Experiment 4

Determining the Rate Law and Activation Energy for the Methyl Blue Reaction:

An exercise in experimental design

Pre-Lab Assignment

Before coming to lab:

- Read the lab thoroughly.
- Answer the pre-lab questions that appear at the end of this lab exercise. The questions should be answered on a separate (new) page of your lab notebook. Be sure to show all work, round answers, and include units on all answers. Background information can be found in Chapter 14, especially sections 14.1- 14.4 in your textbook (Brown and LeMay).
- Follow the guidelines in the "Lab Notebook Policy and Format for Lab Reports" section of the lab manual to complete in your lab notebook the following sections of the report for this lab exercise: Title, Lab Purpose, Procedure and Data Tables.
- **You will need to write your own detailed procedure for this lab.**

Purpose

The goal of this lab is to determine the rate law for the reaction between methyl blue and hydroxide ions, and the activation energy for the reaction. This will be accomplished by monitoring the absorption of a methyl blue solution as it fades at it reacts with hydroxide.

Specifically you will need to:

a) Determine the best wavelength of light to use for the experiment (λ_{max})
b) Construct three graphs that will allow you to determine the order of the reaction with respect to methyl blue using the integrated rate laws.
c) Determine the activation energy of the reaction

Background

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

A simplified version of the equation is:

	MB^{+} (aq)	+	OH^{-} (aq)	→	MBOH (aq)
Color:	**Blue**		**Colorless**		**Colorless**

As usual, the rate law for this reaction is in the form: rate = $k[MB^{+}]^{m}[OH^{-}]^{n}$, where k is the rate constant for the reaction, m is the order with respect to methyl blue (MB^{+}), and n is the order with respect to the hydroxide ion.

As the reaction proceeds, the blue-colored reactant will be slowly changing to a colorless product. You will measure the absorbance change with a Vernier Spectrometer as the reaction proceeds.

We will assume that absorbance is proportional to the concentration of methyl blue (Beer's Law) and therefore can use absorbance in place of concentration of MB in constructing our graphs. By determining which of your graphs is linear, you will be able to determine order of the reaction with respect to MB (m in the above rate law).

Because hydroxide (OH^-) is colorless and therefore unable to be detected with a spectrometer, we will not be determining the order of the reaction with respect to OH^- (n in the above rate law). To insure that the concentration of OH^- is a constant as the reaction proceeds and therefore does not affect your results, we will use a concentration of OH^- more than 1000 times as large as the concentration of methyl blue, $[OH^-]$ will not change appreciably during this experiment. Thus, you will find the order with respect to methyl blue (*m*), but not the order with respect to hydroxide (*n*).

To determine the activation energy (E_a), you will need to repeat the experiment while varying the temperature. This will allow you to determine the value of the rate constant (k). Note that the value of the rate constant we will be determining will only be valid when the concentration of OH^- is not changing. For this reason, it is important that the concentration of OH used in each trial is consistent.

Procedure

Safety

GENERAL SAFETY: Methyl Blue is a stain. Avoid spilling it on your skin or cloths. Sodium hydroxide solution is caustic. Avoid spilling it on your skin or clothing. Students must wear safety goggles at all times. The hot-water baths used in Part B of this experiment can become hot enough to burn your skin. Use caution when working with them.
WASTE DISPOSAL: All solutions used in this lab may be disposed of in the sink.

Materials and Equipment you will be provided beyond what is in your drawer:

computer
Vernier Spectrometer
cuvettes
two 10 mL pipettes

0.10 M sodium hydroxide, NaOH, solution
2.5×10^{-5} M methyl blue solution

-hot-water baths set at different temperatures (available in lab room)
-ice-water bath (obtain a bucket of ice from the stockroom)

A detailed procedure is not provided in this experiment- only a general outline. You will need to write out a step by step-by-step procedure as part of your pre-lab.

Part A: Determine the best wavelength of light to use for the experiment (λ_{max})

Using the Vernier Spectrometer, you will need to determine the wavelength of light that methyl blue absorbs most strongly (λ_{max}). This will be the best wavelength of light to use for the rest of the experiment.

Write out a detailed procedure of how you will accomplish this in you lab notebook. Be sure to include the steps necessary to calibrate the spectrometer. ***The procedure should include numbered steps- at least four for this part of the lab including the amounts and concentrations of chemicals to be used.***

Part B: Construct three graphs that will allow you to determine the order of the reaction with respect to methyl blue using the integrated rate law.

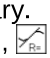
You will be mixing 0.10 M NaOH with 2.5×10^{-5} M methyl blue in order to construct three graphs that will allow you to determine the order of the reaction with respect to methyl blue. We will assume that absorbance is proportional to the concentration of methyl blue (Beer's Law). Absorbance will be used in place of concentration in constructing our graphs.

Write out a detailed procedure of how you will accomplish this in you lab notebook***. The procedure should include numbered steps- at least eight for this part of the lab including the amounts and concentrations of chemicals to be used.***

Some details regarding the proper use of the Vernier Software is given below.

- Absorbance data will need be collected for at least three minutes.
- Analyze the data graphically to decide if the reaction is zero, first, or second order with respect to methyl blue. Print your graphs!
- To help construct one of your graphs, you will need to create a calculated column, **ln Absorbance**. To do this,

  a. Choose New Calculated Column from the Data menu.

  b. Enter "ln Absorbance" as the Name, and leave the unit blank.
  c. Enter the correct formula for the column into the Equation edit box by choosing "ln" from the Function list, and selecting "Absorbance" from the Variables list. Click Done
  d. Click on the y-axis label. Choose ln Absorbance. A graph of ln absorbance *vs.* time should now be displayed. Change the scale of the graph, if necessary.
  e. To see if the graph is linear, click the Linear Regression button, .
  f. Close the Linear Regression box by clicking the X in the corner of the box.

- To help construct one of your graphs, you will need to create a calculated column, 1/Absorbance. To do this,

a. Choose New Calculated Column from the Data menu.

b. Enter “1/Absorbance” as the Name, “1/Abs” as the Short Name and leave the unit blank.
c. Enter the correct formula for the column into the Equation edit box by choosing “1/”. Then select “Absorbance” from the Variables list. Click Done
d. Click on the y-axis label. Choose 1/Absorbance and uncheck any other boxes. A graph of 1/Absorbance *vs.* time should now be displayed. Change the scale of the graph, if necessary.
e. To see if the graph is linear, click the Linear Regression button, . Write down the slope value in your data table as the rate constant, *k*.
f. Close the Linear Regression box by clicking the X in the corner of the box.

Part C: Determine the activation energy of the reaction

You will be mixing 0.10 M NaOH with 2.5×10^{-5} M methyl blue in order to construct at least four more graphs where the temperature is varied and find the value of the rate constant at each temperature. Note that the rate constant you are finding is what is referred to as a pseudo rate constant, because it does not take into account the effect of the other reactant, OH^-. In your experiment, $[OH^-] >> [MB^+]$, so $[OH^-]$ is essentially constant throughout the experiment. We will again, as in Part B, assume that absorbance is proportional to the concentration of methyl blue (Beer's Law) and therefore use absorbance in place of concentration of methyl blue in constructing our graphs.

After you repeat the experiment four more times, you will then need to construct another graph to determine the value of the activation energy (E_a). Do this graph using Excel. Be sure your graph is well labeled and print this graph. Be careful with your units of temperature. Be sure to report your activation energy in J/mol and the more common unit of kJ/mole.

Write out a detailed procedure of how you will accomplish this in you lab notebook. The procedure should include numbered steps- at least eight for this part of the lab and amounts and concentrations of chemicals you plan on using.

Data Tables and Calculations

Prepare a data table for each part of the lab. Include both measured values and calculated values. Be sure to properly label each value and include the units.

Post-Lab Questions

1. Suggest two specific improvements in your procedure from Part B of the experiment you could make to improve the reliability of your data.

2. Suggest two specific improvements in your procedure from Part C of the experiment you could make to improve the reliability of your data.

3. Calculate the half-life of methyl blue for each of your trials from Part C.

4. Using E_a and A from your graph, calculate the rate constant of the reaction at 125^oC.

Pre-Lab Questions

1. Methyl Blue is (not surprisingly) blue in color. At approximately what wavelength should it most strongly absorb light? Note: You will be determining the exact wavelength in lab.

2. In this experiment, you will need to construct three graphs to determine if the reaction is zero, first or second order with respect to methyl blue.

   a. For a zero order reaction a graph of _________ versus ____________ will be a straight line. The slope of the line is equal to _________.
   b. For a first order reaction a graph of _________ versus ____________ will be a straight line. The slope of the line is equal to _________.
   c. For a second order reaction a graph of _________ versus ____________ will be a straight line. The slope of the line is equal to _________.

3. In order to experimentally determine the activation energy of a reaction, what variables should be plotted against each other?

4**.** The following data were collected for a reaction of type: A → Products.
Complete the last two columns and answer the questions below:

Time (s)	**[A] (M)**	**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}		

Determine the order of the reaction with respect to A and the find the value of the rate constant. You must graph the data to determine the order. Use Excel to graph your data and include a brief explanation.