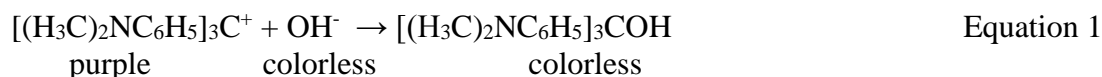


INTRODUCTION

It is thought that the birth of chemical kinetics occurred in 1850 when a German chemist, Ludwig Ferdinand Wilhelmy, 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 a colored dye, crystal violet, and hydroxide ion:



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

THE CHEMICAL RATE LAW

Consider the following reaction:



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

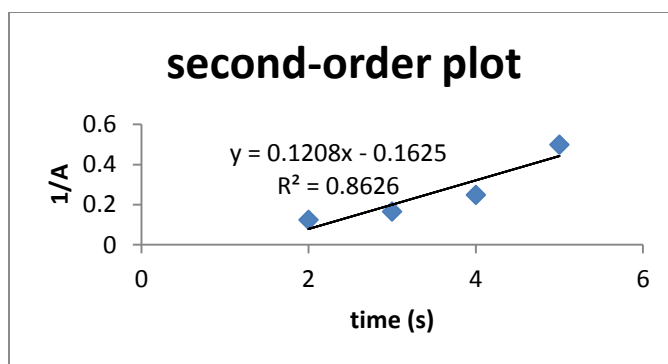
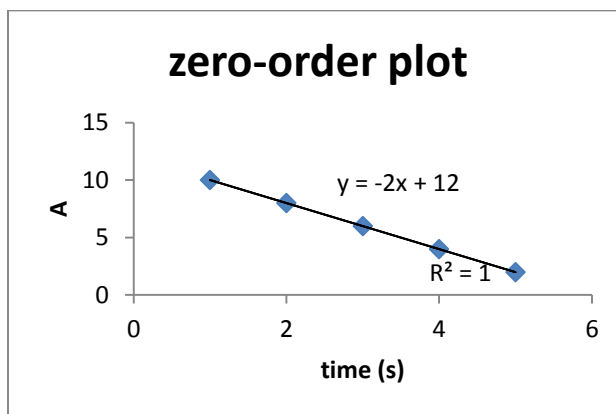
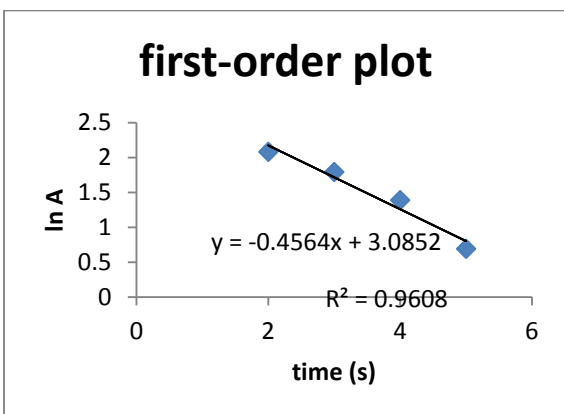
$$\text{rate} = k[D]^x[B]^y \qquad \text{Equation 3}$$

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 $[D]^x=[D]^1$, which means the reaction rate doubles when the concentration of D is doubled. If $x=2$, we have $[D]^x=[D]^2$, 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 D 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 crystal violet reaction with hydroxide ion in equation 1, such a method would work well for determining the order with respect to the purple colored crystal violet. What about the colorless hydroxide oxide? 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:

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

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

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:

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

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

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

Consider the following chemical reaction:



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:

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

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 OH^- in the reaction in Equation 1 because OH^- 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:



The rate law for Equation 9:

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

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 OH^- . 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 OH^- 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 also reflects in an increasing slope and is $-k$.

To get the order of the OH^- we must use the method of initial rates. Remembering that the $[\text{dye}]$ is constant in both trials, in the first trial the initial $[\text{OH}^-] = 0.050 \text{ M}$ and the slope of the plot of $\ln A$ versus t was -0.101 . For the second trial $[\text{OH}^-] = 0.10 \text{ M}$ 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:

$$\ln a^y = y \cdot \ln a$$

$$\ln 0.251 = \ln (0.50)^y = y \cdot \ln 0.50$$

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

Now we can combine result and say

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

Experimental Procedure

Note: Nothing should go down the sink in this experiment. Place all waste in the discard container.

- 1) Turn on the SPEC 20 and set to the wavelength to 595 nm and %T. Allow 15 minutes to stabilize. Follow the instructor's directions for calibrating the SPEC 20. Water can be used as the blank.
- 2) Rinse a cuvette with deionized water. Be sure to use only Kim wipes on the cuvette to avoid scratches.
- 3) Accurately obtain 10 mL each of 0.040 M NaOH and 1.5×10^{-5} M CV using a graduated cylinder. Record the concentrations on your data sheet.
- 4) To begin the reaction, mix the all of the 0.040 M NaOH and 1.5×10^{-5} M CV together in a beaker.
- 5) After about 1 minute, rinse the cuvette with aliquots of the NaOH/CV solution and fill the cuvette $\frac{3}{4}$ full.
- 6) After 3 minutes place the cuvette in the SPEC 20 and record the %T. Alternatively, your instructor may have you read Absorbance directly.
- 7) Continue recording the %T in 1 minute intervals for 20 minutes. Be sure to remove the cuvette from the SPEC 20 between reading to prevent the solution from warmig in the SPEC 20 cavity.
- 8) Repeat step 3-7 with 10 mL of 0.020 M NaOH and 1.5×10^{-5} M CV.

Calculations

- 1) If Absorbance was not measured directly, convert %T to A. This can be done in a spreadsheet using the relationship: $A = 2.000 - \log(\%T)$
- 2) Use the spreadsheet to convert A to $1/A$ and $\ln A$.
- 3) Use the spreadsheet to make 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 OH^- .

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 CV in Equation 1? _____
- 4) What is the order of the $[\text{OH}^-]$ in Equation 1? _____
- 5) What is the rate law for the reaction in Equation 1? _____
- 6) How would doubling the concentration of CV alter the reaction rate? _____

7) Would you have determined the same rate law if you had used $[\text{OH}^-] = 0.080 \text{ M}$ instead of 0.040 M ? Briefly explain?

8) Consider a generic reaction $\text{A} + \text{B} \rightarrow \text{C}$ where C is colored.

a) What happens to the absorbance of solution at the analytical wavelength of C 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 CV or OH^- in this experiment?

2) Consider the following reaction:



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

Time (s)	$[\text{NO}_2]$, M	$\ln [\text{NO}_2]$	$1/[\text{NO}_2]$
0	0.4167		
20	0.2084		
40	0.1389		
60	0.1042		

b. Make plots of $\ln [\text{NO}_2]$ versus t , $[\text{NO}_2]$ versus t , and $1/[\text{NO}_2]$ versus t . Which graph is the most linear?

c. What is the NO_2 reaction order? Explain.

d. What is the reaction rate law?

3) Consider the following data collected for the reaction $\text{A} + 2\text{B} \rightarrow \text{D} + \text{C}$

initial rate (M/hour)	initial [A] (M)	initial [B] (M)
0.041	0.0058	0.0032
0.080	0.0058	0.0064

a. Use these to determine the order of the reaction with respect to [B].

b. From these data is it possible to determine the reaction order with respect to [A]? Explain.