Kinetics of a Dye Decolorization
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Objectives
In this experiment you will study the kinetics of a reaction in which a colored dye fades upon reacting with hydroxide ion and determine the exponents for a chemical "rate law" that describes the reaction. You will determine the order of the reaction as well as the equilibrium constant for the reaction

Introduction
Chemical reactions can proceed quickly or slowly. The "quickness" of a reaction is expressed in terms of the reaction's rate. The rate is the increase in the concentration of products (or the decrease in the concentration of reactants) during a given unit of time. In this experiment you will investigate the rate of a reaction in which a purple dye becomes colorless. You will see how the rate depends on different concentrations of reactants. You will specify a mathematical equation that shows the dependence of the rate on concentrations. This equation is known as a kinetic rate law.

The Chemical Reaction
In neutral solution, crystal violet dye exists as a cation with an intense purple color. In basic solution, the dye cation combines with an OH⁻ ion and becomes a colorless neutral molecule, as shown below in Figure 1. Experimentally, when NaOH is added to a solution of the dye, the purple color gradually fades.

We can also describe the change with this simple ionic equation:

\[
dye^+_{\text{purple}} + \text{OH}^-_{\text{(aq)}} \rightarrow \text{dye(OH)}_{\text{colorless}}
\]

**Figure 1:** hydroxide anions turn purple dye cations into colorless products.
**Kinetic Rate Law**

The kinetics of this or any other reaction can be described in terms of a chemical rate law, a mathematical expression of the relationship between the rate and the reactant concentrations. In this case, the rate at which the dye fades can be defined as the decrease in dye cation concentration (-d[dye']) as a function of time (dt). This rate depends on the concentrations of both reactants: the hydroxide anion and dye cation.

(eq. 1)

\[ \text{Rate} = \frac{-d[dye']}{dt} = k[OH^{-}]^{m}[dye']^{n} \]

**The exponents m and n:**

The exponents m and n represent the order of the reaction and are most likely to be 0, 1, or 2, although non-integral values are possible. These exponents indicate how the rate is affected by the concentration of each reactant. The exponent \( m \) is the order of the reaction with respect to hydroxide concentration; the exponent \( n \) is the order of the reaction with respect to the dye. The overall reaction order is the sum of the exponents; in this case \( m + n \).

**How is a rate law useful?**

Once we measure experimental values for the order (m and n) and the rate constant (k), we could use the rate law to predict the rate of the reaction at a variety of concentrations. The value of the rate constant k is dependent on temperature, the presence of catalysts, and other factors. We will measure the rate law for the reaction in water at room temperature with no catalysis.

**Simplifying a complex experiment:**

Since the concentrations of both reactants change during the reaction, it is not possible which of the two concentrations is causing any rate changes we observe. Therefore we must look at one variable at a time. Using a technique, called "swamping", will simplify the mathematical treatment of the results by keeping the concentration of hydroxide ion essentially constant, so we can first focus on [dye] and its exponent, n.

In our experiment the dye concentration will be a thousand times lower than the OH\(^-\) ion concentration. Therefore the change in the hydroxide ion concentration during any given trial will be less than 0.1%. It is reasonable to approximate that the hydroxide ion concentration, [OH\(^-\)], is constant, not variable, during a given trial. As long as [OH\(^-\)] is approximately constant, so is \( k[OH^{-}]^{m} \) (k is a constant). We can designate a new variable, the pseudo-rate constant, \( k_p \), for this expression.

\[ k_p = k[OH^{-}]^{m} \quad (eq. 2) \]

Substitution of \( k_p \) into Equation 1 simplifies it to the pseudo rate law of equation 3:
Note that Equation 3, with fewer variables on the right, is simpler to work with than Equation 1.

**Monitoring the concentration of [dye']**

A spectrophotometer will be used to obtain measurements of the rate of this reaction. A spectrophotometer is a device which passes light of a selected wavelength (color) through the sample solution. Since some of the light is absorbed by the sample solution, less light reaches a detector to be converted into an electrical signal. If the concentration of a light-absorbing chemical species (the chromophore) is high, the solution will be intensely colored and will have a high absorbance. It is thus possible to measure the concentration of a colored solution by measuring its absorbance. The absorbance and concentration are directly proportional using a relationship called the Beer Lambert law.

\[ A = Ebc \]

Where \( A \) is the solution absorbance at a determined wavelength, \( E \) is a constant called the molar absorptivity or extinction coefficient, \( b \) is the path length in cm (a function of the instrument), and \( c \) is the molar concentration.

We need to monitor how the concentration of the purple dye cation changes as a function of time. The purple dye absorbs most efficiently when the light has a wavelength of 590 nm. If the absorbance \( A \) is directly proportional with purple dye cation concentration, then we can use the changes in absorbance as our way of monitoring the dye concentration. A spectrophotometer can display the changing absorbance good to 3 digits as the purple color fades.

**Solving for n: the order in dye concentration**

To determine \( n \) we graph the data.

If \( n = 0 \), the changing dye cation concentration would have no influence on the rate. If this is true, the dye concentration would decrease at a constant rate, and the best fit for a plot of [dye'] or absorbance versus time would be a straight line for every trial, with a slope equal to \(-k_p\).
Only if $n=1$, the best fit for a plot of $[\text{dye}^+]$ or absorbance versus time would be an exponential curve. When $n=1$, the pseudo-constant $k_p$ can be taken as the exponential constant from the displayed equation $A=A_0e^{-kp \times t} + B$. The fading reaction would slow down as the concentration of dye cation decreased.

Aside from computer curve-fitting, how could we tell if the curve is exponential? Integration of equation 3 assuming that $n = 1$ provides:

$$\ln [\text{dye}^+]_t = \ln [\text{dye}^+]_o - k_p t \quad (\text{eq. 4})$$

$$\ln A_t = \ln A_0 - k_p t \quad (\text{eq. 5})$$

The natural log of the purple dye cation concentration, represented by $\ln[\text{dye}^+]$, can be plotted as a function of time. (The subscript $t$ designates dye concentrations at any time $t$ once the reaction has begun; the subscript $o$ designates the initial dye concentration, prior to any fading, at time $= 0$.) Measured absorbances, as in the analogous Equation 5, can be taken more directly from the spectrophotomer.

If you prepare a derived plot of $\ln A$ versus time, and it is highly linear, it would confirm that $n=1$, and that the reaction is first order in dye concentration. The slope equals $-k_p$ in Eq.5 and its linear graph.
If and only if \( n = 2 \), meaning that the reaction is second order in dye concentration, the best fit of \( A \) versus time would be an inverse curve. A graph of \( 1/A \) vs. time would provide the most linear fit for the data and confirm the second order.

**Solving for \( m \):**

**Order of the Reaction in OH\(^-\) ion:**

Once we have determined the order of the reaction with respect to the dye cation concentration, we can separately consider the influence of the hydroxide concentration on the rate. A second trial with twice the concentration of \([OH^-]\) will indicate the value of \( m \). Refer to equation 1. Notice that if the exponent \( m \) is equal to zero, doubling \([OH^-]\) would have no effect on the rate. If \( m = 1 \), then doubling \([OH^-]\) would double the rate. If the exponent \( m = 2 \), then doubling \([OH^-]\) would make the rate increase by a factor of \( 2^2 = 4 \). The relationship between hydroxide ion concentrations and rates for the two trials can be expressed as an algebraic rearrangement of equation (1), with constant terms cancelling:

\[
\frac{\text{rate trial 2}}{\text{rate trial 1}} = \left(\frac{[OH^-]_2}{[OH^-]_1}\right)^m \quad (eq.6)
\]

Taking the natural log of both sides gives:

\[
\ln\left(\frac{\text{rate trial 2}}{\text{rate trial 1}}\right) = m \ln\left(\frac{[OH^-]_2}{[OH^-]_1}\right) \quad (eq.7)
\]

Rearranging to solve for \( m \) gives this result:

\[
m = \frac{\ln\left(\frac{\text{rate trial 2}}{\text{rate trial 1}}\right)}{\ln\left(\frac{[OH^-]_2}{[OH^-]_1}\right)} = \frac{\ln\left(\frac{k_{p2}}{k_{p1}}\right)}{\ln 2} \quad (eq.8)
\]
Since the rate of each trial is proportional to the value of the pseudo-constant, \( k_p \), for that trial, and since the second trial used twice the concentration of hydroxide, Eq. 8 can be simplified as:

\[
m = \frac{\ln \left( \frac{k_{p2}}{k_{p1}} \right)}{\ln 2} \quad \text{(eq. 8)}
\]

Values for \( k_p \) to use in Eq. 9 can be obtained by examination of the graphs, as described on the previous page.

**Experimental Assumptions**

In this experiment, some assumptions must be made.

1. The experiment is assumed to follow the Beer-Lambert law; the dye concentration is expected to be directly proportional with absorbance.
2. It is assumed that the dye absorbs most efficiently at a wavelength of 590 nm, as reported in the literature.
3. It is assumed that the amount of dye that comes out of solution and clings (adsorbs) to pipette tips or the walls of the spectrophotometer cells is too small to see or measure.
4. It is assumed that the drift in the instrument is small enough that a series of measurements can be completed before drift correction is necessary. ("Drift" refers to a gradual change in the signal from the instrument which is not due to a change in concentration.)
5. It is assumed that the temperature remains constant (to within 1°C) so that temperature does not significantly affect the rate of the reaction.

**Observations**

Do not concentrate exclusively on the numerical data. Look closely at how the color fades with time. Describe what the reaction looks like with passing time.

**Prelab Questions**

1. What do you observe when crystal violet dye is made basic?
2. What is the x-axis variable in all of the graphs you will prepare today? How is this related to the study of reaction kinetics?
3. What specific pattern or feature, seen on what graph, would convince you that the reaction in this experiment is first order with respect to the dye?
4. What can we learn about the reaction by performing two trials, one having twice the concentration of NaOH as the other?
5. What are the hazards associated with each?
   (a) NaOH solution
   (b) crystal violet dye
6. In every reaction mixture you prepare, the NaOH concentration will be over 1000 times higher than the dye cation concentration. How does this approach make your data treatment simpler?

**In the Laboratory - Procedural outline**
Work in teams as directed. Plan ahead so that your team is efficient and swift.

Caution!
NaOH is caustic and toxic.
The dye causes stains.

The square cuvettes are optical devices (like eyeglasses or contact lenses), so treat them with care. Hold them only by the ridged sides near the top, not by the transparent faces. Do not handle these sample cells with brushes or paper towels.

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Spectrum of Crystal Violet

1. **Instrument setup.** Log on to a computer that is connected by USB cable to a spectrophotometer. Run the Vernier LOGGERpro 3.6.0 program, found in the CHEMISTRY folder. (If popup boxes appear asking permission to install drivers, continually say yes until the program runs.) Open the file named “Crystal Violet Spectrum.” (This file can be found in I:\Doherty\Logger). The screen should look like a rainbow.

2. **Preparing a calibration blank.** Taking care to handle only by the ridged sides near the top, fill your square cuvette 2/3 full with distilled water. Cap the cuvette. Insert the cuvette so that the transparent sides are in the light path of the spectrophotometer.

3. **Instrument calibration.** The spectro-photometer must be calibrated to display an absorbance of zero when your blank cuvette is in position. Under the “experiment” menu, click on “calibrate” and select “spectrometer 1.” Allow a 60-second warmup as directed, and “finish calibration.” Click “OK.”

4. **Preparing a stable 1/3 dilution of dye stock.** Empty your cuvette. Using a micropipette as directed, deliver 1.000 mL of distilled water into the cuvette. Repeat a second time to bring the transferred volume of distilled water up to 2.000 mL. Move to the dye dispensing station. Using a single transfer, pipette 1.000 mL of crystal violet dye solution. Record the precise concentration from the bottle. Cap the cuvette tightly. Holding by the top and bottom, shake vigorously, insert it in the spectrophotometer.

5. **Obtaining the spectrum.** Click the green start arrow. Within seconds, a spectrum will appear. Hit the red “stop” button. Answer the questions on the data page about the spectrum.

6. **Printing the spectrum.** Under “file”, use the “Print Graph” command to print your spectrum, including your name in a footer.

7. **Examining the peak absorbance.** Drag a small gray box around the top region of your peak,
and right-click to “zoom graph in”. Comment in your data page on how near the top of the peak is to 590 nm, a figure reported in the literature. Right-click and select “zoom graph out” to restore the full spectrum.

8. **Selecting absorbance versus time.** If you have stopped data collection, there should be a rainbow spectrum icon two boxes to the left of the “start” button. Click this, and configure the spectrometer to record “Abs vs time”. Whatever wavelength gave the highest absorbance reading in your spectrum will be automatically selected. If this is not between 589 and 592 nm, uncheck this wavelength and select the nearest available wavelength to 590.0 nm, (You only want 1 wavelength checked, not 2.) Click “OK.” Do not store the spectrum when asked.

9. **Preparing for kinetic runs.** The instrument defaults to 200 seconds. We would prefer 300. Under “Experiment”, select “Data Collection.” Change the length to 300 seconds. Also change the sampling rate to 0.5 samples/second. (This will be one data point every 2 seconds.)

**Standard Solution Absorbance**

10. **Standard solution.** Use your cuvette filled with diluted purple standard solution, as prepared for the spectrum. If our experimental assumptions are true, the color and absorbance of this solution will not change at all over time. Click the green “start” arrow. Allow the LOGGER to gather the absorbance for at least 120 seconds before hitting the red button to stop data collection.

11. **Checking for drift or adsorption.** Drag across the entire absorbance-time trace to highlight it. Under “analyze,” select “statistics.” Record the minimum, average, and maximum absorbances in the trace. Note if the absorbance is trending upwards or downwards.

12. **Saving your standard solution data.** Use “Save As...” to save your standard trace to your log-on folder or USB memory stick. Create a descriptive filename such as “DYEFÄDE STANDARD yourinitials CHEMLAB”.

**TRIAL 1**

13. **Preparing the instrument for trial 1.** After data collection stops, under “Experiment,” select “Store Latest Run.” The trace dims on the screen. This readies the computer for you to record the next run in a moment.

14. **Preparing solution for dye fading trial 1.** Drain your cuvette into the sink. Rinse with distilled water. Shake away any loose drops. Using the appropriate pipettes and tips in turn, pipette 1.000 mL each of distilled water and 0.1000M NaOH solution into your cuvette. Move to the station with the crystal violet dye pipette.

15. **Trial one: the first ten seconds**

With the cuvette cap ready, pipette 1.000 mL of dye into the cuvette. Cap tightly. Holding between the thumb and index finger, shake vigorously up and down several times to mix the solution within. Immediately insert your cuvette in your spectrophotometer. Immediately click the green arrow to begin data collection.
16. **Saving Trial 1 data.** Allow the instrument to gather data for the full 300 seconds without stopping. Use “Save As...” to save your Trial 1 trace to your log-on folder or USB memory stick with a descriptive filename.

17. **Is “n” equal to zero?** Starting at the right margin, drag from right to left across the entire curve to highlight it. Under “Analyze” try “linear fit” for the latest trial. If this is an ideal fit, n=0 and the reaction is zero order in dye.

18. **Or is “n” equal to one?** Making sure the trace is highlighted, under “Analyze” choose ”Curve Fit” and specify for the latest trial a “natural exponential” fit. This corresponds to a first-order reaction in dye, with n=1.

19. **Or is “n” equal to 2?** Also try fitting the latest trial to an “inverse” or A/t curve. This corresponds to a second-order dye fading, with n=2. Choose which of these three curves fits the data most closely. Indicate the value of “n”.

20. **Determining a value for \( k_p \).** You should be able to determine a value for the pseudo-constant, \( k_p \), from the boxed equation remaining on your absorbance plot.

**Trial 2, double NaOH**

21. **Preparing the instrument for trial 2.** Under “Experiment,” select “Store Latest Run.” The standard trace and Trial 1 should be dimmed on the screen together in two colors.

22. **Preparing solution for dye fading trial 2.** Drain your cuvette into the sink. Rinse with distilled water. Shake away any loose drops. Using the appropriate pipette and tip, pipette twice to transfer 2.000 mL of 0.1000M NaOH solution into your cuvette. Move to the station with the crystal violet dye pipette.

23. **Trial two: the first ten seconds** With the cuvette cap ready, pipette 1.000 mL of dye into the cuvette. Cap tightly. Holding between the thumb and index finger, shake vigorously up and down several times to mix the solution within. Immediately insert your cuvette in the spectrophotometer. Immediately click the green arrow to begin data collection for the full 300 seconds.

24. **Saving Trial 2 data.** Use “Save As...” to save your Trial 2 trace to your log-on folder or USB memory stick with a descriptive filename.

25. **Compare** the appearances of the remaining solution to the standard solution made earlier, and record your observation on the data sheet.

26. **Solving for “m” by comparing both trials.** Once data collection has stopped, fit the best curve to your Trial 2 data. Find the value of the pseudo-constant, \( k_p \), for trial 2. Use Equation 9 to determine the value for “m”, the order of the reaction in hydroxide ion.

27. **Graph finishing and printing.** Use the mouse move the equation boxes out of the way of
your data curves. Use the “print graph” command to send one copy of your graph to the printer for each of the members of your team. Resave your file one last time.

28. **Cleanup.** Rinse your cuvette with distilled water and store it upside-down on a paper towel. Wipe your bench. Check that the pipettes are properly hung at the pipette stations. Disconnect the USB cable to your spectrophotometer to turn off its lamp.

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**Postlab Questions**

1. We assume that the solution temperature, which would affect the rate, is constant as the reaction proceeds. But the solution sits directly next to a warm light bulb. Design an experiment to test how much the temperature is actually changing. Describe the tools, timing, and measurements of your experiment.

2. (a) Use your rate law to predict what would be the initial rate at the start of a trial if $[\text{OH}^-] = 0.010\, M$ and $[\text{dye}] = 5 \times 10^{-6}\, M$.

   (b) Is this faster or slower than the start of your trial 1? Why?

3. An insecticide decomposes slowly in moist air. This insecticide can be measured spectrophotometrically when dissolved in mixtures of water and methanol. In designing an experiment to see how sensitive the rate of decomposition is to dissolved oxygen, list at least three variables you would need to keep constant in all trials.

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**Data Analysis**

You will need to determine the molarity of the diluted NaOH and the diluted stock solution.

Determine and record the concentration of the dye stock solution.

Determine $k_p$, the pseudo-rate constant using equation 3.

Prepare three plots to examine the order of the dye using Excel. Prepare a zero order test plot (absorbance vs. time), a first order test plot ($\ln$ absorbance vs time) and a second order test plot($1/\text{absorbance}$ vs. time). Determine which plot has the best linearity. Use this to determine $n$, the order of the dye.

Determine $m$, the order of hydroxide using equation 9.

Write the rate law for the equation based upon your data.