# Rate of Reaction, Part I: The Method of Initial Rates

Some chemical reactions are complete within the time it requires to mix the reactants, such as most acid-base reactions. Others may take place as we observe them, and we can see concentrations of reactants and products change by a variety of techniques. Some are so slow, that even though a reaction *ought* to proceed spontaneously, it is so slow under typical conditions that we never detect any change taking place. Wood, left to itself in air, does not burn. In the presence of certain bacteria and fungi, wood slowly decomposes. In the presence of a flame to start the process, wood will burn spontaneously.

Chemical reaction rates, or kinetics, provide a wealth of information not only about how fast reactions proceed, but also what concentrations are expected in the future or were present in the past, and how the reaction itself proceeds on a molecular level. Chemical reaction rates are fundamentally experimental; they may have explanations that come from theory, but the actual rates themselves are determined by experiments. The purpose of this experiment is to introduce you to chemical reaction rates through observation, rather than from a rigorous study of their theory.

A rate, by definition, is a change in a variable as time changes. Velocity is a rate; it is the change of distance ($\Delta s$) within a specific change of time ($\Delta t$). In finance, an interest rate is the change in money ($\Delta \$$) with respect to time ($\Delta t$). A chemical reaction rate is the change in concentration ($\Delta c$) with respect to time ($\Delta t$). (When the concentration is molar, it is expressed with square brackets, [C].) A rate is expressed as the change in the "dependent" variable (the result of the operation or experiment) divided by the change in the independent variable (time). Velocity could be expressed as ($\Delta s$) / ($\Delta t$), or a reaction rate as ($\Delta c$) / ($\Delta t$). You will recognize this form as the slope ($\Delta y$) / ($\Delta x$) of a line on a graph with time plotted along the x-axis. In chemical reactions, very few graphs of concentration vs. time are straight lines. It is still possible to obtain the rate from a graph that is a curve, either by estimating or by calculating the slope of the tangent at one specific point on a curve. It can be estimated by drawing the tangent with a ruler and calculating ($\Delta c$) / ($\Delta t$). If you are familiar with calculus, you know it also can be computed from the "first derivative" of the curve, which is possible with many computers.

Concentration vs. time data are rarely linear, but some exponential relationship. However, in the early phase of most reactions the changes are nearly linear, thus the rate ($\Delta[C] / \Delta t$) can be obtained as the slope of the line (or the slope of the tangent drawn to the origin). This technique is known as the "Method of Initial Rates," and uses experiments in which concentrations of some reactants are deliberately held constant, and large changes are made in the others. The initial rates might be proportional to the initial concentration (rate = k [C] ) or they may have an exponential relationship (rate = k [C]$^n$ , where n is the "order"). For example, if doubling the initial concentration quadrupled the rate, the order is 2. If doubling the concentration doubled the rate, the order is 1. We will explore this method in the first part of the experiment.

Part I: The Bleaching of Phenolphthalein

Phenolphthalein is a compound that is used in titration analyses and in some forensic work. Its most familiar use is its color change from clear to a purplish pink color with small amounts of excess hydroxide ion above a pH of about 8.5. However, in more concentrated hydroxide solutions, the phenolphthalein anion decomposes and its color fades. This color change does not occur instantaneously, and the rate of its bleaching depends on the hydroxide concentration. In this experiment we will observe the change in color intensity of phenolphthalein solutions as they react with hydroxide by monitoring their absorbance with a spectrophotometer. Absorbance is proportional to concentration, as expressed in Beer's Law, A = a b c (where a and b are constants).

(**Note**: The Prelaboratory Assignment is the 2 last pages of this document, which must be completed and turned in at the start of lab.)

**Procedure:**

1. Turn on a spectrophotometer and set it to a wavelength of 550 nm.  Select Absorbance.

2. Materials:
    5.2 x 10⁻³ M Phenolphthalein solution in ethanol (dispense with an Eppendorf pipet)
    1.0 M NaOH solution                    (dispense with a 2.00 mL measuring pipet)
    Deionized water                    (dispense with a 10.00 mL measuring pipet)
    Dropper pipet, 30 mL beaker, cuvet, spectrophotometer

You will be assigned to start with either experiment A or B.  However <u>read all of step 4 before preparing your solutions</u>.  In all cases we will assume volumes add quantitatively to 10.0 mL.

| Expt. | μL 5.2 x 10⁻³M Phenolphthalein solution | mL Deionized water | mL 1.0 M NaOH | M Phenolphthalein | M NaOH |
|-------|------|------|------|------|------|
| A | 50 | 9.20 | 0.80 | 2.6 x 10⁻⁵ | 0.080 |
| B | 50 | 9.00 | 1.00 | 2.6 x 10⁻⁵ | 0.10 |
| C | 50 | 8.40 | 1.60 | 2.6 x 10⁻⁵ | 0.16 |
| D | 50 | 8.00 | 2.00 | 2.6 x 10⁻⁵ | 0.20 |

3.  After a 10 minute warm-up period, calibrate your spectrophotometer at 0.000 Absorbance using deionized water.  Then empty and dry the cuvet.

4. Have all three pipets, the dropper, the beaker, the cuvet, and a timing device ready.  Read ALL the following before starting:

    a) Add the appropriate amount of 1.0 M NaOH to the beaker.
    b) Add the appropriate amount of deionized water to the beaker.
    c) With the timer ready, add the phenolphthalein solution to the 30 mL beaker with the
        Eppendorf pipet, starting the timer when the first phenolphthalein hits the beaker's solution.
    d) Immediately draw part of the beaker solution up into a plastic dropper and flush back into the
        beaker; repeat once.  This accomplishes mixing.  Then fill the cuvet to the mark with the
        dropper.
    e) Record the absorbance at 30 seconds (if possible), then every 30 seconds for 240 seconds
        total.

5. Dispose of the solutions in the beaker and cuvet into a waste container, rinse the beaker, the dropper, and the cuvet thoroughly with deionized water, and dry the beaker and cuvet.

6.  Conduct a second experiment (C or D) in which the NaOH molarity is twice the first experiment you ran; details are in the table above.
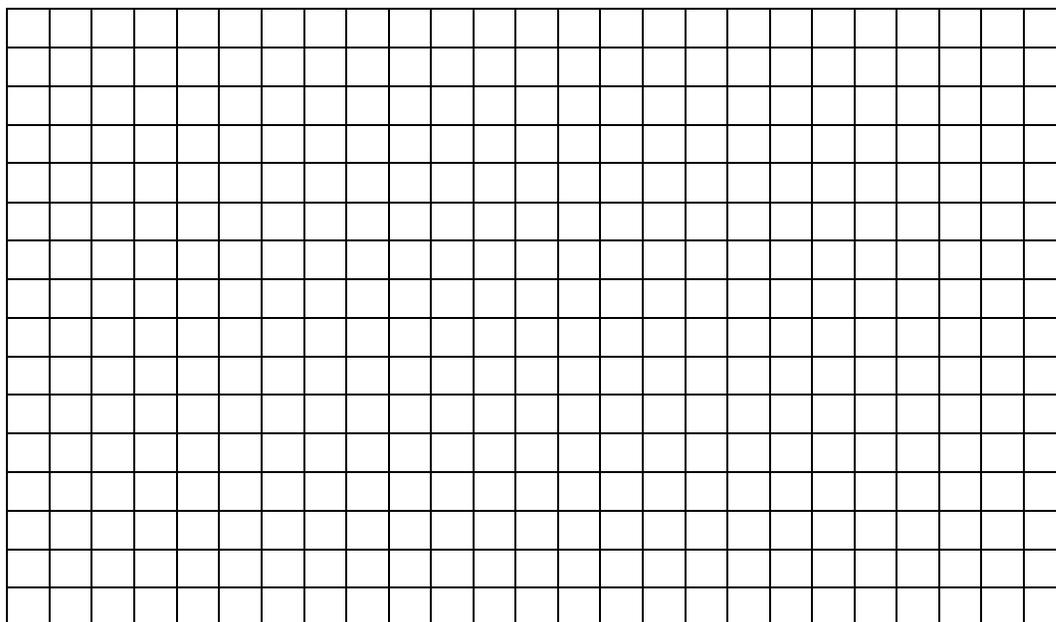
**Name** _____

**Partner** _____

**Report:**

**Data:**

First run: Letter _____          Second run: Letter _____

$[OH^-] = $ _____          $[OH^-] = $ _____

| Time (sec) | A, first run | A, second run |
|---|---|---|
| 30 | | |
| 60 | | |
| 90 | | |
| 120 | | |
| 150 | | |
| 180 | | |
| 210 | | |
| 240 | | |

Make a graph showing all data from both runs with two symbols on one set of axes; clearly indicate which run each symbol corresponds to.  Using a ruler, place a straight line through each set of data for 30 to 120 seconds <u>only</u>, and extend the line to the y-axis intercept (at t = 0).

Critical Thinking Questions:

Over the time period of 0 to 120 seconds, are these data approximately straight or curved?

Are <u>all</u> the data for a single run straight or curved?

**Calculations** (using Absorbance in place of [C] throughout)

Using regression (or the straight line on the graph), determine the slope ($\Delta A / \Delta t$) for <u>only</u> the data between 30 and 120 seconds, which is the initial rate. Include units.

Initial slope (initial rate), first run:

Initial slope (initial rate) second run:

Would these slopes be the same or different if you picked a later time interval?
"Faster" or "slower"?

Determination of Order:

Qualitative: When comparing runs where [OH⁻] doubled, did the rate remain the same (zero order), approximately double (first order), or increase approximately four times (second order)?

Quantitative: Set up two equations for the rate, using the format rate = k [OH⁻]$^n$. Substitute known experimental values for rate and [OH⁻]. Divide the equation with the faster rate by the equation with the slower rate, cancel k, and solve for n. Show both the decimal value and the closest integer value for n.

Determination of the rate constant, "k":

Substitute your experimental values of rate (using their absolute values), [OH⁻], and your unrounded, experimental n in each of the two rate equations. Solve for k in each; include units.

Is k constant or not constant (considering appropriate significant figures)?

In this experiment, we did not study the influence of the phenolphthalein concentration. How could an experiment be designed to find out its influence? Give specific quantities.

## Rate of Reaction, Part II: The Integrated Rate Laws
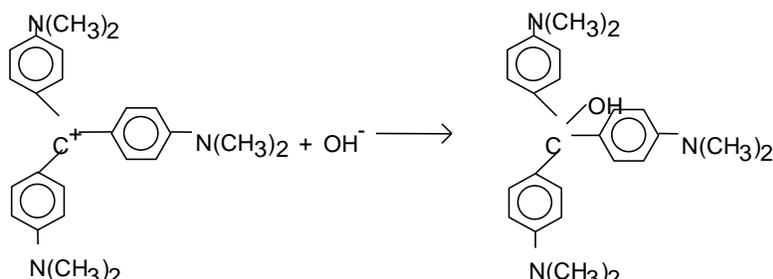Determination of the Rate Law for the Reaction of Crystal Violet with Hydroxide Ion

Another method for determining orders and rate laws is to find a mathematical relationship that transforms concentration-time data into a straight-line form, and then solving "y = mx + b" for the slope. You may have done this in experiments using absorbance to replace transmittance, or natural log of pressure (ln P) to replace pressure. Many chemical reactions can be fitted using the natural log of concentration (ln c) vs. time and others can be fitted using the inverse of concentration (1 / c) vs. time. These are the two most common cases, which we will explore in the second part of this experiment.

It has been proven (and it can be derived mathematically) for those reactions with ln c vs. t having a straight line, that the experimental reaction rate is proportional to concentration; these are first order. It has been proven (and it can be derived mathematically) for those reactions with 1/c vs. t having a straight line, that the rate is proportional to the square of concentration; these are called "second order". These relationships are called the "integrated rate laws." We will assume that absorbance is proportional to the concentration of crystal violet (Beer's law: A= a b c, where a and b are constants). Thus, using Absorbance to monitor c,
- Absorbance vs. time: A linear plot indicates a *zero order* reaction (k = −slope).
- ln Absorbance vs. time: A linear plot indicates a *first order* reaction (k = −slope).
- 1/Absorbance vs. time: A linear plot indicates a *second order* reaction (k = slope).

(The text of Part II was modified from Vernier Software, copyright obtained.)

In this experiment, you will observe the reaction between crystal violet and sodium hydroxide. One objective is to study the relationship between concentration of crystal violet and the time elapsed during the reaction. The equation for the reaction is shown here:



A simplified (and less intimidating!) version of the equation is:
$$CV^+ \quad + \quad OH^- \quad \longrightarrow \quad CVOH$$
$$\text{(crystal violet)} \quad \text{(hydroxide)}$$
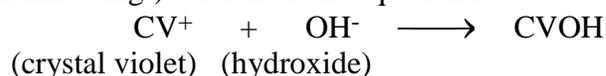
The rate law for this reaction is in the form: rate = $k[CV^+]^m[OH^-]^n$, where $k$ is the rate constant for the reaction, $m$ is the order with respect to crystal violet ($CV^+$), and $n$ is the order with respect to the hydroxide ion. Since the hydroxide ion concentration is more than 1000 times as large as the concentration of crystal violet, $[OH^-]$ will not change appreciably during this experiment. Thus, you will find the order with respect to crystal violet (m), but not the order with respect to hydroxide (n).

As the reaction proceeds, a violet-colored reactant will be slowly changing to a colorless product. Using the green (565 nm) light source of a computer-interfaced colorimeter, you will monitor the absorbance of the crystal violet solution with time.

Once the order with respect to crystal violet has been determined, you will also be finding the rate constant, k, and the half-life for this reaction.

**Part II Materials:**

| | |
|---|---|
| IBM-compatible computer | 0.020 M NaOH |
| Interface | $1.8 \times 10^{-5}$ M crystal violet |
| Logger Pro | deionized water |
| Vernier Colorimeter | two 10-mL graduated cylinders |
| two plastic cuvettes | 3 plastic droppers (labels: NaOH, CV, R) |
| 100 mL beaker, two 50 mL beakers | |
| 5% bleach solution for clean-up | |

**Part II Procedure:**

1. Obtain and wear goggles.  Obtain and label 3 plastic droppers as noted above.

2. Turn on the colorimeter to "0%T" and allow it to warm up for at least 5 minutes (while doing step 3). Prepare a *blank* by filling a cuvette 3/4 full with deionized water. To correctly use a colorimeter cuvette, remember:

   • All cuvettes should be wiped clean and dry on the outside with a tissue.
   • Handle cuvettes only by the top edge of the ribbed or frosted sides.
   • All solutions should be free of bubbles:  Tap the base of the cuvette gently on a benchtop.
   • Always position the cuvette with its clear sides facing toward the white reference mark at the right of the cuvette slot on the colorimeter.

   Place the cuvette in the slot facing the correct direction.

3. Pour about 25 mL of 0.020 M NaOH solution into one 50 mL beaker and about 25 mL of $1.8 \times 10^{-5}$ M crystal violet solution in another 50 mL beaker.  Transfer 10.0 mL of the NaOH solution in the beaker to a 10-mL graduated cylinder using a plastic dropper (label and use this dropper only for NaOH throughout).   Transfer 10.0 mL of the crystal violet solution to another 10-mL graduated cylinder (with a dropper labeled CV).

4. Prepare the computer for data collection:  If the program is open, close it.  Double click the "Rate of Reaction Part II" icon on the desktop, and click Connect in the Sensor Confirmation dialog box that appears. Confirm that "Rate of Reaction Part II" is on the title bar.

5. You are now ready to calibrate the colorimeter.

   On the top bar click Experiment, then Calibrate ▶ Colorimeter, then Calibrate now.
   Check the blank cuvette for bubbles, place it with the clear faces aligned with the white scribe in the
      cuvette slot of the colorimeter and close the lid.
   Confirm the wavelength knob of the colorimeter is in the *0%T* position. On the screen, enter 0 in the
      Reading 1 box, then click the Keep button.
   Turn the wavelength knob of the colorimeter to the Green LED position (565 nm). Type 100 in the
      Reading 2 box and wait at least 1 minute. Then click Keep and Done.

   READ STEPS 6 and 7 COMPLETELY BEFORE MIXING THE REACTANTS.

6. Rinse and dry a 100 mL beaker.  You will use the computer to acquire both absorbance and time: Simultaneously pour the 10-mL portions of crystal violet and sodium hydroxide into the beaker and click on the Collect button (This will start the computer's timer; you will not use a stopwatch.)  Stir the reaction mixture with the dropper marked "R". Note: Because the initial data are sometimes sporadic, you will not actually take a reading until 3 minutes have passed. Empty the water from the cuvette. Using the dropper, rinse the cuvette twice with ~1-mL amounts of the reaction mixture and then fill it 3/4 full. Do not put the cuvette in the colorimeter yet. To keep the solution from warming

inside the colorimeter, the cuvette is left outside the colorimeter between readings. Keep the cuvette away from direct sunlight.

7. After about 2.5 minutes have passed since combining the 2 solutions, place the cuvette (correctly aligned) in the cuvette slot of the colorimeter and close the lid. As close as possible to the 3 minute mark, click on the Keep button. Clicking on the Keep button saves both the absorbance and time data values. Remove the cuvette from the colorimeter (do not discard the solution). After 45 seconds more (0.75 min) have elapsed, again place the cuvette in the colorimeter, and click on Keep as close as possible to the 4 minute mark. After keeping this second data pair, remove the cuvette again. Continue in this manner, collecting data about once every minute, until 15 minutes have elapsed. (If you accidentally collect a "bad" data point, collect a "good" point as soon as practical, and continue taking data.) RECORD YOUR TIME AND ABSORBANCE DATA IN YOUR NOTEBOOK AS THEY ARE BEING COLLECTED. After 15 minutes, click Stop. (After clicking Stop you can eliminate any accidental data by highlighting its row, then Edit / Strike Through Data Cells.)

8. Discard the beaker and cuvette contents in a waste container.

9. Use the "M=" button on the toolbar to explore whether the slope is constant or changing. Write down the value of the slope at the data point closest to 10 minutes. Then click the button again to turn the slope function off.

10. Determine the half-life at several points from the graph:
a) Double click anywhere on the graph area. In the dialog box (under the Graph Options tab) click the "Connect Points" check box, then Done.

b) Measure three half-lives using the "Δx" feature of Logger Pro: Make a table in your lab notebook with two columns, "starting time" and "half life" for the following data.
- Place the cursor (which will appear as a "+" sign) over the first data point you recorded. Note that the "(x,y)" coordinates are shown at the bottom left corner of the graph space; do not be concerned if they are "off" in a non-significant figure.

- Click and hold the left mouse button down while you "drag" the cursor down the connecting line through the data points. Stop and release the mouse button when the "y" coordinate (Absorbance) is exactly half of the "y" starting value and directly on the line.

- Then record the Δx value (the change in time) shown just to the right of the parentheses. This is the half-life from the initial value you chose, i.e., the time it took for the Absorbance to drop by half.

c) Repeat 10b ending at the longest-time point on the graph: Calculate double its absorbance, place the cursor at the earlier point on the connecting line that has this absorbance, and click and drag to the last point.

d) Repeat 10b for one additional set of points between those of (b) and (c). Then uncheck the Connect Points option.

11. Examine the data graphically to decide if the reaction is zero, first, or second order with respect to crystal violet. If the current graph of absorbance vs. time is linear the reaction is *zero order*. If not, click and drag the cursor around all the data, then click Analyze / Curve Fit, and scroll down through the functions and select "Natural Exponent". Click Try Fit. Note the RMSE error of the fit. Then choose "Inverse sum" (not "Inverse") from the functions menu, Try Fit, and decide which curve gave the best fit based on the error. If the exponential fits best, it is first order; if the inverse sum fits best, it is second order. When you have found the function that best fits the data, cancel the Curve Fit box and return to the original graph.

12. Use Logger Pro in the lab* to change the original graph to a linear form. Choose Data / New Calculated Column and give the new column a name and an identical short name in the respective boxes: either ln(a) or 1/a. Then click the Expression box. Click the Function box, choose ln or Inverse; click the Variables box, choose Absorbance, then click Done. To place the linearized data on the graph, double-click the y-axis, click Axes options, uncheck Absorbance and check your new function's name, then Done. From the upper tool bar click on the icon with the graph axes and the capital A to autoscale the axes. Get the slope and intercept by clicking the R= icon. The linear regression line appears in the box on the graph. Copy down the equation in your notebook BEING CAREFUL to look for minus signs (which may appear as "+-"). Move the results box with the mouse if necessary. Print one copy of your graph using File / Print Graph. **DO NOT SAVE** the file. Then close the Logger Pro program.

13. If you are doing a second run, close and restart the experiment file. Recalibrate, and repeat the reaction using an unused cuvette and a second concentration directed by your instructor. (The droppers should be re-used, but not interchanged.) Watch the data values as they are acquired; if the absorbance does not drop by at least half (i.e., one half-life), extend your data collection beyond 15 minutes until a half-life is passed. Carry out data analysis for Run 2* as you did for Run 1.

14. At the end, all glassware should be rinsed with 5% bleach and then DI water during final cleanup.

*If time is short at the end of the second run, skip step 10, do step 11 while in the lab, and you can do steps 10 and 12 later from any computer that has Graphical Analysis installed, as follows:

Open a Graphical Analysis file from another computer and double-click each table column heading to set it up: type in time as the x-axis column and Absorbance as the y-axis column names, and under Options specify significant figures. Type in your data and do step 10, if needed. (To turn the connecting line on/ off, double-click anywhere on the graph and check / uncheck the Connect Points box. It should be on for step 10 and off for steps 11 and 12.) From the top bar, click Data / New Calculated Column and give it a name and an identical short name (ln(a) or 1/a depending on your previous choice). Click the Equation box, then drop down the Function box and choose ln(); if you chose inverse simply type 1/. Drop down the Variables box and choose Absorbance, then click OK. Double-click the y-axis on the graph, choose Axes options, uncheck Absorbance and check your new function. On the top bar click on the Autoscale button (an A inside a set of axes). Click the R= icon to get a linear fit and record the equation in your notebook. Print your "linearized" results using File / Print Graph.

Name _____

Partner(s) _____

**Rate of Reaction, Part II Report:**

**Data: Run 1**                    **Run 2:** (if performed: give specific amount of CV: _____)

| Time (min) | Absorbance | | Time (min) | Absorbance |
|---|---|---|---|---|
| | | | | |
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**Questions 1 – 3 refer to the original absorbance vs. time data. Questions 4 – 7 refer to the linearized data and graph that you obtained by applying a natural logarithm or inverse function. Items with a * are omitted if you performed only one run.**

1. Calculate ΔA/Δt using the data points at about 3 and 4 minutes, which we will assign as the "initial rate". Also report the instantaneous rate at about the ten minute point (i.e., the instantaneous slope of each absorbance vs. time graph at 10 minutes from step 9 of the Procedure).   *Repeat for the second reaction.

                                   Initial rate                    Rate at 10 min.
          Rates, first reaction


          Rates, second reaction*


     A) Does rate remain approximately constant or change as each reaction progresses?

     B) *Is the rate of the second reaction faster or slower than the first?

     C) *Calculate the ratio (as a decimal value) of the second reaction's initial rate to the first:

2. Report your three half-life determinations for each run (or fewer if the data did not permit). For each reaction, place these in the order of increasing start times:

|  | Reaction 1 | Reaction 1 | Reaction 1 | Reaction 2* | Reaction 2* | Reaction 2* |
|---|---|---|---|---|---|---|
| Start Time (min) |  |  |  |  |  |  |
| Half-life (min) |  |  |  |  |  |  |

3. One test of order is to determine if half-life is constant (as it is only for a first-order reaction) or if it changes with time. Decide if the half-life is approximately constant or if it is clearly changing as each reaction progresses. Then make a conclusion about order: _____

4. Attach graphs showing both* sets of data in their linear form (or one each per partnership).

5. A) Based <u>on these graphs</u>, was the reaction zero, first, or second order, with respect to the concentration of crystal violet? B) Explain your reasoning. C) Compare your conclusion to #3.

6. Report the rate constant, k, for each run using the *slope* of the linear regression line from your linear graphs (k = − slope for zero and first order, and k = slope for second order). Be sure to include correct units for the rate constant (Absorbance has no units). Note: This constant is sometimes referred to as the *pseudo rate constant*, because it does not take into account the effect of the other reactant, OH⁻, nor the conversion between absorbance and concentration from Beer's Law.

First run: Regression equation:         *Second run: Regression equation:

        Rate constant with units:         *Rate constant with units:

        Ideally, should it be constant or change as concentration changes?

*Calculate the average rate constant, and the average deviation for the two runs:

*Revise the significant figures in the average rate constant based on the error (average deviation); write the average and the error as a confidence interval:

7. Calculate the half-life for each reaction from the *two rate constants in step 6 using the appropriate equation. (These should agree with your approximate values in step 2.)

8. Which method of half-life determination (step 2 or step 7) do you consider to be more reliable? Why? Consider both the precision of the data and the number of data points used.

(Page intentionally left blank.)

Name _____

Rate of Reaction, Parts I and II
Prelaboratory Assignment
(1 – 5 are for Part I)

1.  In a graph of the concentration of a reactant vs. time, what parameter gives the rate?

2.  Write Beer's Law as an equation.  Show how absorbance can be used to monitor concentration.

3.   A rate equation could be written as $(\Delta c/\Delta t) = - k [c]^n$.  Define (name) the following as they pertain to the rate equation:

   a)  $(\Delta c/\Delta t)$

   b)  k

   c)  [c]

   d)  n

4. Assume n in #3 is not zero.

   a)  Does $(\Delta c/\Delta t)$ change or remain constant as a reaction progresses in time?

   b)  Does k change or remain constant as a reaction progresses?

5.  Why can we use absorbance in place of [c] in this experiment?

(6 – 9 are for Part II)

6. Using your textbook, look up the "Integrated Rate Laws."  For each of zero, first and second order reactions, write down the algebraic form of these laws.

   Zero order:


   First order:


   Second order:


7. Use the information in your text and the information in the introduction to this experiment to indicate how a graph would be constructed to use an integrated rate law as a test of order. Specifically for each, what is plotted on the "x" axis and what is plotted on the "y" axis?

   |  | x-axis variable | y-axis variable |
   |---|---|---|

   Zero order:


   First order:


   Second order:


8. Use the information in your text and the information in the introduction to this experiment to indicate when a graph produces a straight line, what part of its integrated rate law is equal to the slope.

   Zero order:


   First order:


   Second order:


9. Transcribe the *simplified* version of the reaction equation into your lab notebook.