**RATE LAW DETERMINATION OF THE CRYSTAL VIOLET/SODIUM HYDROXIDE REACTION**

Reaction kinetics is defined as the study of the rates of chemical reactions and their mechanisms. Reaction rate is simply defined as a change in a measurable quantity divided by the change in time. In chemistry, the “measurable quantity” is usually molar concentration or absorbance. Consider the generalized chemical reaction equation: A + B → C + D. Symbolically it can be represented in multiple ways: *Rate* = − Δ[A] = *k*[A]*m*

Δ *time*

Note that the units on rate are always *M/*time which can also be expressed as *M* time−1. The negative sign on the first expression indicates that the molar concentration of reactant A will decrease as time goes by. The second expression is simply the differential rate law expression where the rate constant *k,* and the *order* of reactant A (the exponent *m*) must be experimentally determined. Never forget that the value of *k* is temperature dependent. Since two reactants are present in our example reaction we can write comparable expressions for reactant B, but beware that the order of B will not necessarily be the same as the order for A, so we often use a different variable, such as *n*, for the exponent on B. The differential rate law can be integrated to link changes in concentration with time as opposed to rate. In this experiment you will investigate the reaction of crystal violet with sodium hydroxide. Crystal violet, in aqueous solution, is often used as an indicator in biochemical testing. Crystal violet belongs to a class of intensely colored organic compounds called triphenylmethane dyes.

The structure and color of crystal violet depend on pH, making it a valuable acid−base indicator as well as an excellent dye. The major structural form of crystal violet is the monovalent cation, abbreviated CV+, which is shown in Figure 1a. CV+ is the predominant form of crystal violet in the solid state and in aqueous solution across a broad range of pH values from pH 1 to 13. The positive charge shown on the central carbon atom in Figure 1a is delocalized via resonance to the three nitrogen atoms. See Figure 1b for one of the three additional resonance forms with the positive charge on a nitrogen atom. Delocalization of the charge across the system of double bonds in the benzene rings stabilizes the carbocation and is responsible for the vibrant purple color of the dye. In strongly basic solutions, the purple CV+ cation slowly combines with hydroxide ions to form a neutral product, CVOH, which is colorless (see Figure 2). The rate of this reaction (Equation 1) is slower than typical acid–base proton transfer reactions and depends on the initial concentration of both crystal violet and hydroxide ions.

Purple

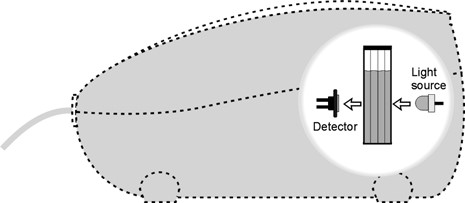
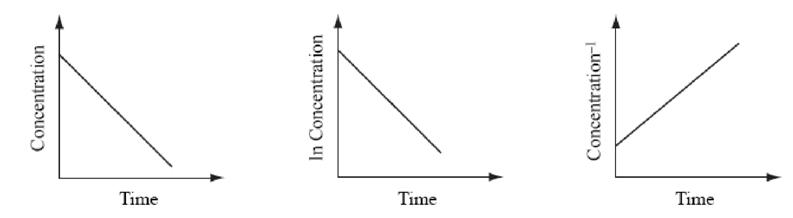
Colorless

CV+ + OH– → CVOH Equation 1

Purple Colorless

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. By keeping the concentration of [OH-] ***very large*** compared to the concentration of [CV+], for all practical purposes the concentration of [OH-] remains ***constant*** and does not change (the system is swamped with [OH-]. In fact the technique is called “swamping”. The concentration of crystal violet will change dramatically though, allowing the order and rate constant with respect to crystal violet to be determined with only one reaction. The rate constant obtained in this manner is called the pseudo rate constant (k’), because it only applies to part of the reaction. The reaction is said to follow pseudo mth order kinetics. Under these conditions, the rate equation simplifies to:

Rate = k’[CV+]m, where the pseudo rate constant k’ = k[OH-]n.

As the reaction proceeds, a violet-colored reactant will be slowly changing to a colorless product. You will use a Vernier Colorimeter to measure the absorbance by the fading violet color over time. Recall that the absorbance *(A)* for a specific concentration *(c)* of a solution with a fixed path length *(b)* varies directly with the absorptivity coefficient *(a)* of the solution. This relationship is known as Beer’s Law: *A = abc*  Since *absorbance varies directly with concentration*, the following plots can be used to determine the order of the reaction with respect to crystal violet concentration.

• 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)

Another important part of the kinetic analysis of a chemical reaction is to determine the activation energy, *Ea*. Activation energy can be defined as the energy necessary to initiate an otherwise spontaneous chemical reaction so that it will continue to react without the need for additional energy. An example of activation energy is the combustion of paper. The reaction of cellulose and oxygen is spontaneous, but you need to initiate the combustion by adding activation energy from a lit match.

We can use a different graphical analysis method to easily determine the activation energy of a chemical reaction. Each laboratory group will simply repeat the reaction between crystal violet and sodium hydroxide at different temperatures, while keeping the initial concentrations of the reactants the same for each trial. Recall that the value of *k* is temperature dependent. Class data will be collected, graphed and analyzed to find the activation energy.

(

)

1

1

K

*T*

−

*E*

*a*

*=*

*−*

*R × slope*

ln *k*

**MATERIALS:** Labquest, colorimeter, thermometer, 2 plastic cuvettes with lids, hot plate, ice, 250mL beaker,

0.10M sodium hydroxide, 25μM crystal violet stock solution, 2-(1 mL) graduated pipets, kimwipe

**PROCEDURE**: <https://www.youtube.com/watch?v=4k-1TdxN-kk>

1) Connect the colorimeter to the Labquest and turn on the power. Choose NEW from the file menu. Allow the colorimeter to warm up for 5 minutes while you prepare for the lab.

2) Set up a 250mL water bath for your assigned temperature. (5, 15, 25, 35 or 45oC)

3) Obtain 1.5mL of 0.10M NaOH solution and 1.5 mL of 25μM crystal violet solution in separate graduated pipets. ***Caution:*** *NaOH is caustic and crystal violet stains!* Submerge the pipet bulbs in your water bath as shown by the instructor in order to bring the solutions to the assigned temperature (*about 5 minutes*). ***Monitor the bath temperature.***

4) Prepare a “blank” to calibrate the colorimeter by filling a cuvette ¾ full with 0.1M NaOH. (use clean pipet)

Cap the cuvette. Remember to correctly use the cuvettes:

* All cuvettes should be wiped clean and dry with a Kimwipe after filling with solution and applying cap.
* Handle the cuvette only by the ribbed sides.
* All solutions should be free of bubbles.
* Position the cuvette so the light passes thru the clear sides (align with arrow on colorimeter)

5) Calibrate the colorimeter. Place the blank (capped!) in the cuvette slot of the colorimeter and close the lid. Press the < or > buttons to set the wavelength to 565nm. Then calibrate by pressing the CAL button. When the LED stops flashing, the calibration is complete. *Remove the blank*.

6) On the *Meter screen*, tap ***Rate***. Change the data collection rate to ***0.20sample/sec*** (Interval 5sec/sample). Change the data collection length to ***500*** seconds. Select OK. Have a clean, dry cuvette ready for step 7. ***The group using 5oC should set the length to 700 seconds****.*

7) ***Do this step quickly!*** When the solutions reach the assigned temperature (1-2oC above for warm or below for cold). Remove the pipets from the water bath. ***Simultaneously*** squirt the contents of each into the clean, dry cuvette – it should be ¾ full. Cap the cuvette and place it into the colorimeter. Close the lid and *tap the green play button to start* the data collection.

8) Absorbance data will be collected for 500 seconds. *You may stop collection if absorbance reaches 0 before 00sec.* ***Save the file by selecting File, Save.***

Remove the cuvette from the colorimeter. Dispose of the solution in this cuvette and the blank. Rinse out the cuvettes with tap water and then distilled. Place in a cuvette rack upside down to dry. Rinse the pipets with tap water. Don’t worry if the one for the CV solution is stained. Return all equipment and materials.

**Data Analysis**

Observe the graph on the Labquest. If the graph of abs (conc) vs time is a straight line, the reaction is zero order. (It should NOT be a straight line.)

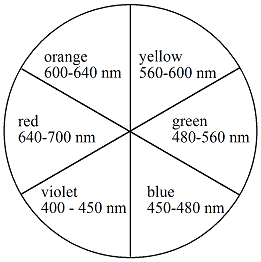
To create a graph of ln(abs) vs time, tap the Table tab to display the data table. Choose New Calculated Column from the Table menu. Enter the “ln abs” as the Name and leave the Units field blank. Select the equation, Aln(X). Use Absorbance as the Column for X and **1** as the value for A. Select OK. A graph of ln absorbance (conc) vs time will be displayed. If this line is linear, the reaction is first order.

To create a graph of 1/abs vs time, tap the Table tab to display the data table. Choose New Calculated Column from the Table menu. Enter “1/abs” the Name and leave the Units field blank. Select the equation, A/X. Use Absorbance as the Column for X and **1** as the value for A. Select OK. A graph of 1/abs (conc) vs time will be displayed. If this line is linear, the reaction is second order.

Sketch the graph which is linear in the analysis section and record the y = ax + b equation of the line next to the graph.

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**Name(s):**

**Pre-Lab Questions**

0

0.2

0.4

0.6

0.8

1

1.2

1.4

1.6

1.8

350

400

450

500

550

600

650

700

750

**Absorbance**

**Wavelength (nm)**

The visible absorption spectrum for crystal violet, CV+, is shown above. The *concentration* of the dye was 12.5 **μ**M (12.5 × 10–6 M).

1) What is the maximum absorbance value? \_\_\_\_\_ What is the wavelength at this value? \_\_\_\_\_\_\_\_

What color does this represent? Examine the color wheel. Why would this color have the highest absorbance?

2) The colorimeter gives best results when the absorbance falls within a range from 0.05–1.0 (transmittance 10−90%).

Based on this, what would be the 2 optimum wavelengths to use to generate a Beer’s Law calibration curve for a 12.5 **μ**M solution of crystal violet and measuring the absorbance of the fading reaction? Explain your choices.

3) A calibration curve requires the use of several concentrations of the test solution. Using 25 μM CV solution as the stock solution, complete the following table to show how you would prepare 2.5, 5, 7.5, 10 and 12.5 μM solutions of CV+. (1/10th fold dilutions) Assume that the final solution volume should be 10.0 mL in all cases.

Show *one* dilution calculation next to the table.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | **CV Stock Solution** | **A** | **B** | **C** | **D** | **E** |
| Concentration  (micromolar, μM) | 25 μM | 2.5 μM | 5.0 μM | 7.5 μM | 10.0 μM | 12.5 μM |
| Water (mL) | 0 |  |  |  |  | 5.0 mL |
| Stock Solution  (mL) | 10.0 |  |  |  |  | 5.0 mL |
| Predicted absorbance |  |  |  |  |  |  |
| Measured absorbance |  | 0.159 | 0.332 | 0.508 | 0.639 | 0.742 |

3) The colorimeter has 4 LEDs (wavelengths = 430, 470, 565 and 635nm). Which of these would be the best choice for the lab? \_\_\_\_\_\_\_\_\_ Determine the absorbance at this value from the graph (it is slightly above the ideal range) and record it in the table for the 12.5 μM solution. Calculate the predicted absorbance for the other solutions based on the fact that Beer’s Law states that absorbance varies directly with concentration. (Path length “b” and absorptivity “a” are constant for the crystal violet at the given wavelength.)

A = abc therefore A = k [CV+] Show *one* calculation below the table. Record the values.

4) Create a graph in your calculator of the

measured absorbance vs concentration.

Sketch the graph. Label each axis and

record the equation of the line.

Determine the concentration of an unknown

solution that has an absorbance of 0.565

5) A 0.1M NaOH solution will be used during the lab. Calculate how many times more concentrated this solution is compared to the *highest and lowest* CV concentrations (A & E) in the table.

**Lab Analysis**

1) Sketch the graph of ln(abs) vs time. *Record* the equation of the line. Temp = \_\_\_\_oC

*The integrated rate equation for this graph is:*

ln(abs)t = -kt + ln(abs)0 abs ≈ to [CV+]

What does the graph indicate about the order of the reaction? ln(abs)

[CV+]

Write the rate law for the reaction and determine

the value of the pseudo rate constant k’ (including units).

*Note: ln(abs) does not have units.* time

*eqn of the line:*\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

2) Estimate the half-life of the reaction by clicking on the data table to find the time at which the *initial* absorbance decreases to ½ of the initial value. Calculate the half-life (including units) of the reaction using the appropriate half-life equation for the order of the reaction. How close are the values?

3) Use the integrated rate equation *(the equation of the line)* to calculate the absorbance of the CV during the reaction at 45 seconds.How does this compare to the value in your data table?

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Temperature (oC) (K)** | 5  278 | 15  288 | 25  298 | 35  308 | 45  318 |
| **k’ (sec-1)** |  |  |  |  |  |

4) Complete the table.

Why do the ***rate constant values*** increase with temperature?

Plot ln k’ vs 1/T (K) in your calculator. Record the equation of the line: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Determine the activation energy for the reaction. Show your calculation including units.

Does the data support the general rule that the rate of a reaction approximately doubles every 10oC?

Support your answer. *Hint: R = k[CV+] rate is directly proportional to k*

5) How would the absorbance values be affected if you forget to wipe finger prints from the cuvette?

How would this affect the rate constant?

6) How would the absorbance values be affected if the cuvettes are only filled ½ full instead of ¾ full?

How would this affect the rate constant?