CHEMISTRY 206

Experiment 4: A KINETIC STUDY

Instructor's Informal Preamble

Chemists are interested in figuring out how reactions happen (*i.e., mechanisms*), and how quickly they occur (*i.e., rates*). Both of these topics lie within the realm of *chemical kinetics*. In this experiment, we will focus on investigating reaction rates. In general, the rate at which a reactant disappears (or a product forms) during a reaction is a function of:

(1) the concentrations of the reactants, *and*

(2) the temperature at which the reaction occurs.

The importance of reactant concentrations is fairly intuitive: the more reactant there is, the more often the molecules will collide with other reactants, and thus, the faster the reaction will be. *[If a reaction is a unimolecular decomposition, we see the same effect: the probability that one molecule will spontaneously fall apart at any given moment is higher when there are more molecules present.]* The dependence of a reaction's rate on reactant concentration is summarized using a *differential rate law*:

$$\text{Rate (mol L}^{-1}\text{ sec}^{-1}) \;=\; k\,[\text{reactant}_A]^p[\text{reactant}_B]^q[\text{reactant}_C]^r\ldots$$

where the superscripts (p, q, r…) denote the order of the reaction with respect to reactants A, B, C respectively, and k is the rate constant. You should recall that if a reaction's rate is *linearly dependent* on a reactant's concentration, then the reaction is described as *first order* with respect to that reactant; similarly, if the rate depends on the *square* of the concentration, it is called *second order*. Experimentally, the rate law for a reaction is usually determined using one of two methods:

(1) by changing the reactant concentrations one at a time and seeing how the initial rate changes (the *method of initial rates*), which yields the differential rate law;

(2) by monitoring each reactant's concentration over a long period of time, and plotting the data various ways to match it with a possible integrated rate law.

In this experiment, you will be using *a combination of these two methods* to figure out the rate law for a particular reaction.

This brings us to the second important factor to consider: temperature. The *rate constant*, k, accounts for the fact that not all collisions between reactants actually lead to reaction. Collisions must be energetic enough *and* occur in an orientation that encourages the appropriate bonds in the reactants to start breaking and new bonds to start forming. The Arrhenius equation summarizes these requirements:

$$k = Ae^{-(Ea/RT)} \quad \text{where R is the gas constant, R = 8.31451 J mol}^{-1}\text{ K}^{-1}$$

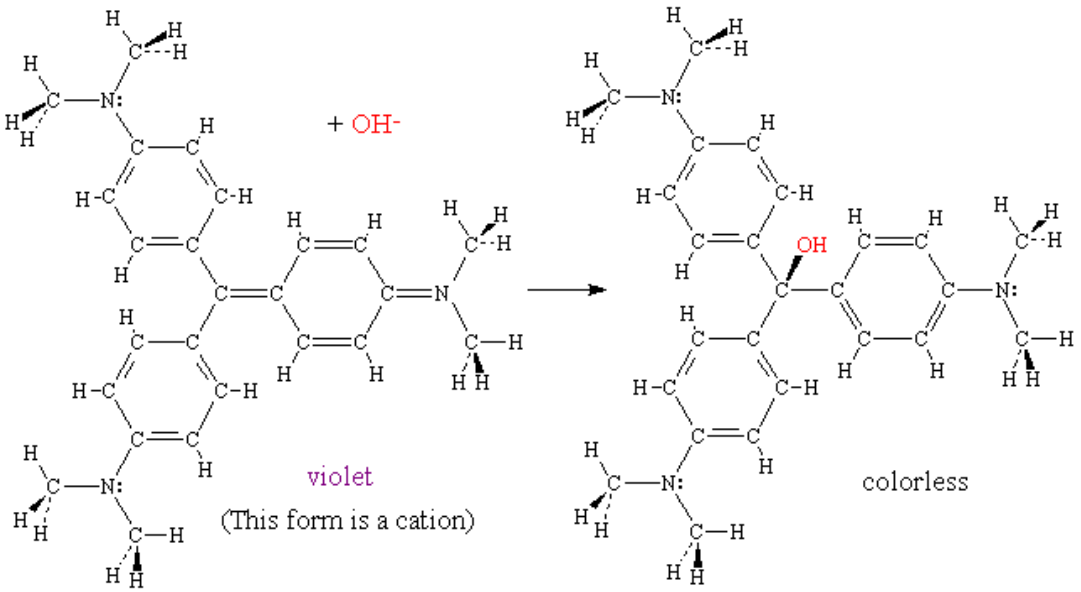
The constant A contains information about how common collisions with a reaction-inducing orientation are, while the exponential term compares the energy required (*activation energy*, E_a) with the thermal energy available at that temperature. At higher temperatures, reactions proceed more quickly for two reasons: more collisions occur, and more of them have sufficient energy to lead to reaction.

CHEMISTRY 206

Experiment 4: A KINETIC STUDY: THE REACTION OF CRYSTAL VIOLET WITH SODIUM HYDROXIDE

Introduction

In this experiment, you will study the kinetics of the reaction between a dye called crystal violet and the hydroxide ion. The reaction is depicted below:



The large molecule on the left is the crystal violet cation ("cv^+") – we have left out the anion associated with it (*e.g.,* Cl^- or Br^-) for clarity. Notice that every carbon atom in the central part of the cv^+ molecule has a double bond to a neighbouring atom plus two other single bonds; thus, every one of these C atoms is sp^2-hybridized. This allows the electrons in the π-bonds to be spread out over the p-orbitals of all the carbons in the rings of the molecule; we describe this as a large *conjugated* system. Conjugated molecules like this are typically intensely coloured (explanations as to *why* are beyond the scope of this course); the cv^+ cation itself is violet in colour. When an OH^- group bonds to the central carbon (which is therefore no longer sp^2-hybridized), the conjugation between the rings is disrupted and the species becomes colourless.

This colour change makes the reaction of cv^+ with hydroxide ion easy to follow *colorimetrically*, that is, by monitoring the intensity of the violet colour, which disappears as the reaction proceeds. To monitor this, we use a device called a colorimeter, which measures the amount of light that passes through a solution (*i.e.*, the *percent transmittance*). This quantity can be converted mathematically (by taking the logarithm) into another number called the *absorbance*, which is useful because absorbance is *directly proportional to the concentration* of the coloured

species. Molar concentration, c, and absorbance, A, are related by the Beer-Lambert Law: $A = \varepsilon bc$, where ε is the species' *molar absorptivity* (whose value depends on molecular structure and solvent), and b is the path length (the distance, in cm, that the light must travel through the solution). With our experimental setup, where light passes through 1 cm of cv^+ solution, the concentration of cv^+ will be calculated by dividing the absorbance by 264488 L mol^{-1}, which is the value of ε for cv^+ in water. *Colorimetry* measurements like this are commonly used to collect concentration *vs.* time data for the purpose of studying reaction kinetics.

In this experiment, your goal is to characterize the kinetics of the reaction between crystal violet and hydroxide anion. The differential rate law will have the form:

$$\text{Rate} = k\,[cv^+]^p[OH^-]^q$$

First, you will collect cv^+ concentration *vs.* time data and then apply the graphical (or trial-and-error) method to determine the reaction's order, p, with respect to cv^+. Because hydroxide is colourless, it cannot be monitored directly by colorimetry. Thus, to determine the order, q, with respect to hydroxide ion, you will use a trick that lets you once again monitor cv^+ concentration; the trick is outlined in the Part 2 description and is roughly similar to the method of initial rates. Once you have determined the values of both p and q, you will determine the value of the rate constant, k, at room temperature. Finally, you will investigate the temperature dependence of the reaction's rate constant, in order to determine the activation energy of the reaction.

PART 1: Determination of the Order of the Reaction with Respect to Crystal Violet

In Part 1, in order to determine the order of the reaction with respect to crystal violet, you will monitor the disappearance of the crystal violet as a function of time. The reaction will be done using a very large excess of hydroxide ion, because under these conditions the concentration of hydroxide, $[OH^-]$, will change so little during the course of the reaction that it can be treated as a constant. Thus, any changes in reaction rate observed as the reaction proceeds will be caused solely by the fact that the cv^+ concentration will be continually decreasing; this will enable us to evaluate the reaction's dependence on $[cv^+]$ alone. Because both k and $[OH^-]^q$ will be approximately constant, we combine the two and call this term k_{eff} (*i.e., effective rate constant*). The rate law therefore becomes:

$$\text{Rate} = k\,[OH^-]^q[cv^+]^p = k_{eff}\,[cv^+]^p$$

The constant, k_{eff}, is formally known as a pseudo rate constant: it is a combination of a rate constant and a concentration term that stays roughly constant under the reaction conditions used.

Most reactions are either zeroth order (p = 0), first order (p = 1), or second order (p = 2) with respect to any particular reactant, and normally chemists use a trial-and-error approach to determine which one applies. Using calculus, the equation above can be integrated to give the following three potentially correct integrated rate laws:

If p = 0 ("zeroth order"): $[cv^+]_t = -k_{eff}\,t + [cv^+]_o$

If p = 1 ("first order"): $\ln[cv^+]_t = -k_{eff}\,t + \ln[cv^+]_o$

If p = 2 ("second order"): $1/[cv^+]_t = k_{eff}\,t + 1/[cv^+]_o$

These equations all define straight lines ($y = mx + b$).

To analyze the data collected in Part 1, you will make the above three trial plots. Only one of the plots will appear as a reasonably straight line: the one corresponding to the reaction's actual order with respect to crystal violet, p. The slope of the line will provide a value for the pseudo rate constant, k_{eff}. [You will label this constant as $k_{eff\text{-}1}$, because you found it in Part 1.]

PART 2: Determination of the Order of the Reaction with Respect to Hydroxide

In Part 2, you will collect another set of concentration *vs.* time data, this time using *half* the hydroxide concentration used in Part 1; the other experimental conditions ($[cv^+]$, T) will remain the same. Analyzing the data the same way as in Part 1 will yield a new value for the pseudo rate constant k_{eff}, this time labeled $k_{eff\text{-}2}$.

The next step in your analysis will resemble a Method of Initial Rates problem: the initial OH^- concentration was lowered by a factor of 2, so you must determine if a similar change in reaction rate occurred – by comparing the pseudo rate constants $k_{eff\text{-}2}$ and $k_{eff\text{-}1}$. This will reveal whether the reaction is 0^{th}, 1^{st} or 2^{nd} order in OH^-. The analysis can be done algebraically as follows:

From Part 2:	$k_{eff\text{-}2} = k\,[OH^-]_2^{\,q}$
From Part 1:	$k_{eff\text{-}1} = k\,[OH^-]_1^{\,q} = k\,(\,2[OH^-]_2\,)^q = k\,2^q\,[OH^-]_2^{\,q}$
Divide to compare:	$k_{eff\text{-}1} / k_{eff\text{-}2} = k\,2^q\,[OH^-]_2^{\,q} / k\,[OH^-]_2^{\,q} = 2^q$
Take log of both sides:	$\log(k_{eff\text{-}1} / k_{eff\text{-}2}) = q\,\log(2)$

Once you have solved for q, the order with respect to hydroxide, you will be able to write a complete differential rate law for the reaction between crystal violet and hydroxide: Rate $= k\,[cv^+]^p[OH^-]^q$. Having done this, you will be able to go back and solve for the numerical value of the true rate constant, *k*.

PART 3: Determination of the Reaction's Activation Energy

In Part 3, you will investigate the dependence of reaction rate on temperature. A general "rule-of-thumb" for most organic reactions is that the reaction's rate will be between doubled and tripled for every 10 ^oC rise in temperature (assuming all else is kept constant). If we know the activation energy, E_a, for a reaction, we can accurately predict the dependence of the reaction's rate constant on temperature, rather than simply estimating it with the rule-of-thumb. In this last part of the experiment, we will determine the E_a for the reaction of crystal violet with hydroxide.

The rate constant for a reaction is a function of the activation energy and the temperature according to the Arrhenius equation, which can be written in logarithmic form:

$$\ln(k) = \ln(A) - E_a/(RT)$$

Remember: A is a constant characteristic of the reaction, R is the gas constant (R = 8.3145 J mol^{-1} K^{-1}) and T is the temperature in Kelvin. A plot of ln(*k*) versus 1/T, called an Arrhenius plot, has the form of a straight line with slope = $-E_a/R$. Thus, by experimentally determining the (true) rate constant at several different temperatures and constructing an Arrhenius plot, we can calculate the reaction's activation energy. This information would give us the ability to predict the rate constant for our reaction at other temperatures. It could also shed light on the mechanism of the reaction, since it could provide information about what the transition state of the reaction looks like (which is beyond the scope of this course).

Experiment Summary

Parts 1 & 2: Determining the Rate Law

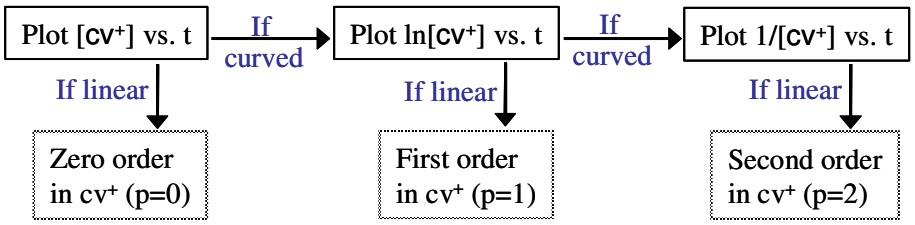
You will acquire kinetic data at room temperature, consisting of the percent transmittance of the solution as a function of time for two different concentrations of (excess) sodium hydroxide. Using the software's spreadsheet, you will convert the percent transmittance data into absorbance data, which you will then convert into concentration data. The trial-and-error graphical analysis of the first set of concentration *vs.* time data (Part 1) will allow you to determine the order of the reaction with respect to the crystal violet concentration. A comparison of the first and the second (Part 2) sets of data will allow you to determine the order of the reaction with respect to the hydroxide ion concentration. You will then be able to calculate the rate constant for the reaction at room temperature, and write a complete rate law for the reaction.

Part 3: Determining the Activation Energy

By measuring the kinetic data for one starting concentration at several temperatures, you will be able to construct an Arrhenius plot and obtain the reaction's activation energy.

Goals: for reaction $cv^+ + OH^- \rightarrow cv{-}OH$**, determine rate law** rate = $k\,[cv^+]^p[OH^-]^q$**, and** E_a

PART 1: To find p, the order of reaction with respect to crystal violet, cv^+ :
- Choose large initial $[OH^-]_1$ so that $[OH^-]_1^q \sim$ constant ⇨ rate = $k_{eff\text{-}1}\,[cv^+]^p$
- Monitor $[cv^+]$ over time by following disappearance of colour
- Graphically analyze data to test for the three common orders (see flowchart below)
- Use graph that matches order with respect to cv^+ to determine value of $k_{eff\text{-}1} = k\,[OH^-]_1^q$



PART 2: To find q, the order of reaction with respect to hydroxide, OH^- :
- Choose new large initial $[OH^-]_2$ ⇨ rate = $k_{eff\text{-}2}\,[cv^+]^p$ *(but now p is known…)*
- Monitor $[cv^+]$ over time & graph *(once…)* to find value of $k_{eff\text{-}2} = k\,[OH^-]_2^q$
- Compare $k_{eff\text{-}1}$ & $k_{eff\text{-}2}$ to determine value of q
- Sub p & q into rate law to yield the complete differential rate law
- Use data from Parts 1 & 2 to find average value of true rate constant *k* at room temperature

PART 3: To find the reaction's activation energy, E_a :
- Perform four more runs (at 40, 35, 30, 25°C) using Part 2's initial concentrations
- Use k_{eff} values from 40, 35, 30, 25°C to determine rate constant *k* at each temperature
- Make Arrhenius plot (ln*k* vs 1/T for T = 40, 35, 30, 25°C and room temperature)
- Use graph to determine E_a

Prelaboratory Assignment

Read the procedure and answer the Prelaboratory Questions before coming to the lab. Your demonstrator will inspect and collect in your prelab before you are permitted to begin the experiment - keep a copy of it for yourself, and have the TA sign your receipt record.

Materials

Apparatus

- Computer running Logger Pro 3 (with a colorimeter and Go!Link interface)
- 1 cuvette *[Do not clean plastic cuvettes with acetone – it etches the plastic.]*
- Kimwipes to clean cuvette *[Do not use paper towel – it scratches them.]*
- wash bottle
- waste beaker
- 2 small test tubes
- hot plate, 250 mL beaker (water bath), stand, and 2 clamps
- thermometer
- 0.5 mL volumetric pipette for NaOH solution
- Pasteur pipette bulb
- 1000-5000 µL automatic pipettor for crystal violet solution (one for the whole lab)

Reagents and Materials

- 0.1 M sodium hydroxide (prepared by technical staff)
- 2.25×10^{-5} M crystal violet (prepared by technical staff)
- 6 pieces of Parafilm, or a rubber stopper or cork

Procedure

The colorimeter should be connected to the interface and ready for use. You will need to calibrate the instrument (described below) before performing your experiment. Then, the reaction will be monitored by mixing the reactants and placing them in the cuvette so that the percent transmittance can be measured.

Initial Set-up of the Colorimeter

1. Connect the colorimeter to your data collection interface, called "Go!Link". (Go!Link is a single-channel interface that connects directly to the computer's USB port.)
2. On the computer, double click the "CHEM 206 Experiment 4" icon to open the data acquisition window. The program will automatically display the current transmittance reading from the colorimeter.

3. Using the arrow keys on the front panel of the colorimeter, select the red LED with λ = 565 nm. *Note: Crystal violet has maximum visible-light absorbance (λ_{max}) at 590 nm. A linear Beer's law curve (i.e., absorbance vs. concentration) can usually be obtained at any wavelength in the vicinity of a substance's λ_{max}. Thus, to monitor the crystal violet concentration, we select the LED with the wavelength closest to 590 nm.*
4. Let the instrument stabilize ("warm-up") for 5 min prior to calibration.

Calibration of the Colorimeter

1. Inspect your cuvette. If it is stained purple after rinsing it with water, ask for a new one.
2. *Insert the "blank" sample:* Open the colorimeter's lid. Insert a cuvette filled $^3/_4$ -full with distilled water (this will define 100 % transmittance, or 0 absorbance, at 565 nm). *Make sure one of the clear sides of the cuvette is lined up with the arrow at the top of the cuvette slot.* Close the colorimeter's lid.
3. *To begin calibration:* Hold down the CAL button on the colorimeter. Release the button when the red LED stops flashing. *(You do not need to go to a special calibration menu in the data collection program.)* The transmittance shown on the computer display should read 99.99-100.01 %. If not, let the colorimeter warm up a little longer and try again.
4. *When calibration is complete:* Remove the cuvette from the colorimeter, empty it, and dry it gently (both inside and out) with a Kimwipe. Proceed with the experiment.

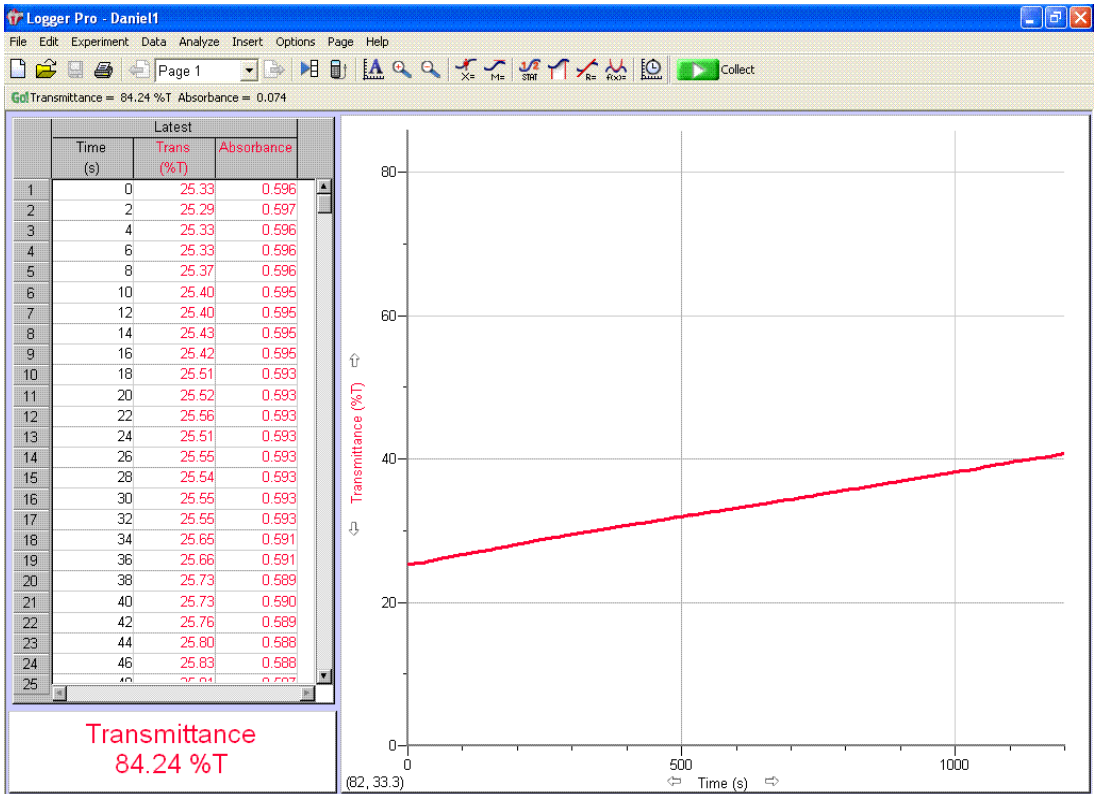
Part 1: Determining the order of reaction with respect to crystal violet

1. To a clean dry test tube, add exactly 4.500 mL of crystal violet solution, using an automatic pipettor equipped with a disposable plastic tip. *Important: ask your TA to show you how to use the pipettor – it is an expensive piece of equipment that can be damaged by pushing too hard on the plunger or by turning the volume dial too far.*
2. Into a second clean dry test tube, pour roughly 2 mL of 0.1 M NaOH stock solution.
3. Using a 0.50 mL volumetric pipette equipped with a small Pasteur-pipette bulb, transfer exactly 0.50 mL of the NaOH solution from the test tube into the crystal violet solution. *To use a volumetric pipette: Draw the liquid up to <u>above</u> the calibration line, lift the pipette out of the liquid, then gently replace the bulb with your fingertip. Holding the pipette vertical, carefully lower the liquid level (by very slightly moving your finger) until the bottom of the meniscus lies <u>exactly</u> at the calibration line. Touch the pipette tip to the side of the tube to remove any clinging droplets. Then, position the pipette over the receiver tube and let gravity control how much flows out – do not force out the last drop.*
4. As quickly as possible, mix the contents of the test tube by covering it with a piece of Parafilm or a stopper and inverting it twice. Then fill a cuvette to $^3/_4$ full with the mixture, wipe the outside of the cuvette with a Kimwipe, place it in the colorimeter (clear side aligned with the arrow), and close the lid.
5. Immediately click COLLECT on the computer to start the data acquisition. *While acquiring, do not touch the calorimeter or bench – vibrations cause "noise" in the data.*

6. After about 1000 seconds, click on STOP to stop the data collection.
7. Click on FILE, then SAVE AS, and save the data file under a logical name *(e.g., jd-Ex4-Part1-data)* onto the computer's Desktop, into the folder called *Chem 206 Expt 4 Data*. (If a folder like this does not yet exist: right click inside the Save As window, choose New, then Folder, then name the new folder as specified above).
8. Dispose the contents of the cuvette into the waste beaker, rinse it with distilled water, and dry it inside and out with a Kimwipe to prepare for the next run.

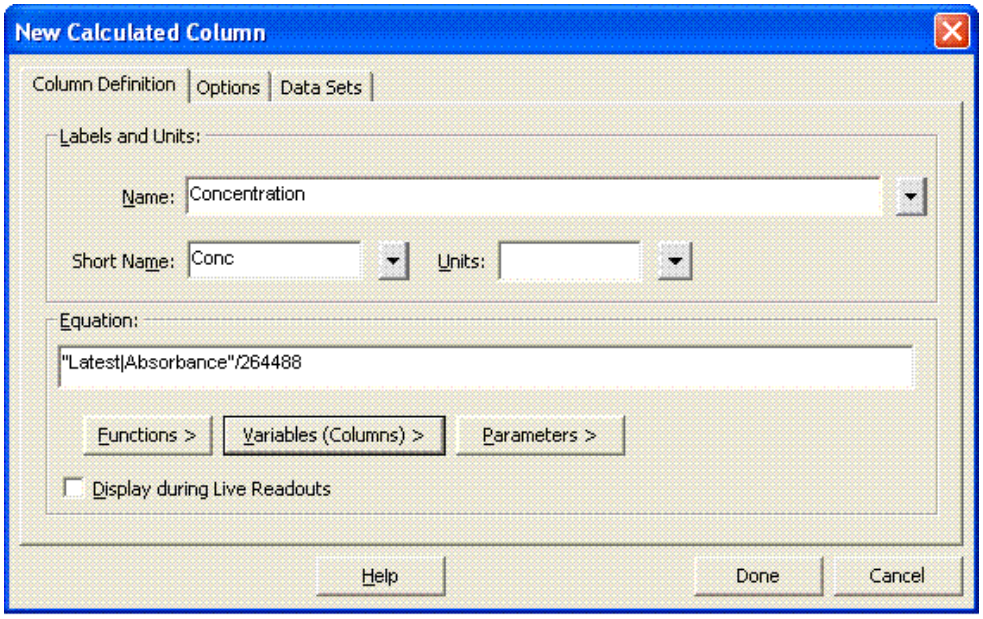
Data Analysis for Part 1

1. Select the file to be opened (click on FILE, then OPEN…), and open it.
2. The screen should look like the following figure. The left part of the window contains a spreadsheet with three columns, containing time values (headed "s"), percent transmittance values (headed "%T") and absorbance values. The right part of the window shows a plot of percent transmittance *vs.* time in seconds.



To determine the order of the reaction with respect to cv^+ and to determine the rate constant, $k_{eff\text{-}1}$, some data treatment must be done using the spreadsheet.

3. Four new data columns must be created. To do this, click on DATA in the menu bar, then NEW CALCULATED COLUMN. A window like the one shown on the next page will appear. For each new column, you will need to provide a name, short name (can be same as name) and equation - see details in step 4.



4. The names and equations for the new columns are given in the table below.

Name	Conc	–Conc	–ln(Conc)	1/(Conc)
Equation	(Absorbance)/264488	–(Conc)	–ln(Conc)	1/(Conc)

- If your equation involves simple arithmetic: click "Variables (Columns) > ", then scroll down and choose the column's name (*e.g.*, to calculate concentration, select the Absorbance column). Use the keyboard to complete the equation. Press DONE.
- If the calculated values in the new column are displayed as 0.000, you need to change to scientific notation. Double click on the column, then click OPTIONS, then click USE SCIENTIFIC NOTATION, then click DONE.
- If your equation makes use of a function: first click on "Functions > ", then scroll down and select the desired function (*e.g.*, natural logarithm, *ln*). You will then see the cursor blinking inside the function. Click on "Variables (Columns)>" and follow the above instructions to complete your equation.

5. When the columns are made, save your changes: Click on FILE in the menu bar, then SAVE AS, but use the same filename as earlier.

6. Now, the following three graphs must be plotted (*see instructions on p. 4-10*):

   Zeroth order test: –Conc *vs.* time (seconds)
   First order test: –ln(Conc) *vs.* time (seconds)
   Second order test: 1/Conc *vs.* time (seconds)

   These will allow you to determine the reaction's order with respect to crystal violet. The Laboratory Report questions will lead you through the analysis.

Preparation of graphs:

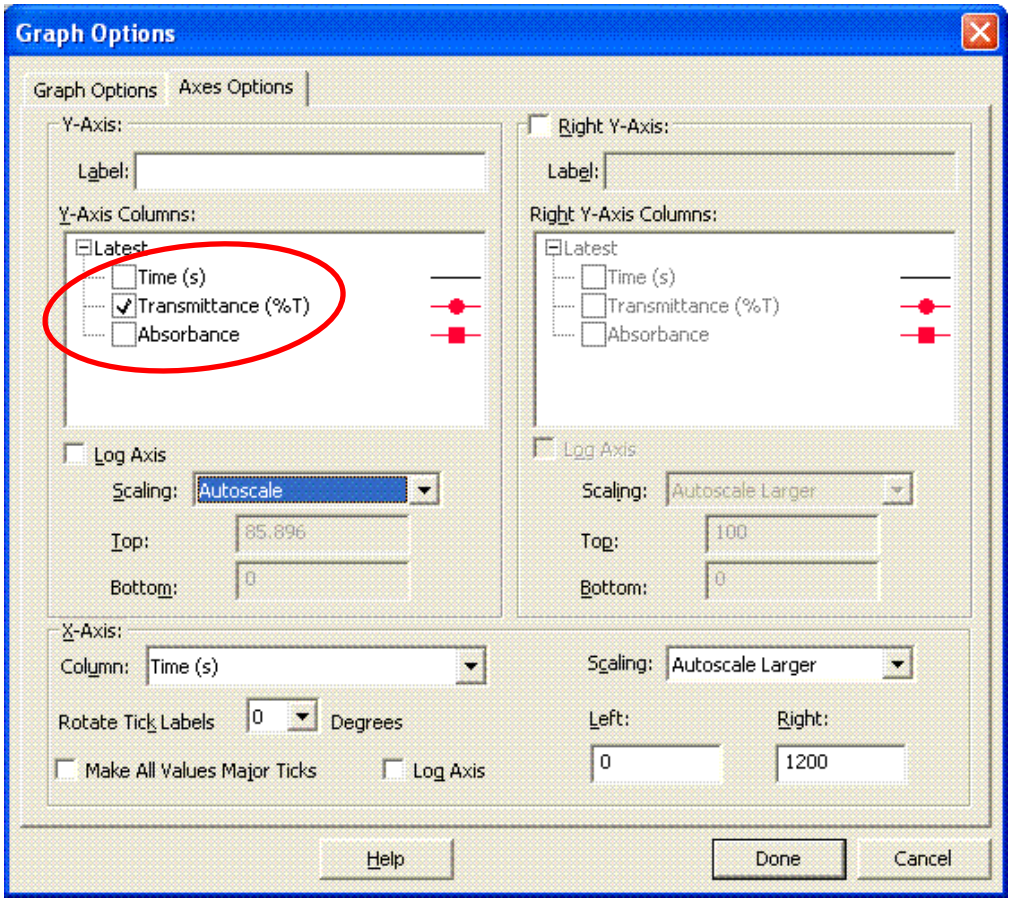
a) To display a new graph (or modify the one displayed):

Right click on the graph side of the window. A menu will appear; click Graph Options, which will bring up a window similar to the one shown below.

In the Axes Options tab:

- In the Y-Axis Columns area (left side only, circled), select the box for the parameter you want to plot (***i.e.*, do not choose %T as shown below**), and then deselect any other columns currently checked. In the Scaling drop-down menu, choose Autoscale.
- In the X-Axis Columns drop-down menu, select Time (s). To the right of the X-axis menu is the Scaling menu; choose Autoscale.
- Then press DONE. The graph will now be displayed.

In the Graph Options tab: Enter a title (*e.g.*, J.D. Part 1, $0^{th}/1^{st}/2^{nd}$ order test).



Save your changes: Click on FILE in the menu bar, then SAVE AS; use a name that matches the graph (*e.g.*, *jd-Ex4-Part1_ln-plot*, or *jd-Ex4-Part1_reciprocal).*

b) To print a graph:

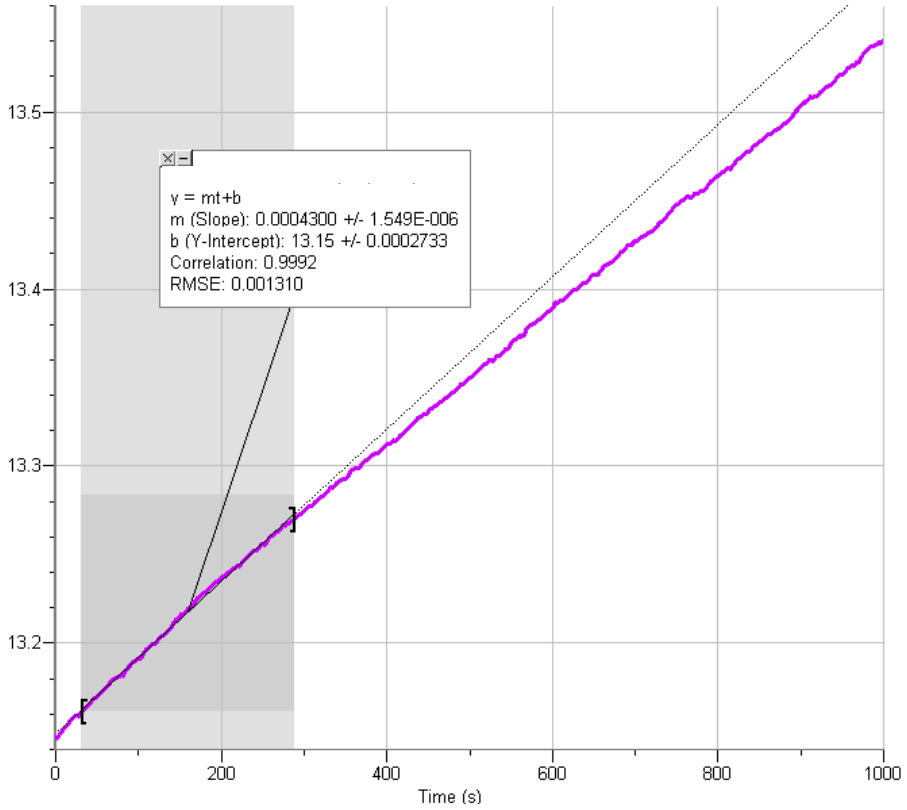
Click on FILE in the menu bar, then PRINT GRAPH, then OK. Do this in duplicate (one for each partner) for each of the three required graphs.

c) To fit the linear data to a best-fit line:

i.) Examine your three graphs and visually identify the one that is *closest* to a straight line over the entire time range (even the best may be slightly curved). This one corresponds to the reaction's order with respect to crystal violet. *After careful examination, confirm your choice with your TA.* Redisplay this straightest graph.

ii.) By dragging the mouse with left mouse key depressed, select the linear portion of the graph (the first ~20% of the data, ignoring the first few seconds when the colorimeter was settling). Keep the desired data inside the darker gray small box. *If the desired portion is covered only by the lighter gray box, your best-fit line will not properly represent the desired data.* Release the mouse button, then click Analyze, then Curve Fit. A small window displaying your plot will appear. In the section General Equation, select the linear equation, "mt + b". Select the Fit Type as Automatic, then press OK.

Your graph will look similar to the one shown here (*i.e.,* slight curvature is normal).



iii.) Square brackets indicate the selected data range, which can be fine-tuned by moving the brackets with the mouse. Note the "Correlation" coefficient – the closer it is to 1.00, the better the best-fit line matches the data.

iv.) The value of $k_{\text{eff-1}}$, the pseudo rate constant, is obtained from the slope of this line. Print the graph, label it, and note the value of $k_{\text{eff-1}}$.

v.) When you have completed the analysis, click on FILE in the menu bar and select EXIT. When you are asked if you want to save changes, click YES.

Part 2: Determining the order with respect to hydroxide ion.

In this part of the experiment, a smaller initial concentration of hydroxide will be used, so the pseudo rate constant $k_{eff} = k[OH^-]^q$ will have a different value than in Part 1. Comparison of the data obtained in Parts 1 and 2 will allow the value of q, the reaction's order with respect to hydroxide, to be determined.

1. Open one of your data files from Part 1 and immediately save the file under a new file name for Part 2. *This saves you the work of recreating the set of columns from Part 1; the transmittance data will be replaced and manipulated as it is collected.* Change the Graph Options to display % Transmittance.
2. Place 2.0 mL of 0.1 M NaOH stock solution and 2.0 mL of distilled water into a clean dry test tube, then cover the top with parafilm and invert the tube to mix. *This yields 0.05 M NaOH, in order to half the NaOH concentration in the reaction mixture compared to Part 1.*
3. Into a second clean dry test tube, add exactly 4.500 mL of crystal violet solution, measured with the automatic pipettor.
4. Pipette exactly 0.50 mL of the diluted NaOH solution into the crystal violet solution using the volumetric pipette. As quickly as possible, mix the contents of the test tube by covering it with a piece of Parafilm or a rubber stopper and inverting it twice. Then fill a cuvette to $^3/_4$ full with the mixture, wipe the outside of the cuvette with a Kimwipe, place it in the colorimeter (clear side aligned with the arrow), and close the lid.
5. Immediately click COLLECT on the computer to start the data acquisition (and then don't jiggle the instrument!).
6. After about 300 seconds, click on STOP. Save the data (*important!*).
7. Change the Graph Options to display the data in linear format (*i.e.*, plot the one graph that matches the reaction's order with respect to cv^+, as determined from Part 1)
8. Fit this graph to a linear equation using Analyze and Curve Fit, as done in Part 1 (p.4-11). *Important: use ~90% of the data, leaving out the very beginning and very end of the run.*
9. Record room temperature, to know the temperature of your solutions from Parts 1-2. The exact temperature is required for the data analysis in Part 3.

Primary data analysis for Part 2:

You *only* need to display and print the one graph that corresponds to the cv^+ order you determined in Part 1. This graph's slope will yield a value for the pseudo rate constant $k_{eff\text{-}2}$ (see the Laboratory Report section for details). *Important: verify with your TA the correctness of your conclusion about the reaction's order with respect to cv^+ to be sure you are using the correct type of graph for Parts 2 & 3.*

Once the form of the differential rate law has been determined (*i.e.*, the values of p & q), you can use your two data sets to calculate two values for the reaction's *true* rate constant (k_1 and k_2) and its average value k. You should report the temperature along with your rate constant; for example, label it as $k_{23°}$ if the value was determined at 23°C. Instructions for the remainder of the data analysis (*i.e.,* determining the value of q) are given in the Laboratory Report section.

Part 3: Determining the activation energy

In this part of the experiment, you will see how the magnitude of the rate constant *k* changes with temperature. You will run the reaction at four higher temperatures (25, 30, 35 and 40 °C) using 0.1 M NaOH as in Part 1, and determine the *pseudo* rate constants $k_{\text{eff-25°}}$, $k_{\text{eff-30°}}$, $k_{\text{eff-35°}}$ and $k_{\text{eff-40°}}$. From these, you will calculate the corresponding values of the *true* rate constant: $k_{25°}$, $k_{30°}$, $k_{35°}$ and $k_{40°}$. Including the room temperature rate constant obtained in Parts 1-2, you will have rate constants for five different temperatures. This will permit you to make an Arrhenius plot (ln(*k*) *vs.* 1/T) and thereby determine a value for the reaction's activation energy.

Note: If this type of experiment were being performed under ideal conditions, the colorimeter cell holder would be thermostatted to maintain the desired reaction temperatures. Our simplified equipment does not have this feature, so the strategy is to perform each run at *approximately* the desired temperature by starting about 1 °C too high, and then collecting transmittance data over a short time period. *It is essential that you work with the warm solutions quickly and place the cuvette into the colorimeter as quickly as possible, otherwise the solutions will cool to significantly below the desired temperature and your data will be quite scattered.*

1. Place 200 mL of ~45 °C water from the hot water tap into a 250 mL beaker to serve as a warm water bath. Gently clamp a thermometer in place to monitor the bath temperature. If the tap water is not warm enough, heat the beaker on the hot plate on low-medium until it reaches ~45 °C.
2. Place ~4 mL of 0.1 M NaOH in a test tube and clamp the tube into the water bath. Position the tube so that it will be easy to reach with your 0.5 mL volumetric pipette.
3. Open your data file from Part 2 (or one of your previous Part 3 files), and immediately save the file under a logical Part 3 file name that includes the desired temperature. Change the Graph Options to display % Transmittance.
4. Into another test tube, pipette exactly 4.500 mL of crystal violet (cv^+) solution. Stand this tube in the water bath, but do not clamp it.
5. Keep stirring the water bath gently by moving the cv^+ test tube. When the water cools to 41 °C, prepare your sample. Pipette 0.50 mL of the warm sodium hydroxide solution into the test tube containing the warm crystal violet solution, then quickly mix the solution by inverting the test tube and put a portion into the cuvette. Collect data for about 3 minutes, then save the data.
6. *To work efficiently:* while data is being collected at a particular temperature, measure out another 4.5 mL of crystal violet solution and put it into the water bath, which will probably cool to the next desired temperature just in time. If the cooling is too slow, add a little cool tap water to more rapidly cool the bath.
7. Repeat steps (3) – (6), starting the other three runs at 36, 31 and 26 °C.

Primary data analysis for Part 3: Analyze the data as in Part 2 *(that is, make only the one appropriate plot for each temperature)*, but use only the first ~100 s of data when fitting the data to a best-fit line (to avoid curvature that results from the sample continually cooling down). Remember to leave out the first few seconds of the data. Print out and label your graphs appropriately. The analyses will yield values of k_{eff} at 40, 35, 30 and 25 °C from which you will calculate four rate constants *k*. Instructions for the rest of the analysis (the Arrhenius plot) are given in the Laboratory Report section.

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CHEMISTRY 206

Experiment 4: A KINETIC STUDY: THE REACTION OF CRYSTAL VIOLET WITH SODIUM HYDROXIDE

Prelaboratory Questions

This lab is the most complicated of the experiments in Chem 206. The questions in this prelaboratory exercise illustrate the calculations you will be doing with the results you will obtain, and should help you understand the reason for steps you will follow in the lab. For this reason we are *not* asking you to write the usual brief introduction.

1. (1 mark) The following data were collected for a reaction of type:

   $$A + B \longrightarrow \text{Products}$$

   where [B] was 0.25 M after the reactant solutions were mixed, i.e. a large excess.

   Complete the last three columns:

Time (s)	**[A] (M)**	**– [A]**	**– ln[A]**	**1/[A]**
0	1.00×10^{-3}			
5	6.07×10^{-4}			
10	3.68×10^{-4}			
15	2.23×10^{-4}			
20	1.35×10^{-4}			

2. (1 mark) Determine the order of the reaction with respect to A and the value of the pseudo rate constant, $k_{eff\text{-}1}$. Your answer must include graphs, drawn neatly by hand on graph paper or generated by a computer spreadsheet program, as well as a brief explanation. *Freehand sketches of the graphs are not acceptable.*

3. (2 marks) The following data were collected using a concentration [B] = 0.50 M in the reaction mixture.

Time (s)	**[A] (M)**	
0	1.00×10^{-3}	
5	1.35×10^{-4}	
10	1.83×10^{-5}	
15	2.48×10^{-6}	
20	3.36×10^{-7}	

Using the appropriate function of concentration as determined in Question 3, complete the third column in the table, labeling it to indicate which function you used. Plot a graph to determine the new pseudo rate constant, $k_{eff\text{-}2}$, and then, by comparing it to the value from question 3, calculate the order of the reaction with respect to the reactant, B.

(1 mark) Calculate the average overall rate constant, k, from the two pseudo rate constants from Questions 3 and 4, and write down the complete rate law.

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CHEMISTRY 206

Experiment 4: A KINETIC STUDY: THE REACTION OF CRYSTAL VIOLET WITH SODIUM HYDROXIDE

Laboratory Report

Observations and Data

1. (5 marks) Hand in copies of your graphs (labeled in detail) with this report.

Calculation and Interpretation of Results

Part 1: **Determination of the Order of Reaction with Respect to Crystal Violet**

2. (1 mark) Which graph gave the most linear plot? What is your conclusion about the order (p) of the reaction with respect to crystal violet?

3. (1 mark) What is the value of $k_{\text{eff-1}}$, the pseudo rate constant printed by the curve fitting program for the most linear plot from Part 1? Suppose you were not given the equation at the top of the graph – what calculation would you have had to do in order to determine the value of $k_{\text{eff-1}}$? Show this calculation, and annotate the graph to show the data you used.

Part 2: **Determination of the Order of Reaction with Respect to Hydroxide ion**

4. (2 marks) What is the computer-generated value of the pseudo rate constant $k_{eff\text{-}2}$ found using the mixture prepared with the 0.1 M solution of sodium hydroxide? Determine the ratio of the two k_{eff} values ($k_{eff\text{-}1}$ and $k_{eff\text{-}2}$) and deduce the order (q) of the reaction with respect to hydroxide ion. Show your calculations. *Note: the value of q should be an integer (0, 1 or 2). If it is not, it is because of experimental error. What is the nearest integer value?*

5. (1 mark) Using the k_{eff} values from Part 1 and Part 2, calculate an average value for the true rate constant, k. Show your calculations. *[Take care in each case to correctly calculate the initial concentration of each species after mixing the solutions.]*

Part 3: **Determination of the Activation Energy for the Reaction of cv^+ with OH^-**

6. (1 mark) Calculate the values of the true rate constant k for the reactions at 30, 35 and 40 ^oC, including units. Show your work.

7. (1 mark) Complete the table below (where *k* is the *true* rate constant):

	Temperature (K)	**1/T** (K^{-1})	***k*** (units = ?)	**ln(*k*)** (unitless)
*				
**				
**				
**				

* Data from Part 2. **Data from Part 3.

(2 marks) On graph paper (by hand, not using a computer), make a plot of ln(*k*) *vs.* 1/temperature, and determine the value of E_a. (R = 8.31451 J mol^{-1} K^{-1}). Hand in your graph, and show your calculations in the space below.

8. (1 mark) Using the values of E_a and A from your graph, calculate the expected value of the rate constant for this reaction at 10°C below your value of room temperature (from Part 2). Does it seem that the 2-3× change in rate per 10°C change in temperature "rule of thumb" would apply to this reaction?

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