Preparatory Exercise for A KINETIC STUDY: REACTION OF CRYSTAL VIOLET WITH NaOH
Sample Data Practice

LEARNING OBJECTIVES

The objectives of this sample data practice are:

- To gain familiarity with EXCEL spreadsheet calculations and graphs using the given sample data.
- To be prepared for next week’s laboratory experiment on Kinetic Study of Crystal Violet reaction with NaOH.

BACKGROUND

Reaction Chemistry

Chemical kinetics is the study of reaction rates. In this exercise, the kinetics of the reaction between crystal violet and NaOH will be demonstrated with a sample data set. An EXCEL spreadsheet will be setup with a set of sample data from a Spec-20 spectrophotometer, which was used to monitor the crystal violet concentration as a function of time. The reactant and product structures and the reaction stoichiometry are shown in Figure 1 on the next page.

All of the reactants and products shown in Figure 1 are colorless except for crystal violet which has an intense violet color. Thus, during the course of the reaction, the reaction mixture color becomes less and less intense, ultimately becoming colorless when all of the crystal violet has been consumed. The following is the balanced molecular equation:

\[
C_{25}H_{30}N_3Cl(aq) + NaOH(aq) \rightarrow C_{25}H_{31}ON_3(aq) + NaCl(aq)
\]
The crystal violet color is due to the extensive system of alternating single and double bonds which extends over all three benzene rings and the central carbon atom. This alternation of double and single bonding is termed conjugation, and molecules which have extensive conjugation are usually highly colored. Trace the conjugation in the crystal violet structure and note that in the reaction product, the three rings are no longer in conjugation with one another, and hence, the material is colorless.

**Kinetic Rate Laws**

The rate of the crystal violet/NaOH reaction is given by the following generalized rate law.

\[
    (1) \quad \text{Rate} = k [\text{OH}^{-}]^{x} [\text{CV}]^{y}
\]

In Equation (1), \(k\) is the rate constant for the reaction, \(\text{CV}\) is an abbreviation for crystal violet (\(\text{CV}\) is an aqueous chloride solution), \(\text{C}_{25}\text{H}_{30}\text{N}_{3}^{+}\), \(x\) is the reaction order with respect to \(\text{OH}^{-}\), and \(y\) is the reaction order with respect to \(\text{CV}\). The values of \(x\) and \(y\) can be determined experimentally. Possible \(x\) values are 1 or 2 (first order or second order). Possible \(y\) values are also 1 or 2.
In this sample experiment, the initial [OH\(^-\)] is made much greater than the initial [CV]. Thus, the [OH\(^-\)] change, during the time that the CV is consumed, is negligible. For this reason, [OH\(^-\)]\(^x\) can be treated as a constant and Equation (1) can be written as follows,

\[
\text{Rate} = k'[CV]^y
\]

and if [OH\(^-\)]\(_o\) >> [CV]\(_o\), then

\[
\text{Rate} = k'[CV]^y
\]

Where: \(k' = k[OH^-]^x\) (\(k'\) is termed a pseudo rate constant.)

The integrated form of the pseudo rate law (2) depends on the reaction order with respect to CV. The integrated rate laws for \(y = 1\) and \(2\) are given in Equations (3) and (4). Compare each with the general form of a linear equation, \(y = mx + b\), in which \(y\) is identified as \(\ln [CV]_i\) in Equation (3) and as \(1/[CV]_i\) in Equation (4):

\[
\ln [CV]_i = -k't + \ln [CV]_o \tag{3}
\]

\[
\frac{1}{[CV]_i} = k't + \frac{1}{[CV]_o} \tag{4}
\]

**Calculus Derivation of Equation (3) for \(y = 1\)**

Define: \(\text{Rate} = -\frac{d[CV]}{dt} = k'[CV]^1\);

\[
\int_{[CV]_0}^{[CV]_t} [CV] \frac{d[CV]}{[CV]} = -k' \int_{0}^{t} dt
\]

\[
\ln[CV]_{[CV]_0}^{[CV]_t} = (-k') \cdot t
\]

\[
\ln [CV]_i = -k't + \ln [CV]_o
\]

where: slope = \(m = (-k')\)
In Equations (3) and (4), $[CV]_o$ is the concentration of crystal violet in the reaction mixture at time zero, before any reaction has occurred; $[CV]_t$ is the concentration at any time $t$ during the course of the reaction. If a plot of $\ln [CV]_t$ versus time is linear, $y = 1$ and the reaction is first order in CV. Similarly, a linear plot of $1/[CV]_t$ versus time indicates a second order reaction in CV. Only one of these plots will be linear. For the one that is linear, the resulting straight line slope (its absolute value) equals the pseudo rate constant, $k'$. In order to do the graphing just described, we need to have data showing how the CV concentration changes with time. The % Transmittance data from a Spectronic-20 spectrometer have been manually recorded in an EXCEL spreadsheet. The spreadsheet can be setup to simultaneously convert %T to Absorbance and provide active graphs of %T versus Time and Absorbance versus Time.

Crystal violet solutions obey Beer’s law. Thus, the relationship between percent transmittance and the CV concentration is given by:

$$A_t = -\log \left( \frac{\%T}{100} \right) = \varepsilon bc$$

In Equation (5), $A_t$ is the reaction solution absorbance at any time $t$; $\varepsilon$ is the CV molar absorptivity, $5.0 \times 10^4$ L cm$^{-1}$ mol$^{-1}$; $b$ is the cell path length (1.00 cm); and $c$ is the CV molar concentration at time $t$, $[CV]_t$. Thus, Beer’s law can be used to calculate $[CV]_t$ from each photocell percent transmittance reading during the kinetic run.

SAFETY PRECAUTIONS

None for this sample data practice.
EXPERIMENTAL PROCEDURE (PART 1)

Measurements (Done by Sample Experimenter)

1. The spectrometer was on for at least 20 minutes before operation.

2. The spectrometer wavelength was set to 590 nm.

3. Before beginning the kinetic measurements, a 0% and 100% transmittance calibration was performed according to the instructions on the Spectronic-20 spectrometer; [0%T with no cuvet (left knob); 100%T with H₂O-cuvet (right knob)]. Distilled water was used as the blank. Any fingerprints were wiped off the outside of the cuvet. When completed, the cuvet was dry before samples were placed inside.

4. The EXCEL spreadsheet columns were set up [Col-A: Time; Col-B: %T (read from Spec-20); Col-C: ABS (= - log(%T/100) ]]. Two active graphs were created ( %T versus Time and ABS versus Time ) on the same spreadsheet. They were resized so that both data entered and graph profiles can be seen simultaneously. Before experimental runs, a few %T values were entered to check graphing action.

5. Using the buret provided, 9.00 mL of 1.5 x 10⁻⁵ M crystal violet solution was dispensed into a clean, dry 50 mL beaker. Using a 1-mL disposable volumetric pipet, 1.00 mL of 0.050 M NaOH was added to the CV solution as rapidly as possible without splashing.

6. The CV/NaOH solution was thoroughly mixed in a beaker and then the cuvet was filled ¾ full. The cuvet was placed in the spectrometer and %T was collected as a function of time. **All the operations in steps 5 and 6 were completed as quickly as possible.** This insured that the first measurement will be made as close to the reaction start as possible.

Data was collected for approximately 35 minutes. The data was saved after each trial.

EXPERIMENTAL PROCEDURE (PART 2)

Measurements (Done by Sample Experimenter)

Recall that the k’ just obtained is a pseudo rate constant, whose value depends upon the OH⁻ concentration, i.e. k’ = k[OH⁻]ˣ. In this part of the experiment, the value of x will be determined as well as the value of the true rate constant, k.

In part 1 of the experimental procedure, 9.00 mL of 1.50 x 10⁻⁵ M crystal violet and 1.0 mL of 0.050 M NaOH were combined to form the reaction mixture. In this second part, a second kinetic run was made in exactly the same way except that the NaOH concentration was doubled to 0.10 M.
Therefore, PART 2 was performed by following the last two experimental steps in PART 1 (steps 5 and 6) using 1.0 mL of 0.10 M NaOH in place of 0.050 M NaOH.

**SAMPLE EXPERIMENTAL DATA**

*(Collected by Sample Experimenter)*

Sample data for Parts 1 and 2: used to calculate the theoretical rate constant, k.

<table>
<thead>
<tr>
<th>CV + 0.050 M NaOH</th>
<th>CV + 0.10 M NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total Min</strong></td>
<td><strong>% T</strong></td>
</tr>
<tr>
<td>0.891</td>
<td>19.93716</td>
</tr>
<tr>
<td>4.892</td>
<td>26.83577</td>
</tr>
<tr>
<td>8.892</td>
<td>34.08174</td>
</tr>
<tr>
<td>12.893</td>
<td>40.62858</td>
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<td>16.893</td>
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<tr>
<td>20.893</td>
<td>53.91303</td>
</tr>
<tr>
<td>24.894</td>
<td>60.12763</td>
</tr>
<tr>
<td>30.894</td>
<td>68.38302</td>
</tr>
</tbody>
</table>

**DATA ANALYSIS (PART 1)**

*[To be performed by your lab group during the Check-in lab period one week before your actual Kinetic experiment]*

1. In an EXCEL spreadsheet, type in the above sample data for the 0.050 M NaOH experiment. Column A for Total Min and column B for %T. For column C \(A_t\), type in an equation for Absorbance using Equation (5). Then, in the next column, compute \([CV]_t\) for each data point using Beer’s law \([\text{Absorbance} = \frac{A_t}{5.0\times10^4}]\). Format the display of the values in this column in scientific notation. In columns E and F compute \(1/[CV]\) and \(\ln(CV)\). Be sure to properly label all columns.
2. Plot %T (y-axis) versus time in minutes (x-axis). Then plot A_t versus time. Observe the trend in both graphs. Now plot [CV] versus time. Which of these three graphs would you choose to illustrate rates of a chemical reaction?

3. Plot 1/[CV], (y-axis) versus time in minutes (x-axis). If the reaction between crystal violet and NaOH is second order in crystal violet, this plot will be linear. If it is not second order, this plot will be curved. Test for linearity with a first order (or linear regression) curve fit. Look at the actual data points. If they clearly follow a curved departure from the regression line it should be concluded that the reaction is not second order in crystal violet.

4. Repeat step (2), substituting ln [CV], for 1/[CV]. A linear graph in this instance would indicate a first order dependence on crystal violet. Closely examine your data as done in step 3 above.

5. Prepare and print a carefully labeled graph for the plot which exhibited the best linear relationship. Include the first order (or linear regression) curve fit line. With this plot you have identified y, the reaction order with respect to [CV]. Record the value of y on the sample report data sheet. The absolute value of the slope for the straight line (shown in the regression equation at the top) is the best value of k’. Record this value with proper units and to the correct number of significant figures.

**DATA ANALYSIS (PART 2)**

[To be performed by your lab group during the Check-in lab period one week before your actual Kinetic experiment]

1. Repeat data treatment steps 1, 2, 3, 4 and 5 (for 0.10 M NaOH data) as listed above and again record the k’ value.

2. From the ratio of the two k’ values, determine the reaction order with respect to OH\(^{-}\) (the value of x). Clearly show your calculation of x. You will need to use the NaOH concentrations after dilution with CV. Note: The value of x should be an integer. If your value is not an integer, it is because of experimental error (probably in measuring and adding the NaOH solutions). If necessary, round your x value to the nearest integer.

3. Calculate the true rate constant (k) value from each of the k’ values. Be sure to use OH\(^{-}\) concentrations that have been adjusted for dilution. Finally, average the two k values obtained. Again, be sure to watch significant figures and use proper units.

4. Check your results against the Sample Data Answer Key and show your graphs and calculations to your lab instructor before leaving the lab.
REACTION OF CRYSTAL VIOLET WITH NaOH: A KINETIC STUDY

Data Sheet (Sample Data)

CV Reaction Order (y)
Key equation: \[ \text{rate} = k' [\text{CV}]^y \] (y = 1 or 2)
Part 1 (using 0.050 M NaOH) \[ y _____ k' \text{ (give units)} \]
Part 2 (using 0.10 M NaOH) \[ y _____ k' \text{ (give units)} \]

Hydroxide Reaction Order (x)
Key equation: \[ k' = k [\text{OH}^-]^x \] (x = 1 or 2)
\[
\frac{k' \text{ (part 2)}}{k' \text{ (part 1)}} = \frac{k[\text{OH}^- \text{ (part 2, after dilution)}]^x}{k[\text{OH}^- \text{ (part 1, after dilution)}]^x} \]
\[ x _____ \text{ rounded } x _____ \]
Show one of the above dilution calculations and the calculation of x.

Rate Constant (k)
Key equation: \[ k' = k [\text{OH}^-]^x \] (use rounded x)
Part 1 \[ [\text{OH}^-], \text{after dilution} \] \[ k' \text{ (part 1)} \] \[ k \]
Part 2 \[ [\text{OH}^-], \text{after dilution} \] \[ k' \text{ (part 2)} \] \[ k \]
\[ \text{Average } k \text{ (with units)} \]

Summary
Final rate law
Rate constant (k) with units
REACTION OF CRYSTAL VIOLET WITH NaOH: A KINETIC STUDY

Data Sheet (Sample Data) [Answer Key]

CV Reaction Order (y)

Key equation: \( \text{rate} = k'[\text{CV}]^y \) (\( y = 1 \) or 2) \{via plot of ln[CV] vs. time\}

Part 1 (using 0.050 \( M \) NaOH) \( y = 1 \) \( k' \) (give units) \( 0.048 \text{ min}^{-1} \)

Part 2 (using 0.10 \( M \) NaOH) \( y = 1 \) \( k' \) (give units) \( 0.094 \text{ min}^{-1} \)

Hydroxide Reaction Order (x)

Key equation: \( k' = k[\text{OH}^-]^x \) (\( x = 1 \) or 2)

\[
\frac{k'(\text{part 2})}{k'(\text{part 1})} = \frac{k[\text{OH}^- (\text{part 2, after dilution})]^x}{k[\text{OH}^- (\text{part 1, after dilution})]^x} \]

\( x = 0.97 \) rounded \( x = 1 \)

Show one of the above dilution calculations and the calculation of \( x \).

Part 1 \( \Rightarrow \) \( [\text{OH}^-] = 0.050 \text{M} \times \left( \frac{1}{10} \right) = 5.0 \cdot 10^{-3} \text{M} \)

Part 2 \( \Rightarrow \) \( [\text{OH}^-] = 0.10 \text{M} \times \left( \frac{1}{10} \right) = 1.0 \cdot 10^{-2} \text{M} \)

\[
\begin{align*}
\{\text{Part (2)}\} & \Rightarrow 0.094 \text{ min}^{-1} = \frac{k \cdot [1.0 \cdot 10^{-2} \text{M}]^x}{k \cdot [5.0 \cdot 10^{-3} \text{M}]^x} = (2.0)^x \Rightarrow 1.96 \\
\{\text{Part (1)}\} & \Rightarrow 0.048 \text{ min}^{-1} = \frac{k \cdot [5.0 \cdot 10^{-3} \text{M}]^x}{k \cdot [1.0 \cdot 10^{-2} \text{M}]^x} = (2.0)^x \Rightarrow 1.96 \\
\end{align*}
\]

\[
\ln(2.0)^x = \ln(1.96)
\]

\[
x = \frac{\ln(1.96)}{\ln(2.0)} = 0.292 = 0.971 = 1
\]

Rate Constant (k)

Key equation: \( k' = k[\text{OH}^-]^x \) (use rounded \( x \))

Part 1 \quad Part 2

\begin{align*}
[\text{OH}^-], \text{after dilution} & \quad 5.0 \times 10^{-3} \text{M} \quad \text{[OH}^-], \text{after dilution} & \quad 1.0 \times 10^{-2} \text{M} \\
k' (\text{part 1}) & \quad 0.048 \text{ min}^{-1} \quad k' (\text{part 2}) & \quad 0.094 \text{ min}^{-1} \\
k & \quad 9.6 \text{ L mol}^{-1} \text{ min}^{-1} & \quad k & \quad 9.4 \text{ L mol}^{-1} \text{ min}^{-1} \\
\end{align*}

Average \( k \) (with units) \( 9.5 \text{ L mol}^{-1} \text{ min}^{-1} \)

Summary

Theoretical Final rate law \( \text{Rate} = k[\text{CV}] \cdot [\text{OH}^-] \)

Theoretical Rate Constant (k) with units \( k = 9.5 \text{ L mol}^{-1} \text{ min}^{-1} \)