

Experiment M: Effect of Concentration on Rate of Reaction

Reading

Sections 13.2 to 13.5 from The M. Friedman, TD and Sh. C. E. *Chemistry: A Molecular Approach* 2nd Edition, 2005, © 2005 Pearson Education, Inc.

Objectives

Your objectives for this experiment will be to:

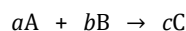
- Prepare a calibration curve for the spectroscopic determination of crystal violet concentration
- Determine the overall rate constant for the reaction between crystal violet and hydroxide at room temperature
- Experimentally determine the reaction order with respect to each reactant, the overall order of reaction, and the rate law for the reaction

Introduction

Reaction Rates and the Rate Law

Kinetics is the study of reaction rate: how fast a reaction occurs. There are several factors that influence how fast a reaction occurs: temperature, the concentration of each of the reactants, and the presence of catalysts. This experiment will focus on the influence of reactant concentrations on the reaction rate; Experiment N investigates the influence of temperature.

For a simple bimolecular reaction of the form:



Reaction rate is simply the change in concentration of the products or reactants with respect to time, and may be described in terms of either the disappearance of the reactants or the formation of the products:

$$rate = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = k[A]^m[B]^n \quad (1)$$

The above equation is the *differential rate equation*. In this equation, k is the overall rate constant of the reaction and m and n are the reaction orders with respect to reactants A and B. The overall order of the reaction is found by summing the reaction orders with respect to the reactants, i.e. $m + n$. The orders of the reaction with respect to each reactant and the overall order of reaction are not necessarily the same as the stoichiometric coefficients of the reaction; in other words, m and n are not necessarily equal to a and b , respectively. Neither the individual reaction orders (m

and n) nor the rate constant (k) can be predicted from the balanced chemical equation alone: these parameters must be determined experimentally.

For reaction (1), the rate can be expressed either in terms of the rate of disappearance of a reactant or by the rate of formation of a product. These rates are related through the stoichiometry of the reaction, as shown in Equation 1. The reaction rate must, by definition, always be a positive number: since reactant concentrations diminish as the reaction proceeds, the rate of change of each reactant will be a negative number and thus must be multiplied by a factor of -1 to furnish a positive value for reaction rate.

Integrated Rate Laws

Equation (1) is an example of a differential equation and shows the relationship between the rate of the reaction and the concentrations of the reactants. Integrating the equation yields the corresponding integrated rate law, which relates the concentration of reactants to time. The form of the integrated rate law depends on the overall order of the reaction.

Zero-Order Integrated Rate Law

The rate of a zero-order reaction, where $m + n = 0$, is not dependent on the concentration of the reactants. The rate of a zero-order reaction can be described as follows:

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^0 = k \quad (2)$$

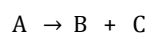
Integrating this equation with respect to time yields:

$$[A]_t = -kt + [A]_0 \quad (3)$$

where $[A]_t$ is the concentration of reactant A at time t , $[A]_0$ is the initial concentration of reactant A at the start of the reaction, and k is the overall rate constant. Notice that this equation is in the form of a straight line, $y = mx + b$. If the reaction is zero-order, plotting $[A]_t$ versus t will yield a straight line with slope $-k$ and a y-intercept of $[A]_0$.

First-Order Integrated Rate Law

First-order reactions are typically of the form:



In first-order reactions, the rate of reaction is directly proportional to the concentration of the reactants:

$$\text{Rate} = -\frac{d[A]}{dt} = k[A] \quad (4)$$

For a first-order reaction, the order of the reaction with respect to the reactant is 1, which is often omitted from the rate law (if m or n do not appear in the rate law you can assume that they are 1). The overall reaction order is also 1. Integrating this equation with respect to time yields:

$$[A]_t = [A]_0 e^{-kt} \quad (5)$$

where $[A]_0$ is the initial concentration, $[A]_t$ is the concentration at time t , and k is the overall rate constant. Taking the natural logarithm of both sides of the first-order integrated rate law transforms the equation into an equation of the form $y = mx + b$:

$$\ln[A]_t = -kt + \ln[A]_0 \quad (6)$$

From this equation it can be seen that a plot of $\ln[A]_t$ vs. t will yield a straight line, with slope = $-k$ and y-intercept of $\ln[A]_0$.

Second-Order Integrated Rate Law: Single Reactant

Second-order reactions have one of two forms. The first occurs when a reaction has a single reactant and the rate is second order with respect to it. For example, for the following reaction:



Assuming an elementary reaction, the overall rate would be proportional to the square of the concentration of the reactant:

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^2 \quad (7)$$

Notice that in this situation, the order of with respect to reactant A is 2 and the overall reaction order is also 2. Integrating the differential equation with respect to time and rearranging so that a straight-line relationship can be obtained yields:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \quad (8)$$

From this equation it can be seen that a plot of $\frac{1}{[A]_t}$ vs. t will yield a straight line, with slope = k and y-intercept of $\frac{1}{[A]_0}$.

Second-Order Integrated Rate Law: Two Reactants

Second-order reactions may also have two different reactants. For example:



The overall rate of reaction would be:

$$\text{Rate} = -\frac{d[A]}{dt} = k[A][B] \quad (9)$$

Notice that in this situation, the order of the reaction with respect to each reactant is 1, and the overall reaction order ($m + n$) is 2. Integrating the differential equation with respect to time and rearranging so that a straight-line relationship can be obtained yields:

$$\ln \frac{[B][A]_0}{[A][B]_0} = k([B]_0 - [A]_0)t \quad (10)$$

Thus, a plot of $\ln \frac{[B][A]_0}{[A][B]_0}$ versus t will yield a straight line, with slope $= k([B]_0 - [A]_0)$.

Pseudo-First Order Reactions

Many second (and even third!) order reactions can be transformed into *pseudo-order reactions*, which can greatly simplify the quantification of the reaction dynamics. In order to transform a second or third order reaction into a more simple pseudo-order reaction, the concentrations of one (or more) of the reactants must stay constant through the course of the reaction. As an example, consider the following second-order reaction:



where one of the reactants (let's say B) is present at much higher concentrations ($>100\times$) than the other reactant A. As the reaction progresses to completion, very little of reactant B will be used up ($<1\%$) and the concentration of reactant B will remain approximately constant throughout the reaction. By assuming that $[B]$ is constant, we can combine it with the overall rate constant (k ; another constant), to form a new rate constant called the *pseudorate constant*, k' , where $k' = k[B]$. Therefore, our second order rate equation:

$$\text{Rate} = -\frac{d[A]}{dt} = k[A][B] \quad (11)$$

Can be simplified to:

$$\text{Rate} = -\frac{d[A]}{dt} = k'[A], \text{ where } k' = k[B] \quad (12)$$

where k' is the *pseudo-first-order rate constant*. It should be noted that because we assume that the concentration of B is unchanging, at any point in time during the reaction $[B]_t = [B]_0$.

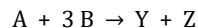
By running reactions under conditions where they will behave as pseudo-order reactions (*i.e.* when one or more of the reactants is in much higher concentration than the other), our mathematics and data interpretation are simplified.

In the above examples, which is an example of a pseudo-first order reaction, the order of the reaction with respect to A is, by definition, 1 (first order with respect to reactant A). However, the overall rate of reaction will still depend on $[B]$, and our simplification makes no assumption of the reaction order with respect to B.

To find the effect $[B]$ on the reaction rate (the order of reaction with respect to $[B]$), we must proceed systematically, that is, by changing one independent variable (in this case a

concentration of B) while the other variables and parameters remain fixed. By observing how the overall rate of reaction changes as we change $[B]$, we can deduce what the reaction order is with respect to B; an example of this is shown below.

Example: Consider the reaction of the hypothetical species A and B to yield Y and Z according to the balanced chemical equation:



The strategy to solve this problem experimentally is as follows:

Step 1. Assume that the reaction fulfils the simple rate law: $\text{rate} = k [A]^m [B]^n$

Step 2. Design an experiment that follows the pattern illustrated in the table below. For instance, in runs 1 and 2, the initial molarity of A is unchanged (in this case, at $0.0010 \text{ mol L}^{-1}$) and the initial molarity of B is doubled.

Run	$[A]_0 \text{ (M)}$	$[B]_0 \text{ (M)}$	$k' \text{ (M}^{-1} \text{s}^{-1})$
1	0.0010	0.100	6.0×10^{-4}
2	0.0010	0.200	1.2×10^{-3}

Step 3. The pseudo rate constant, tabulated above for each run, is determined from a plot based on the appropriate integrated rate law. For instance, in this example, the experimenter found that for each run a plot of $\ln[A]_t$ versus t yielded a straight line, and thus concluded that the reaction is first order with respect to A (and thus is a pseudo-first order reaction when $[B] \gg [A]$). Thus, $m = 1$.

Step 4. To find the reaction order with respect to reactant B (i.e. n), we identify two runs in which the initial concentration of A ($[A]_0$) remains fixed. In this case, runs 1 and 2 are appropriate. We substitute the values of the initial concentration of reactant B ($[B]_0$) and the experimentally determined k' for each run into the expression for k' (e.g. Equation 12). **Note:** the overall rate constant k does not need to be known at this stage as it will be algebraically cancelled shortly. Likewise, the units of k will not be known at this stage and are thus unspecified for now.

	k'	=	k	×	$[B]^n$
For run 1	$6.0 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$	=	k	×	$(0.100 \text{ M})^n$
For run 2	$1.2 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$	=	k	×	$(0.200 \text{ M})^n$

Now we divide the k' equation for run 2 by the equation for run 1. Since the units will cancel, they are now omitted for clarity:

$$\frac{1.2 \times 10^{-3}}{6.0 \times 10^{-4}} = \frac{k(0.200)^n}{k(0.100)^n}$$

The equation can now be further simplified by recognizing that ($k/k = 1$) and that k thus cancels out. Applying a common logarithm to each side of the previous equation and solving for n yields:

M-6

$$\log \left(\frac{1.2 \times 10^{-3}}{6.0 \times 10^{-4}} \right) = \log \left(\frac{k(0.200)^n}{k(0.100)^n} \right)$$

$$\log \left(\frac{1.2 \times 10^{-3}}{6.0 \times 10^{-4}} \right) = \log \left(\frac{0.200}{0.100} \right)^n$$

$$\log \left(\frac{1.2 \times 10^{-3}}{6.0 \times 10^{-4}} \right) = n \times \log \left(\frac{0.200}{0.100} \right)$$

$$\log 2 = n \times \log 2$$

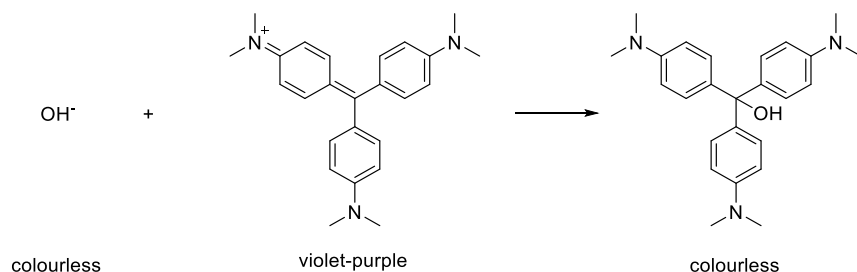
$$n = \frac{\log 2}{\log 2} = 1$$

Thus, this reaction is first order with respect to B and the experimentally derived rate law can be written as:

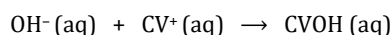
$$\text{Rate} = k[A]^1[B]^1$$

Experimental Method

In this experiment, we will examine the kinetics for the reaction between hydroxide ion and crystal violet (CV⁺). Crystal violet has the structure shown below:



For this experiment, we will adopt the following simplified version of the above equation:



Crystal violet (CV⁺) in water forms a bright purple solution. A colorless product, CVOH, is formed upon reaction with hydroxide. The rate law for this reaction can be described as:

$$\text{Rate} = k[\text{CV}]^m[\text{OH}^-]^n$$

The kinetics of the reaction will be investigated by monitoring the disappearance of the purple colour using spectrophotometry (see Experiment E: Spectrophotometric Determination of Iron). The collected data will be processed by using spreadsheet software such as Google Sheets or Microsoft Excel, and the reaction order with respect to [CV⁺] (in other words, m) will be determined by generating three plots: [CV⁺] versus time, $\ln [\text{CV}^+]$ versus time, and $1/[\text{CV}^+]$ versus time. The pseudo rate constant (k') will be determined from the appropriate plot, and the rate constant k will be calculated from k' . The reaction order with respect to [NaOH] will be determined by varying its concentration amongst three runs.

Advance Study Assignment

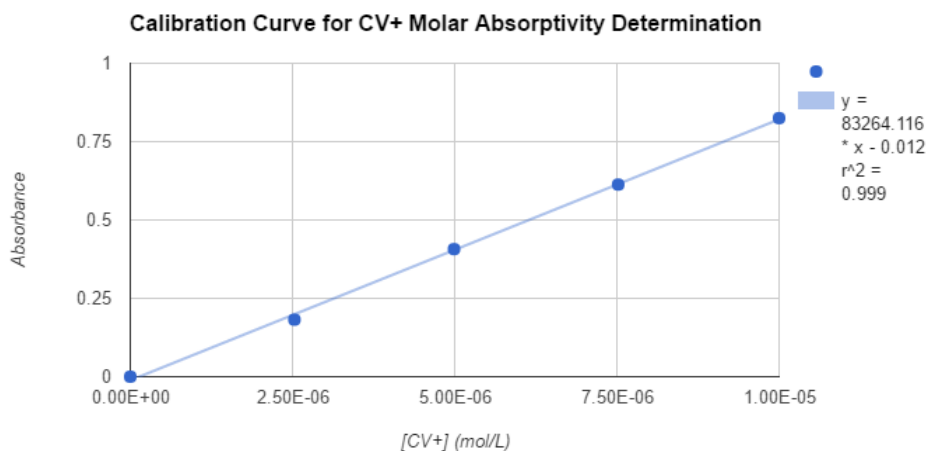
1. Read the following sections at the beginning of the laboratory manual: Volume Measurements (Use of a Volumetric Flask and Use of a Burette), and Absorbance Measurements.
2. In order to determine the molar absorptivity (ϵ) of crystal violet (CV^+) at 588.5 nm, it is normally necessary to prepare a series of solutions of CV^+ at differing (but known) concentrations and then to measure the absorbance of each solution and construct a plot of absorbance versus concentration for CV^+ at 588.5 nm. Such a plot is described as a **calibration curve** for CV^+ ; you will have prepared a calibration curve as part of the Iron Spectroscopy experiment in CHEM 101.

To ensure adequate time to complete Experiment M and to allow time to process data in the lab, the calibration curve for CV^+ at 588.5 nm has been prepared in advance for you, but you must use this curve to determine the molar absorptivity before arriving for the experiment.

A chemist prepared a series of standard solutions of known concentration and acquired the following calibration data using a cuvette with a pathlength (b) of 1.00 cm.

Sample	[CV^+] (mol/L)	Absorbance
1	1.00×10^{-5}	0.825
2	7.52×10^{-6}	0.613
3	4.99×10^{-6}	0.407
4	2.53×10^{-6}	0.182
5 (Blank)	0	0.000

A plot of absorbance versus concentration for CV^+ at 588.5 nm based on this data was then prepared (next page). Note that the linear equation for the best-fit line is (after rounding) $y = (8.32 \times 10^4 \text{ L/mol})x - 0.012$. Based on this equation and the known pathlength ($b = 1.00 \text{ cm}$), determine the molar absorptivity (ϵ) of crystal violet (CV^+) at 588.5 nm. Answer: $8.32 \times 10^4 \text{ L/mol cm}$



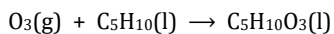
- What is the concentration of $\text{OH}^-(\text{aq})$ at the point of mixing but before reaction when 5.00 mL of 0.400 mol/L NaOH are mixed with 5.00 mL of 6.00×10^{-5} mol/L CV+? Answer: 0.200 mol/L.
- The following kinetic data was collected for a reaction: $\text{A} \rightarrow \text{B}$. Use the methods described on pages M-2 through M-4 (plotting graphs) to determine the order of the reaction with respect to A, and the rate constant k . Write the rate law for the reaction.

Time (s)	[A] (mol/L)
0	5.37×10^{-4}
5	4.68×10^{-4}
10	4.05×10^{-4}
15	3.61×10^{-4}
20	3.20×10^{-4}
25	2.80×10^{-4}
30	2.47×10^{-4}

Answer: 1st order; $k = 0.0256 \text{ s}^{-1}$; Rate = $k[\text{A}]$

- Compare the equation: $\ln [\text{B}]_t = -k't + \ln [\text{B}]_0$ to the straight-line equation, $y = mx + b$. How can the value of k' be extracted from a data set of $[\text{B}]_t$ as a function of time? Answer: Plot a graph in which $\ln [\text{B}]_t$ is on the vertical axis, t is on the horizontal axis, and calculate the slope. Your k' will be equal to the negative of the slope of the line.

6. Assuming that the reaction: $\text{OH}^- + \text{CV}^+ \rightarrow \text{CVOH}$ goes to completion during a run of this experiment; what percent of OH^- has been consumed when 5.0 mL of 0.10 mol/L NaOH was mixed with 5.00 mL of 2.5×10^{-5} mol/L CV⁺? Answer: 0.025 %.
7. For the ozonation of 1-pentene the following data are reported at 27.0 °C:CV



$[\text{C}_5\text{H}_{10}]$ (mol/L)	$[\text{O}_3]$ (mol/L)	$-\Delta[\text{C}_5\text{H}_{10}] / \Delta t$ (mol L ⁻¹ s ⁻¹)
0.010	0.0028	2.19×10^{-5}
0.027	0.0028	1.60×10^{-4}
0.010	0.0045	3.50×10^{-5}

- a. What is the order of the reaction with respect to O_3 and C_5H_{10} ?
Answer: First order in O_3 and second order in C_5H_{10}
- b. Determine the rate law for this reaction.
Answer: rate = $k[\text{O}_3][\text{C}_5\text{H}_{10}]^2$
- c. Calculate the rate constant for one of the runs.
Answer: $k_{\text{run1}} = 78.2 \text{ (mol/L)}^{-2} \text{ s}^{-1}$, $k_{\text{run2}} = 78.4 \text{ (mol/L)}^{-2} \text{ s}^{-1}$,
 $k_{\text{run3}} = 77.8 \text{ (mol/L)}^{-2} \text{ s}^{-1}$

Reagents and Equipment

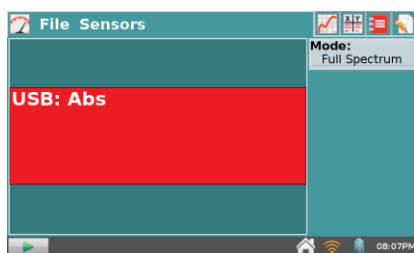
- LabQuest 2 Device with SpectroVis Spectrometer and temperature probe
- Disposable (Pasteur) pipettes
- 3 plastic test tubes (for NaOH)
- Kimwipes to clean/dry the cuvettes
- 50-mL burette
- 3 cuvettes (test tubes)
- 250-mL beakers (2)
- 50-mL volumetric flasks (5)
- 1 mol/L HCl for rinsing cuvettes
- Parafilm (to cover test tubes)
- ~~2.53~~0 $\times 10^{-5}$ mol/L crystal violet
- NaOH (0.10 mol/L, 0.~~25~~20 mol/L, and 0.~~40~~30 mol/L)

Procedure (Partnered)

Setup and Calibration of the Lab Quest 2 Unit and Visible Light Spectrometer

You may use deionized water as the blank solution during calibration for this experiment. As well, you should use the same cuvette

1. Ensure that the Lab Quest 2 unit is plugged in and turned on. Although the unit may be run on battery power, the spectrometer will drain power quickly and thus it is best to run the unit on AC power.
2. Connect the SpectroVis Plus spectrometer to the Lab Quest 2 unit by USB cable. The Lab Quest 2 display should appear as follows:
3. Tap anywhere within the red USB: Abs box and then select “Calibrate...” from the menu that appears. While the 90-second warmup proceeds (see figure below) you can complete steps 4, 5, and 6.



4. Before filling the cuvette with the blank solution, rinse it three times by filling it about $\frac{1}{3}$ full with fresh blank solution each time and rotating the cuvette to ensure all the sides are coated with the blank.
5. Fill the cuvette about $\frac{2}{3}$ full with the blank solution. Wipe the cuvette with a Kimwipe to remove any fingerprints or particles from the glass. Check that no particles or air bubbles are present in the solution.

- Place the cuvette into the spectrophotometer sample holder, making sure the cuvette is securely in place and properly aligned. If there is an arrow or identifiable marking on the cuvette, make sure it is always on the left side so that the cuvette is consistently placed into the spectrophotometer the same way each time.
- Once the warmup is complete and the blank cuvette is correctly inserted into the sample slot, select "Finish Calibration". After a few seconds, the "Calibration completed" message will appear, and you can select "OK".



Preparation of solutions for kinetic measurements

- Reagents are dispensed from bottles fitted with automatic dispensers. Each run requires a glass test tube cuvette (with a white line) and a plastic test tube. Thoroughly wash 3 glass test tube cuvettes and 3 plastic test tubes and completely dry the inside of each test tube with a Kimwipe.
- Into the first clean and dry glass test tube cuvette, dispense 3.00 mL of the stock crystal violet solution. Into the first clean and dry plastic test tube, dispense 3.00 mL of 0.300 mol/L NaOH solution. Cover each test tube with a piece of Parafilm and place the test tubes into a water-bath containing ~150 mL of room temperature water in a 250-mL beaker.
- Into the second clean and dry glass test tube cuvette, dispense 3.00 mL of the stock crystal violet. Into the second clean and dry plastic test tube, dispense 3.00 mL of 0.200 mol/L NaOH solution. Cover each test tube with a piece of Parafilm and place the test tubes into the water-bath containing ~150 mL of room temperature water in a 250-mL beaker.
- Into the third clean and dry glass test tube cuvette, dispense 3.00 mL of the stock crystal violet. Into the third clean and dry plastic test tube, dispense 3.00 mL of 0.100 mol/L NaOH solution. Cover each test tube with a piece of Parafilm and place the test tubes into the water-bath containing ~150 mL of room temperature water in a 250-mL beaker.
- Ensure that the temperature probe is connected to the Lab Quest 2 unit.

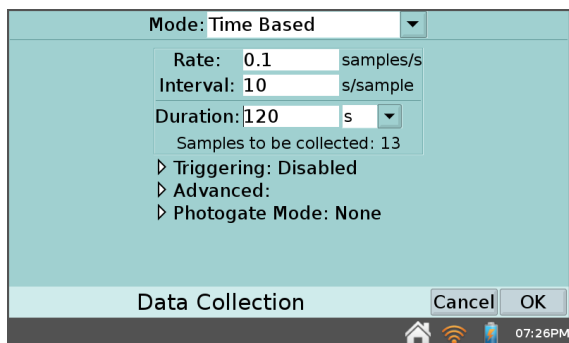
Temperature Probe Setup:

6. If other lab sections have completed this experiment before you, your temperature probe may already be ready for you to use: it must be equipped with a small plug of parafilm wrapped tightly around the probe in the correct position such that when it placed into the test-tube during the experiment, the tip of the probe is immersed into the tube but is held just above the beam of light in the spectrophotometer. This is important: if correctly position, the temperature probe will report accurate temperature values for the solution without blocking the light as it passes through the sample.

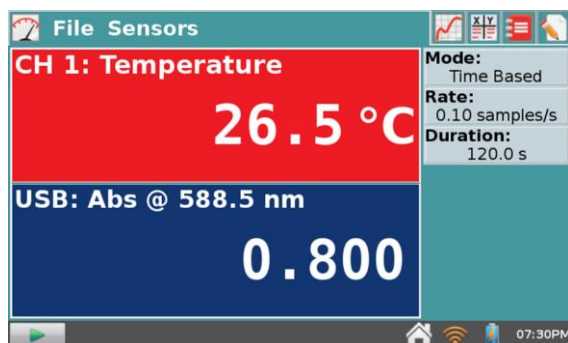


Part II: Spectrophotometric measurements

1. The spectrometer will need to be set to the correct wavelength for today's experiment, which must correspond to the wavelength we used to generate the calibration curve in the pre-lab: 588.5 nm. Tap the red "USB: Abs" box, select "Change Wavelength..." and then enter the new wavelength. The instrument does have limited resolution, so if you input 588.5 nm, the instrument might set to a value very close to (but not equal to) 588.5 nm. This is fine!
2. On the Meter screen, tap Mode and change to "Time Based". See sample screen display below:

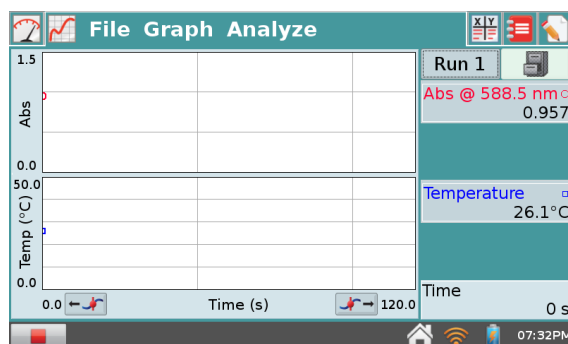


3. Tap on the "Interval" box, change the interval to 10, and press OK. Tap on the "Duration", change the duration to 120 seconds and press OK until you are returned to the data collection screen. See sample screen display below:

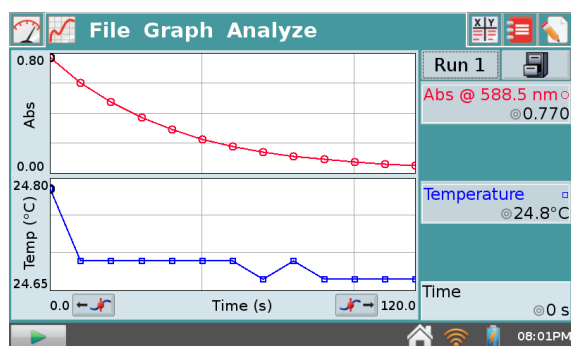


4. This step should be done carefully and quickly. In order to ensure that the reaction solutions are properly mixed, you will pour the reaction solution back and forth between the two reagent test tubes, then place the cuvette test tube into the SpectroVis instrument and tap on Collect  to start data collection. Proceed as follows:

- Pour the NaOH solution into the glass test tube containing the CV⁺ solution; then pour the solution mixture back into the plastic test tube and then back again into the glass test tube. Wipe the glass test tube cuvette with a Kimwipe and then place the cuvette into the spectrophotometer sample holder, making sure the cuvette is securely in place and properly aligned. Tap on Collect  to start data collection. Data collection will begin, and the Lab Quest 2 will graph the data in real time, as shown in the sample screen below. In order to determine the reaction temperature, place the thermometer probe into the reaction solution. Make sure that the probe is not blocking the light beam.



- When the run is over, the Stop  at the left bottom corner of the screen will change back to Collect  and the graph will autoscale the data.
- Tap on the File Cabinet  to store the collected data. The "Run 1" tab will automatically switch to "Run 2", making it possible for you to collect run 2 data without losing run 1 data. Collect data for Run 2 and then Run 3 by repeating steps 4-6 using the solutions for runs 2 and 3, respectively.



- Once you have collected data for all three kinetics runs, tap on the Table screen  to access your data. See sample Table screen below:

Run 1			Run 2		
Time (s)	Temp (°C)	Abs @ 589	Time (s)	Temp (°C)	Abs
0	23.6	0.873	0	24.0	
10	24.3	0.813	10	23.8	
20	24.8	0.754	20	23.8	
30	25.0	0.699	30	24.3	
40	25.2	0.646	40	24.5	
50	25.4	0.601	50	24.7	
60	25.5	0.556	60	24.7	
70	25.5	0.511	70	24.8	

- Copy the values to your observations sheet. Take the temperature value at $t = 30$ s as the initial temperature and the last value as the final temperature. Use the *average* of these values as the reaction temperature.
- If any of the data appears unreasonable, you may wish to perform additional runs. Remember, the more data you have the more accurate your results will be.

M-16

10. Discard remaining solutions of crystal violet into the toxic waste container in the fume hood and rinse the glassware first with ~ 1 mL of 1 mol/L HCl. Then clean the glassware thoroughly with tap water and then rinse three times with deionized water.

IMPORTANT! Because the spectrometer's light source has a limited life, please ensure that the spectrometer is disconnected from the Lab Quest 2 unit before leaving the lab.

Before leaving the laboratory, check that all your equipment is clean and returned to the correct location: complete the sign-out checklist on page M-26 and have it signed by your lab instructor. Remember to have your Observation Sheet(s) checked and signed by your laboratory instructor before leaving.

If time allows, your instructor will ask you to complete the following post-lab data analysis (starting on page M-18). Note that this work will eventually be submitted as part of the first lab report so you should take full advantage of the opportunity to complete this work in-lab with your instructor's supervision.

Before leaving the laboratory, it is strongly recommended that you do the following:

1. Choose 1 of your kinetics runs (**for best results, use the run with the highest concentration of NaOH**) and prepare 3 plots:
 - i. $[CV^+]$ versus t
 - ii. $\ln[CV^+]$ versus t
 - iii. $1/[CV^+]$ versus t

Instructions for plotting using Google sheets begin on page M-18 and (if time allows) your lab instructor will lead your lab section through this exercise. You will eventually submit these **three plots** along with your lab report.

2. Based on the three plots you just prepared, determine the order of reaction with respect to CV^+ . Then, for the other two kinetics runs, prepare the corresponding correct straight-line kinetics plot. These **two plots** will also eventually be submitted with the lab report.

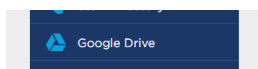
By completing the above plots before leaving the laboratory, you will have completed a significant portion of your lab report (Q1, Q2, and Q3 on page N-13).

Post-Lab Data Analysis

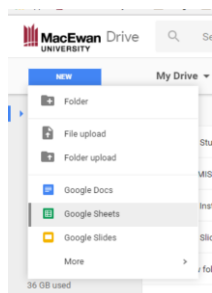
You will generate a fair amount of data as you complete your two kinetics runs and complete the table on the Observations sheet. In principle, this data can be processed and analyzed manually, but it is far more convenient (and accurate) to use a computer spreadsheet program to do this. Much of what follows will probably be demonstrated during the lab and in likelihood will be completed before you depart. The instructions that follow will make use of some typical sample data; you will, of course, be working with your own data during and after the lab!

To the right is some sample data for demonstration purposes. You are welcome to use any spreadsheet software that you have available to you for the purposes of processing the data, but these instructions will assume the use of Google Sheets: if you are using one of the laboratory laptops to input data as you go, that data will be available to you on any network-connected laptop afterwards.

1. Open up a window in a browser (Google Chrome, for example) and log on to your MacEwan account via the MacEwan portal. Towards the left of the screen, you should be able to see a menu option for Google Drive: click on it.

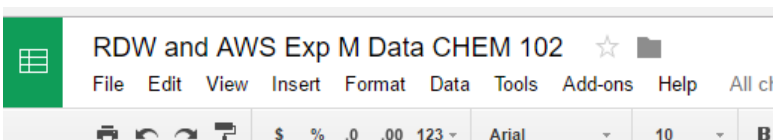


2. Towards the upper-left of the next screen, select “New” and then “Google Sheets”:



3. Give your spreadsheet a meaningful title by clicking in the top-left where it says “Untitled Spreadsheet”. One suggestion is to use your initials as well as your partner’s initials. Also include information about the Experiment itself to make it easier to find the data later on, if necessary:

Run 1 (Example)	
Time (s)	Absorbance
0	0.873
10	0.813
20	0.754
30	0.694
40	0.646
50	0.601
60	0.556
70	0.511
80	0.471
90	0.437
100	0.404
110	0.371
120	0.343
Initial Temp (°C)	Final Temp (°C)
25.0	25.5



4. Begin by transferring the data into the spreadsheet. Label your data columns at the top. If your entry exceeds the default column width, you can make the columns wider or, if you prefer, select the entry in question and then choose the “Wrap” option from the “Text Wrapping” menu. This is merely an optional cosmetic step, and won’t have any influence on the data itself.



5. With the data in place, your spreadsheet should look something like this:

	A	B	C	D	E	F
1	Run 1 Time (s)	Run 1 Absorbance				
2	0	0.873				
3	10	0.813				
4	20	0.754				
5	30	0.694				
6	40	0.646				
7	50	0.601				
8	60	0.556				
9	70	0.511				
10	80	0.471				
11	90	0.437				
12	100	0.404				
13	110	0.371				
14	120	0.343				
15						

6. Ultimately, to determine the order of reaction, you’ll need to prepare three plots: $[CV^+]$ versus time, $\ln [CV^+]$ versus time, and $1/[CV^+]$ versus time. We’ll use the spreadsheet to calculate $[CV^+]$, $\ln [CV^+]$, and $1/[CV^+]$ for each measurement. Start by labelling appropriate columns in the spreadsheet:

M-20

	A	B	C	D	E
1	Run 1 Time (s)	Run 1 Absorbance	[CV+]	ln [CV+]	1/ [CV+]
2	0	0.873			
3	10	0.813			
4	20	0.754			
5	30	0.694			
6	40	0.646			

7. Next, use the absorbance values (column B in the example shown) to calculate the corresponding [CV⁺] using the known value of the pathlength ($b = 1.00$ cm) and the molar absorptivity for CV⁺ at 588.5 nm. Basically, you'll divide the absorbance value (Column B in our example) with the slope of the pre-lab calibration curve on page M-8. Click on cell C2, and then enter:

=B2/83264

In the above entry, B2 refers to the cell containing the absorbance value, and 83264 refers to the slope of the calibration curve: you'll only be able to use three significant digits in your answer because there are only three significant digits in the absorbance. By default, the spreadsheet will show unrounded values in each cell so you'll need to keep this in mind later on when reporting your data.

f_x =B2/83264				
	A	B	C	D
1	Run 1 Time (s)	Run 1 Absorbance	[CV+]	ln [CV+]
2	0	0.873	0.000010484723	
3	10	0.813		
4	20	0.754		

8. Next, select cell D2 and command it to display the natural logarithm of [CV⁺] (in other words, $\ln$ [CV⁺]). Do this by inputting the following in cell D2:

$$=\ln(C2)$$

Be aware that the command contains a lowercase letter L, not a capital letter I nor a number 1.

f_x	=ln(C2)				
	A	B	C	D	E
1	Run 1 Time (s)	Run 1 Absorbance	[CV+]	ln [CV+]	1/ [CV
2	0	0.873	0.000010484723	-11.46559129	
3	10	0.813			
4	20	0.754			

9. Finally, use cell E2 to compute the inverse of [CV⁺] (i.e. $1/[\text{CV}^+]$) by inputting:

$$=1/C2$$

Assuming that you've followed along exactly, you should see:

f_x =1/C2						
	A	B	C	D	E	F
1	Run 1 Time (s)	Run 1 Absorbance	[CV+]	ln [CV+]	1/ [CV+]	
2	0	0.873	0.000010484723	-11.46559129	95376.8614	
3	10	0.813				
4	20	0.754				

10. Rather than repeat this work manually for rows 3 through 14, we'll simply copy the formulae from cells C2, D2, and E2 into the rows beneath. Do this by holding down the left mouse-button and dragging a selection box around these three cells, and then choosing "Copy" from the "Edit" menu (or by using the shortcut CTRL-C).
11. Next, paste the formulae into rows 3 through 14 by holding down the left mouse button and dragging a selection box around the range from C3 to E14. Choose "Paste" from the "Edit" menu (or use the shortcut CTRL-V):

	A	B	C	D	E
1	Run 1 Time (s)	Run 1 Absorbance	[CV+]	ln [CV+]	1/[CV+]
2	0	0.873	0.000010484723	-11.46559129	95376.8614
3	10	0.813	0.000009764123	-11.53679573	102415.7442
4	20	0.754	0.000009055534	-11.61213447	110429.7082
5	30	0.694	0.000008334934	-11.69505488	119976.9452
6	40	0.646	0.000007758455	-11.76672734	128891.6409
7	50	0.601	0.000007218005	-11.83893191	138542.4293
8	60	0.556	0.000006677555	-11.91675855	149755.3957
9	70	0.511	0.000006137106	-12.00115725	162943.2485
10	80	0.471	0.000005656706	-12.08266875	176781.3163
11	90	0.437	0.000005248366	-12.15759365	190535.4691
12	100	0.404	0.000004852036	-12.23611196	206099.0099
13	110	0.371	0.000004455707	-12.32132478	224431.2668
14	120	0.343	0.000004119427	-12.39979639	242752.1866
15					

12. You'll need to generate three plots: you can generate a plot by selecting "Chart" from the "Insert" menu. Don't be concerned if a nonsensical chart is automatically generated (or one that simply says "No data": we'll need to change some settings within the chart editor. **Note: the initial automatically generated chart will vary depending on which cell(s) you have selected before selecting "Chart" from the "Insert" menu. In principle, you should be able to prepare your chart regardless of this initial selection but in the interest of ensuring that these instructions reflect what appears on your screen you may find it helpful to select an empty cell, such as F1, before selecting "Chart" from the "Insert" menu. Even then, Google Sheets will make predictions based on other charts you have created, so it is very likely your first automatically generated chart will differ from the people around you!**

We'll start by generating the first of three plots: [CV+] vs time.

13. In the chart editor, within the "Data" tab, choose the "Scatter chart" Chart type.
14. In the chart editor, within the "Data" tab, set the data that will appear on the y-axis (your dependant variable) by editing the "Series" entry to contain Column C (and only Column C, for this plot). You may need to remove any extra series entries that Google Sheets may have automatically included.
15. In the chart editor, within the "Data" tab, set the data that will appear on the x-axis (your independant variable) by editing the "X-Axis" entry to contain Column A (and only Column A). The Chart editor panel should appear as follows:

Chart editor

×

DATA

CUSTOMIZE

Chart type

Scatter chart

▼

Data range

A1:A1000,C1:C1000

Combine ranges

Horizontally

▼

X-AXIS

123 Run 1 Time (s)

⋮

SERIES

123 [CV+]

⋮

Add Series

☐ Switch rows / columns

☒ Use row 1 as headers

☒ Use column A as labels

☐ Aggregate column A

16. It is likely that you'll need to edit the title as well as the labels along each axis. In the chart editor, within the "Customize" tab, you can edit the chart & axis labels by choosing the item you wish to edit from the "Type" drop-down list. Your overall chart title should be concise but descriptive. Each axis should identify the corresponding quantity and also include units.
17. Also within the "Customization" tab, you can (and should) choose to add a trendline. Do this by expanding the "Series" section within the "Customization" tab and then select the "Trendline" checkbox. You are interested in identifying a linear trend, so you may select "Linear" from the "Type" selection list. Of course, in this example plot the data doesn't appear to be linear, but you can still *show* the best-fit trendline on the plot. To include the linear equation for the best-fit linear trendline, choose "Use Equation" from the "Label" box. As well, it is wise to include the R^2 value, so tick that box as well.

18. At the time of preparing these instructions, the equation for the trendline was not appearing properly on the graph itself. However, the slope and y-intercept for the plot of [CV+] vs time can be calculated independently from the graph:

- To calculate slope, select an empty cell and enter the following command:

```
=slope(C:C,A:A)
```

- To calculate the y-intercept, select an empty cell and enter the following command:

```
=INTERCEPT(C:C,A:A)
```

- In either case, the first range (before the comma) defines the dependant variable (y-axis) and the second range (following the comma) defines the independent variable (x-axis). "C:C" simply tells the spreadsheet to consider all of column C for the y-axis; the software automatically ignores the text headings.

Assessment and report:

Experiments M and N will be assessed together as a combined pair of experiments (**20 points total**), based on the submission of a **lab report (N-13 through N-18)** which is **due at the start of Experiment O**.

Along with the report, you will submit your observation sheets (**M-25 and N-11**)

As well, your report should include hardcopies of **six plots** generated by spreadsheet software:

- Three plots from one of the kinetics runs in Experiment M
- One plot from a second kinetics run in Experiment M
- One plot from the third kinetics run in Experiment M
- The plot of $\ln(k)$ versus $1/T$ from the Experiment N data

You *do not* need to attach hardcopies of the plots generated in Q2, page N-16.

Observation Sheet: Effect of Concentration on Rate of Reaction

Approximate Molarity of stock crystal violet (CV⁺) solution: 3.00x10⁻⁵ mol/L

Wavelength of maximum absorbance ($\lambda_{\max}$): 588.5 nm

Molar Absorptivity of CV⁺ at $\lambda_{\max}$
(from advance study assignment): 8.32 x 10⁴ L/(mol·cm)

Molarity of NaOH used in Run 1: 3.00 x 10⁻¹ mol/L

Molarity of NaOH used in Run 2: 2.00 x 10⁻¹ mol/L

Molarity of NaOH used in Run 3: 1.00 x 10⁻¹ mol/L

Run 1		Run 2		Run 3	
Time (s)	Absorbance	Time (s)	Absorbance	Time (s)	Absorbance
0	<u>0.880</u>	0	<u>1.035</u>	0	<u>1.185</u>
10	<u>0.721</u>	10	<u>0.906</u>	10	<u>1.111</u>
20	<u>0.590</u>	20	<u>0.792</u>	20	<u>1.041</u>
30	<u>0.483</u>	30	<u>0.693</u>	30	<u>0.975</u>
40	<u>0.396</u>	40	<u>0.606</u>	40	<u>0.914</u>
50	<u>0.324</u>	50	<u>0.530</u>	50	<u>0.856</u>
60	<u>0.266</u>	60	<u>0.464</u>	60	<u>0.802</u>
70	<u>0.217</u>	70	<u>0.406</u>	70	<u>0.751</u>
80	<u>0.178</u>	80	<u>0.355</u>	80	<u>0.704</u>
90	<u>0.146</u>	90	<u>0.311</u>	90	<u>0.660</u>
100	<u>0.119</u>	100	<u>0.272</u>	100	<u>0.618</u>
110	<u>0.098</u>	110	<u>0.238</u>	110	<u>0.579</u>
120	<u>0.080</u>	120	<u>0.208</u>	120	<u>0.543</u>
Initial Temp (°C)	Final Temp (°C)	Initial Temp (°C)	Final Temp (°C)	Initial Temp (°C)	Final Temp (°C)
<u>23.4</u>	<u>23.9</u>	<u>23.7</u>	<u>24.4</u>	<u>23.8</u>	<u>24.3</u>

Formatted: Left

M-26

Student: (name) _____ (signature) _____

Instructor: (signature) _____ **Bench #** ____ **Laboratory Section:** _____

CHEM 102: Kinetics I (Concentration) Sign-out Checklist

Equipment Cleaned and Returned to Common Glassware Drawer	Initials
250 mL Beakers	
Equipment Cleaned and Returned to Side/Back Bench	Initials
Test Tubes	
Equipment Remaining on Students Bench	Initials
LabQuest 2 with power cord	
Spectrophotometer with USB Cable	
Temperature probe	
Other Cleaning and/or Upkeep	Initials
Bench wiped with a damp paper towel	
Sinks clear of broken/dirty glassware	
Water bottles returned to end of bench	

Student: (name) _____ (signature) _____

Instructor: (signature) _____ **Bench #** ____ **Laboratory Section:** _____