemical reaction**. Hence, if x=1 and y=2, the overall reaction order would be 3. The order of an individual reactant tells us how many atoms or molecules of that particular reactant are involved in the rate limiting step (the slowest step) of a chemical reaction. For example, in the reaction above if x=2, that means two D molecules are colliding in the slowest step of the chemical reaction. As can be seen in Equation 3, if x=1 we have $[A]^x=[A]^1$, which means the reaction rate doubles when the concentration of D is doubled. If x=2, we have $[A]^x=[A]^2$, and the reaction rate is quadrupled when the concentration of D doubles. An **order** for a reactant is typically any real, positive number including fractions.

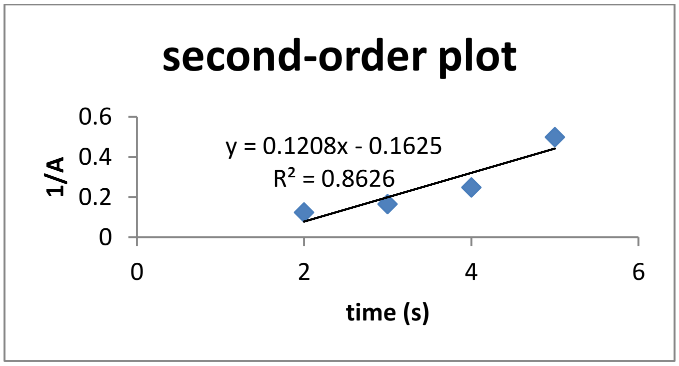
Using Graphical Methods to Determine the Order of a Reactant

By plotting changes in concentration of a given reactant versus time, the order of that reactant can be determined. This is typically accomplished using the **isolation method**. In equation 2 the order with respect to reactant A is to be determined by holding [B], temperature (T), and pressure (P) constant. [B] can be held constant in a chemical reaction by **flooding** the reaction with such a large excess of [B] versus [D] such that the relative [B] does not change as [D] is consumed. For introductory chemistry courses, often only reactions that are 0, 1, or 2 order in a given reactant are considered. To determine if a reactant is first-order in D, ln [D] versus time (t) is plotted. With a second-order reaction, 1/[D] versus t is plotted. A zero-order plot is simply [D] versus t. Then these plots are compared. The plot with the straightest line tells us the order of the reactant. If we assume D is a species that adsorbs visible light, A SPEC-20 can be used to monitor the reaction progress, and we can replace the [D] with absorbance (A) in the plots because [D] is proportional to the adsorbed light.

As an example, here are the first-, second-, and zero-order Excel plots from an experiment that monitored the decrease in absorbance versus time of a generic reactant like D that adsorbs visible light:







Once experimental data are plotted as a scatter plot, a linear regression, or trendline can be added to determine how straight the best fit line is between the data points. R^2 is a correlation coefficient. The closer R^2 is to one, the straighter the trendline. Inspections of the plots above suggest that the order of the generic reactant is 0. The experimental points are also aligned in a perfect straight line because $R^2=1$. Notice that the slopes of the first- and zero-order plots are negative because the reactant concentration and corresponding absorbance is decreasing with t. The slope of the second-order plot is increasing because the plot is now 1/A. If we go back to the blue dye reaction with hypochlorite ion in equation 1, such a method would work well for determining the order with respect to the blue dye. What about the colorless hypochlorite ion? Could we use the above method to determine its order?

Method of Initial Rates

To apply the **method of initial rates**, at least two experimental trials must be performed. Let us use the method of initial rates to determine the order of reactant B in Equation 2. We wish to study the effect of change of concentration in species B to determine the reaction order of B. We will perform two trials. In both trials we will hold the concentration of species D constant, and vary the concentration of species B in trial 1 and 2. For each trial we can now write a rate law:

first trial: $\text{rate}_1 = k[D]_1^x[B]_1^y$ Equation 4a

second trial: $\text{rate}_2 = k[D]_2^x[B]_2^y$ Equation 4b

It is important to realize in equation 4a and 4b that the orders x and y are constant and do not change with concentration. The rate constant k is also constant as long as there is not a change in temperature. Now we can ratio equation 4a and 4b:

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{k[D]_1^x[B]_1^y}{k[D]_2^x[B]_2^y} \qquad \text{Equation 5}$$

In this equation k cancels out. $[D]_1=[D]_2$ because we are starting off with the same initial concentration of A in each trial. The order of species D which is x is also constant. Canceling terms we have left:

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{k[B]_1^y}{k[B]_2^y} \qquad \text{Equation 6}$$

Consider the following chemical reaction:

$$2A + B \rightarrow C + D \qquad \text{Equation 7}$$

Table 1

	Trial 1	**Trial 2**
[A], *M*	0.10	0.20
[B], *M*	0.050	0.050
rate, *M/s*	6.0×10^{-3}	1.2×10^{-2}

The goal of obtaining the experimental data from Trial 1 and 2 in Table 1 is to determine the order of reactant A by varying the concentration of A in dual experiments. Note that the concentration of B is constant in both Trial 1 and 2. We can now use the reaction in equation 7 and the data in Table 1 to derive:

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{k[A]_1^x}{k[A]_2^x} \qquad \text{Equation 8}$$

Substituting data from Table 1:

$$\frac{6.0 \times 10^{-3}}{1.2 \times 10^{-2}} = \frac{(0.10)^x}{(0.20)^x} \quad \text{or} \quad 0.50 = (0.50)^x \quad \text{so } x=1$$

The method of initial rates would be necessary to determine the order of the OCl^- in the reaction in Equation 1 because OCl^- does not adsorb light and we cannot use a SPEC-20 to monitor its concentration versus t.

Experimental Details and Calculations

Consider the following reaction:

$$\text{dye} + OCl^- \rightarrow \text{product} \qquad \text{Equation 9}$$

The rate law for Equation 9:

$$\text{rate} = k[\text{dye}]^x[OCl^-]^y \qquad \text{Equation 10}$$

To determine the order x and y we must perform two trials. We can use one of the trials and the graphical method to determine the order x of the dye. The **Method of Initial Rates** can be used to obtain the order y of OCl^-. In each experimental trial, a SPEC 20 is used to monitor the decrease in dye absorbance versus time at the analytical wavelength for the dye. Different concentrations of OCl^- are used in each trial while the concentration of the dye is constant in both trials. Next, we can prepare plots of A versus t, ln A versus t, and 1/A versus t. The slope of each line can be determined from regression analysis in a spreadsheet. Let us assume that the reaction is first-order in dye concentration so that the plot of ln A versus t was the straightest of the three plots. For the plot of ln A versus t, an increasing rate of reactions would also reflects in an increasing slope and is -k.

To get the order of the OCl^- we must use the method of initial rates. Remembering that the [dye] is constant in both trials, in the first trial the initial $[OCl^-] = 0.050$ M and the slope of the plot of ln A versus t was -0.101. For the second trial $[OCl^-]=0.10$ M and the slope of the plot of ln A versus t was -0.402. The slope of the line of the ln A versus t plots is proportional to the reaction rate for the given trial.

$$\frac{-0.101}{-0.402} = \frac{(0.05)^y}{(0.10)^y}$$

We can now take the natural logarithm of both sides of the equation and use the identity:

$$\ln a^y = y{*}\ln a$$

$$\ln 0.251 = \ln (0.50)^y = y{*}\ln 0.50$$

$$-1.38 = y{*}(-0.693) \text{ so that } y{\sim}2$$

Now we can combine result and say

$$\text{rate} = k[\text{dye}]^1[OCl^-]^2$$

Experimental Procedure

Note: Everything can go down the sink in this experiment. Rinse the containers after discarding the wastes.

1) Turn on the SPEC 20 and set to the wavelength to 630 nm and %T (or absorbance-ask your instructor). Allow 15 minutes to stabilize. Follow the instructor's directions for calibrating the SPEC 20. The blanking for this experiment is done with 0.67M NaCl solution.

2) Rinse a cuvette with deionized water. Be sure to use only Kim wipes on the cuvette to avoid scratches.

3) Accurately obtain 25 mL of the dye solution (5.2×10^{-6} M) and 1 mL of the 0.12M NaClO solution using a graduated cylinder and a disposable pipette. Record the concentrations on your data sheet.

4) To begin the reaction, mix all of the 25 mL dye solution and 1 mL of NaClO solution together in a beaker. Start the timer the moment the two reagents touch. Ensure the reaction mixture is thoroughly mixed and homogeneous. **Quickly** pipette the mixture into a clean cuvette with a new disposable pipette and start the absorbance measurements. **The first absorbance reading at 30 seconds should be somewhere in between 0.6-0.8. If it is not, restart the procedure from step 3.

5) Record the absorbance in 30 second intervals for 20 minutes. Be sure to remove the cuvette from the SPEC 20 between readings to prevent the solution from warming in the SPEC 20 cavity. Be consistent in recording your reading at precisely the time indicated on the timer. Blanking the instrument every few minutes during the measurements is advised to ensure the accuracy of measurements.

6) Repeat step 2-5 with 25 mL of the dye solution and 1 mL of the 0.06M NaClO solution.

Experimental Data

Data for Trial 1

[dye]=________ [OCl^-]=________

Elapsed time, t (min.)	%T	Elapsed time, t (min.)	%T

Data for Trial 2

[dye]=________ $[\mathrm{OCl}^-]$=________

Elapsed time, t (min.)	%T	Elapsed time, t (min.)	%T

Calculations

1) Use a spread sheet to convert %T to A. A = 2.000- log (%T)

2) Use the spreadsheet to covert A to 1/A and ln A.

3) Use the spreadsheet to makes plot of A vs t, ln A versus t, and 1/A versus t. Include on the spreadsheet the best fit line, equation of the line with slope, and R^2. Be sure to clearly label the axes on the plot.

4) Repeat steps 1-3 for both experimental trials.

5) Determine which of the three plot types is most linear. Use the slopes from the most linear plot type and equation such as Equation 11 to determine the order of the OCl^-.

Post-Laboratory Questions

1) Complete the following chart from the graphs:

	Trial 1			Trial 2	
	slope	R^2		slope	R^2
A versus t	___________	__________	A versus t	___________	__________
ln A versus t	___________	__________	ln A versus t	___________	__________
1/A versus t	___________	__________	1/A versus t	___________	__________

2) Which of the three plot types is most linear? _____________

3) What is the order with respect to the dye in Equation 1? _____________

4) What is the order of the $[OCl^-]$ in Equation 1? _____________

5) What is the rate law for the reaction in Equation 1? ______________________________________

6) How would doubling the concentration of the dye alter the reaction rate? ___________________

7) Would you have determined the same rate law if you had used $[OCl^-] = 0.24$ M instead of 0.12 M? Briefly explain?

8) Consider a generic reaction $A + B \rightarrow C$. Assume C is brightly colored.
a) What happens to the absorbance of C at its analytical wavelength as the reaction progresses?

b) Suppose you did an experiment involving this reaction where B is in large excess. If the reaction is first-order in A, would the graph of ln A versus t for P be linear? Explain.

Pre-Laboratory Questions

1) Are there any hazards associated with the use of FD&C Blue #1 or OCl^- in this experiment?

2) Consider the following reaction:

$$2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$$

a. Complete the last twp columns in the Table below.

Time (s)	$[NO_2]$, M	ln $[NO_2]$	$1/[NO_2]$
0	0.4167		
20	0.2084		
40	0.1389		
60	0.1042		

b. Make plots of ln $[NO_2]$ versus t, $[NO_2]$ versus t, and $1/[NO_2]$ versus t. Which graph is the most linear?

c. What is the NO_2 reaction order? Explain.

d. What is the reaction rate law?