

Experiment N: Effect of Temperature on Reaction Rate

Reading

Sections 15.5 to 15.7 from T.0, N), F. Hagen, J.D. and Shaw, L.E. *Chemistry: A Molecular Approach* 2nd Edition, Pearson Education, Inc., 2004.

Objectives

The rate at which a chemical reaction occurs is dependant upon several factors: the chemical nature of the reactant(s), the reactant concentration(s), and (sometimes) the presence of a catalyst. In the Experiment M you studied the effect of reactant concentrations on the rate of the reaction of crystal violet (CV⁺) with hydroxide ion (Reaction (1)) at room temperature.



In this experiment, you will

- Conduct the reaction between crystal violet and sodium hydroxide at four different temperatures.
- Determine the effect of temperature on the reaction rate and rate constant.
- Calculate the activation energy (E_a) for the reaction.

Introduction

Collision Theory

An important part of the kinetic analysis of a chemical reaction is the determination of the activation energy, E_a . The reaction rates of chemical reactions range from imperceptibly slow to essentially instantaneous. This wide range is the result of large differences in the activation energy: the energy needed to bring reactants close enough together to allow for the formation of the transition state (activated complex). In Collision Theory, one assumes that reactant molecules must collide with a total energy equal to or greater than the activation energy, E_a . For example, the collision of two negatively charged ions is expected to have a larger activation energy than a comparable collision of two oppositely charged ions. The larger the activation energy, the slower the reaction.

In a hypothetical elementary reaction, $A + B \rightarrow Y + Z$, having the energy profile plotted in the diagram below, the reactant entities A and B colliding with a total energy equal to or greater than the activation energy, E_a , can bind to form an activated complex $[AB]^{\ddagger}$ at the transition state. The highly unstable activated complex $[AB]^{\ddagger}$ can either break down to give the reactant entities A and B or internally rearrange the bonds to form the product entities Y and Z. The activation energy threshold for the reaction is reached by conversion of the kinetic energy of the reactant entities A and B to potential energy at moment of collision, when the entities A and B bind to form the highly energetic activated complex $[AB]^{\ddagger}$.

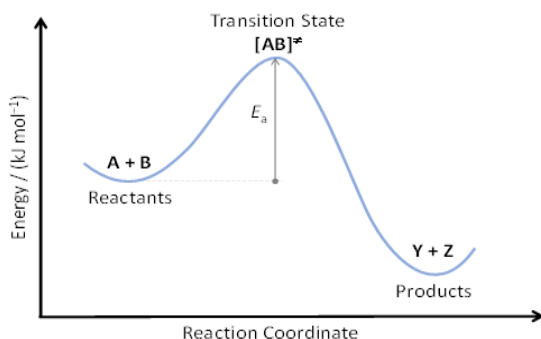


Figure 1. Reaction profile for the hypothetical elementary reaction: $A + B \rightarrow [AB]^{\ddagger} \rightarrow Y + Z$

The E_a is the minimum collisional energy needed to overcome the mutual repulsion of the electron clouds of the colliding molecules and bring them close enough together to permit the formation of the bonds in the product molecules while breaking the appropriate bonds in the reactant molecules. It constitutes an energy barrier for the reactant entities A and B; the higher the barrier is, the fewer the number of successful collisions of A and B that can overcome this barrier. If we compare two reactions with the same overall order occurring at the same temperature, the reaction with the larger E_a has the smaller rate constant, k .

Arrhenius Theory on the Temperature Dependence of Reaction Rate Constants

As you discovered in Experiment M, when we repeat a reaction several times at the same fixed temperature, each time varying the initial concentrations of reactants arbitrarily, we observed that the value of the rate constant k remains constant. However, if we repeat a reaction several times starting with the same initial concentrations of reactants, but each time carrying out the reaction at a different fixed temperature, we will observe that k increases as temperature increases. This is so, because as temperature increases, the reactant molecules have higher kinetic energy on average (because they move faster), and as a result, a greater number of collisions will have enough energy to overcome the activation energy of the reaction and will form activated complexes that can transition into the product molecules. The relation between the rate constant k and the absolute temperature T (in kelvin) is given by the *Arrhenius equation*:

$$k = A e^{-\frac{E_a}{RT}} \quad (3)$$

In Equation (3), A is called the *pre-exponential factor* or *Arrhenius A-factor*, R is the gas constant ($R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$) and e is the Euler's number ($e = 2.718\dots$), which is the base of natural logarithms.

If we take the natural logarithm ($\ln$) of each side of equation (3), we obtain the *linearized Arrhenius equation*:

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \ln A \quad (4)$$

Equation (4) represents the equation of a straight line in the form $y = mx + b$, in which " $\ln k$ " is the y -variable, " $1/T$ " is the x -variable, " $-E_a / R$ " is the slope m , and " $\ln A$ " is the y -intercept b . In this experiment, the activation energy will be found by a graphical method. You will plot several experimentally determined values of $\ln k$ versus $1/T$; you will draw the best fitting line and will calculate the slope. The calculated slope is equal to $-E_a / R$.

The activation energy of a reaction is independent of both temperature and initial reactant concentrations. The activation energy is a characteristic property of a reaction. Always remember that the rate of a reaction and the rate constant k for a reaction are temperature-dependant, whereas the activation energy E_a is not.

Experimental Method

In this experiment, we will examine the kinetics for the reaction between hydroxide ion and CV⁺: $\text{OH}^-(\text{aq}) + \text{CV}^+(\text{aq}) \rightarrow \text{CVOH}$. Crystal violet in water is a bright purple solution and the product of its reaction with the hydroxide ion is colorless. The rate law for this reaction is:

$$\text{rate} = k[\text{OH}^-][\text{CV}^+] \quad (5)$$

The reaction is thus first order with respect to both reactants. As in the previous experiment, the study will be carried out under pseudo-first order conditions: the initial concentration of hydroxide ion, $[\text{OH}^-]_i$, will be much larger than the concentration of CV⁺ so that only the concentration of CV⁺ will effectively change with time. Such a small fraction of the initial $[\text{OH}^-]$ will be consumed that $[\text{OH}^-]$ will remain virtually constant throughout the course of the reaction. This allows for a modified expression for the rate law:

$$\text{rate} = k[\text{OH}^-][\text{CV}^+] = k'[\text{CV}^+] \quad \text{with } k' = k[\text{OH}^-] \quad (6)$$

From the equation (7) we get the overall rate constant, k :

$$k = k' / [\text{OH}^-] \quad (7)$$

You will monitor the reaction at different temperatures, while keeping the initial concentrations of the reactants the same for each trial. In this way, you will isolate and measure the effect of temperature change on the rate of the reaction. From this information, you will be able to calculate the activation energy, E_a , of the reaction.

Overall, the procedure for this experiment is quite similar to the procedure for Experiment M. The major difference in Experiment N is that you will conduct four trials at different temperatures. Because the temperature will change slightly *during* the run, you will use the average temperature for a run during calculations.

Advance Study Assignment

- Compare the equation: $\ln k = -E_a/RT + \ln A$ to the straight-line equation, $y = mx + b$.
 - Is it necessary to know the value of A in order to solve for E_a in this experiment?
Answer: No, E_a is obtained from the slope of the line and A is obtained from the y -intercept (but both may be obtained simultaneously.)
 - How does a change in reaction temperature affect E_a ? Answer: Temperature does not affect the value of E_a .
- What units are used when expressing the pre-exponential factor, A ? Answer: the units used for A depend on the overall order of the reaction and are thus the same as the units of k for the reaction.
- A student performed this experiment and plotted $\ln k$ versus $1/T$. The activation energy, E_a , was determined to be 6.5 kJ/mol and the pre-exponential factor, A , was determined to be $8 \times 10^3 \text{ s}^{-1}$. Answer the following questions using this information:
 - Calculate the slope of the $\ln k$ versus $1/T$ graph. Answer: $-7.8 \times 10^2 \text{ K}$.
 - Calculate the y -intercept of the $\ln k$ versus $1/T$ graph. Answer: 9.
- In a kinetic experiment, a plot of the $\ln k$ versus $1/T$ yields a straight line relationship with the equation $y = (-6582.3 \text{ K})(x) + 14.677$. Determine the value of the pre-exponential factor and the activation energy, assuming that the reaction is a first-order process. Answer: $2.37 \times 10^6 \text{ s}^{-1}$, $E_a = 5.47 \times 10^4 \text{ J/mol} = 54.7 \text{ kJ/mol}$.
- The rate constant, k , for a particular reaction is $1.3 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$ at 50°C and $8.1 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$ at 100°C . Calculate the activation energy, E_a . Answer: 82.8 kJ/mol.
- How would you calculate k from known values of k' and $[\text{OH}^-]$? Answer: $k = k' / [\text{OH}^-]$.

Reagents and Equipment

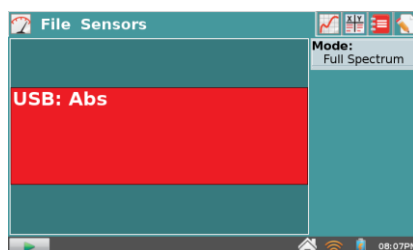
- 0.020 mol/L NaOH
- $2.5 \times 10^{-5} \text{ mol/L}$ crystal violet (120 mL in brown bottles)
- 1.0 mol/L HCl
- 400 mL beaker
- glass test tube cuvettes (4)
- plastic test tube (for NaOH) (4)
- LabQuest 2 Device with SpectroVis Spectrometer and temperature probe

Procedure (Partnered)

Part I: Preparation of the LabQuest 2.

Instructions for the setup and calibration of the instrument are available starting on page 24 in the introductory section of the lab manual, but are summarized below. You should use deionized water as the blank solution during calibration.

1. Ensure that the LabQuest 2 unit is plugged in and turned on. Although the unit may be run on battery power, the spectrometer will drain power quickly and thus it is best to run the unit on AC power:
2. Connect the SpectroVis Plus spectrometer to the LabQuest 2 unit by USB cable. The LabQuest 2 display should appear as follows:

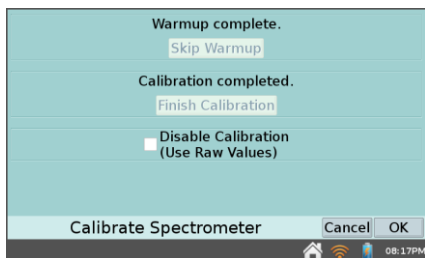


3. Tap anywhere within the red USB: Abs box and then select “Calibrate...” from the menu that appears. While the 90-second warmup proceeds (see figure below) you can complete steps 4, 5, and 6.

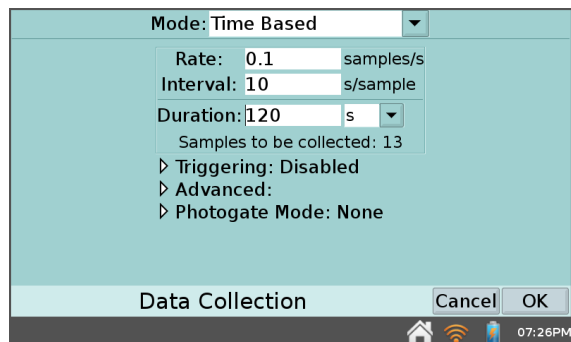


4. Before filling the glass test tube cuvette with the blank solution, rinse it three times by filling it about $\frac{1}{3}$ full with fresh blank solution each time and rotating the cuvette to ensure all the sides are coated with the blank.
5. Fill the cuvette about $\frac{2}{3}$ full with the blank solution. Wipe the cuvette with a Kimwipe to remove any fingerprints or particles from the glass. Check that no particles or air bubbles are present in the solution.

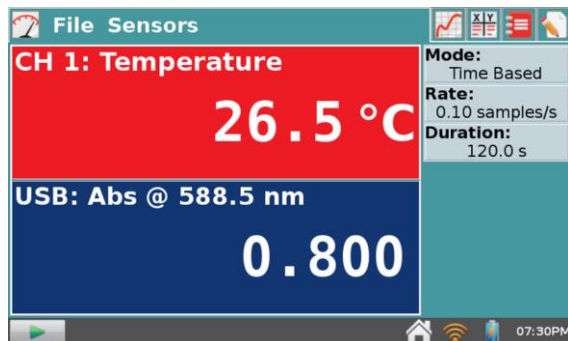
6. Place the cuvette into the spectrophotometer sample holder, making sure the cuvette is securely in place.
7. Once the warmup is complete and the blank cuvette is correctly inserted into the sample slot, select "Finish Calibration". After a few seconds, the "Calibration completed" message will appear, and you can select "OK".



8. The spectrometer will need to be set to the correct wavelength for today's experiment: 588.5 nm. Tap the red "USB: Abs" box, select "Change Wavelength..." and then enter the new wavelength. The instrument does have limited resolution, so if you input 588.5 nm, the instrument might set to a value very close to (but not equal to) 588.5 nm. This is fine!
9. On the Meter screen, tap Mode and change to "Time Based". See sample screen display below:



10. Tap on the "Interval" box, change the interval to 10, and press OK. Tap on the "Duration", change the duration to 120 seconds and press OK until you are returned to the data collection screen. See sample screen display below:



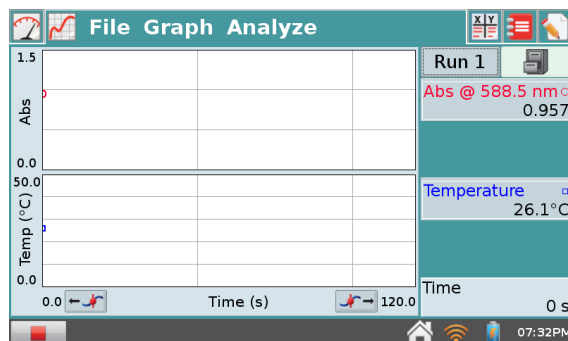
Part II: Solutions for kinetic measurements

You will complete four different kinetics runs at four different temperatures between $\sim 30\text{ }^{\circ}\text{C}$ and $\sim 60\text{ }^{\circ}\text{C}$.

1. Dispense 3.00 mL of crystal violet solution into each of the four glass test tubes.
2. Dispense 3.00 mL of 0.020 M NaOH solution into each of the four plastic test tubes.
3. Dispense $\sim 200\text{ mL}$ of hot water into a 400 mL beaker. Use the hot-water dispenser in the fumehood, and be sure to wear rubber hand-grips to prevent burning yourself.
4. Return to your bench, and quickly place the eight tubes prepared in steps 1 and 2 into the hot-water bath you prepared in step 3. Place the LabQuest 2 temperature probe in the hot water as well, and wait a few minutes for the solutions to warm up.
5. Over the course of the next 30 minutes or so, the hot water bath will gradually cool. You will conduct 4 runs during this time. Aim to conduct runs when the hot-water bath temperature is $\sim 55\text{ }^{\circ}\text{C}$, $\sim 48\text{ }^{\circ}\text{C}$, $\sim 40\text{ }^{\circ}\text{C}$, and $\sim 35\text{ }^{\circ}\text{C}$. See the following section (Part III) for instructions on how to conduct a run.

Part III: Effect of Temperature on Rate

1. Remove a glass tube (with crystal violet solution) from the water bath and quickly wipe the outside with a Kimwipe to dry it off. Remove a plastic tube (NaOH solution) and mix the solutions together by quickly pouring the crystal violet solution into the plastic tube and then returning the mixture to the glass tube.
2. Quickly remove the temperature probe from the water bath, wipe it with a Kimwipe, and place it into the reaction solution. Make sure that the probe is not blocking the light beam. Tap on the Collect  icon to start data collection. Data collection will begin and LabQuest will graph the data in real time, as shown in the sample screen below.



Note: because the thermometer will take some time to acclimatize to and report an accurate temperature for the reaction solution in the tube, you will disregard the first 60 seconds of data in each run: it is the data points from 60s to 120s in each run that you will be analyzing.

Record the temperature value at $t = 60$ s as the initial temperature and the temperature value at 120 s as the final temperature. Calculate the *average* reaction temperature. Dispose of the contents of the cuvette into the toxic waste container. Note: You can always find the solution temperature at 30 s by clicking on Table  and then you can return back to you curve by tapping on "Graph" .

3. Store the data by selection the "cabinet"  in the right upper part of the screen.
4. Repeat steps 1 - 5 as necessary to acquire data for the four different temperature ranges.

Discard remaining solutions of crystal violet into the toxic waste container in the fume hood and rinse the glassware first with ~ 1 mL of 1 mol/L HCl. Then clean the glassware thoroughly with tap water and then rinse three times with deionized water.

IMPORTANT! Because the spectrophotometer's light source has a limited life, please ensure that the spectrometer is disconnected from the LabQuest 2 unit before leaving the lab.

Before leaving the laboratory, check that all your equipment is clean and returned to the correct location: complete the sign-out checklist on page N-13 and have it signed by your lab instructor. Remember to have your Observation Sheet(s) checked and signed by your laboratory instructor before leaving. Submit your observation sheets along with your lab report.

Assessment and report:

Experiments M and N will be assessed together as a combined pair of experiments (**20 points total**), based on the submission of a **lab report (N-13 through N-18)** which is **due at the start of Experiment O**.

Along with the report, you will submit your observation sheets (**M-25 and N-11**)

As well, your report should include hardcopies of **six plots** generated by spreadsheet software:

- Three plots from one of the kinetics runs in Experiment M
- One plot from a second kinetics run in Experiment M
- One plot from the third kinetics run in Experiment M
- The plot of $\ln(k)$ versus $1/T$ from the Experiment N data

You *do not* need to attach hardcopies of the plots generated in Q2, page N-16.

N-10

Observation Sheet: Effect of Temperature on Rate of Reaction

Molarity of stock crystal violet (CV⁺) solution: 5.9 x 10⁻⁵ mol/L

Wavelength of maximum absorbance ($\lambda_{\max}$): 588.5 nm

Molar Absorptivity of CV⁺ at $\lambda_{\max}$ (pre lab): 8.32 x 10⁴ L/(mol·cm)

Volume of CV⁺ used in each run: _____ mL

Molarity of NaOH: 0.0200 mol/L

Volume of NaOH used in each run: _____ mL

Assessment
Report _____ /20

Deductions _____

Total _____ /20

Run 1		Run 2		Run 3		Run 4	
Time (s)	Abs	Time (s)	Abs	Time (s)	Abs	Time (s)	Abs
60	<u>0.436</u>	60	<u>0.547</u>	60	<u>0.725</u>	60	<u>0.894</u>
70	<u>0.386</u>	70	<u>0.498</u>	70	<u>0.685</u>	70	<u>0.868</u>
80	<u>0.342</u>	80	<u>0.454</u>	80	<u>0.648</u>	80	<u>0.843</u>
90	<u>0.303</u>	90	<u>0.413</u>	90	<u>0.612</u>	90	<u>0.818</u>
100	<u>0.268</u>	100	<u>0.377</u>	100	<u>0.579</u>	100	<u>0.794</u>
110	<u>0.238</u>	110	<u>0.343</u>	110	<u>0.547</u>	110	<u>0.771</u>
120	<u>0.210</u>	120	<u>0.313</u>	120	<u>0.517</u>	120	<u>0.748</u>
T _{60s} (°C)	T _{120s} (°C)	T _{60s} (°C)	T _{120s} (°C)	T _{60s} (°C)	T _{120s} (°C)	T _{60s} (°C)	T _{120s} (°C)
<u>50.6</u>	<u>49.8</u>	<u>47.1</u>	<u>46.3</u>	<u>40.7</u>	<u>40.1</u>	<u>33.0</u>	<u>32.4</u>
Average Temp. (°C):		Average Temp. (°C):		Average Temp. (°C):		Average Temp. (°C):	

Student: (name) _____ (signature) _____

N-12

Instructor: (signature)_____ **Bench #** ____ **Laboratory Section:** _____

CHEM 102: Kinetics II (Temperature) Sign-out Checklist

Equipment Cleaned and Returned to Common Glassware Drawer	Initials
250 mL Beakers	
Equipment Cleaned and Returned to Side/Back Bench	Initials
Test Tubes	
Equipment Remaining on Students Bench	Initials
LabQuest 2 with power cord	
Spectrophotometer with USB Cable	
Temperature probe	
Other Cleaning and/or Upkeep	Initials
Bench wiped with a damp paper towel	
Sinks clear of broken/dirty glassware	
Water bottles returned to end of bench	

Student: (name)_____ (signature)_____

Instructor: (signature)_____ **Bench #** ____ **Laboratory Section:** _____

Report: Experiment M (Effect of Concentration on Reaction Rate) & Experiment N (Effect of Temperature on Reaction Rate)

Name: _____ Bench # _____

Section: _____ Date: _____

Laboratory Instructor: _____

Assessment	
Report	_____ /20
Deductions	_____
Total	_____ /20

Part I: Rate Law Determination

For the calculations in Part I use the data from Experiment M, unless instructed otherwise

- Using the molar absorptivity (ϵ , calculated in Question 2 of the Advance Study Assignment on page M-8) convert each of the absorbance values from the kinetic measurements to the corresponding concentration of crystal violet and then prepare plots of $[CV^+]$ versus t , $\ln[CV^+]$ versus t , and $1/[CV^+]$ versus t . Prepare these three graphs for one of your runs, preferably the run using the highest $[OH^-]$. Include these three plots with your Lab Report. **Note:** You will likely have already constructed these plots before leaving the lab during Experiment M and can simply submit them with this report. **(2.0)**
- Based on your plots in Question 1, what is the order of the reaction with respect to crystal violet? Explain how you determined this. **(1.0)**
- Explain how you can determine the pseudo rate constant k' for Run 1 from a graph you prepared in Q1 above. Plot the appropriate graphs for Runs 2 and 3 and **write all three k' values to the table at the top of page N-14**. Be sure to indicate units for k' and to express your k' values using an appropriate number of significant digits. **(1.0)**
- Calculate the initial concentrations of $OH^-(aq)$ for each kinetics run: these initial concentrations represent the concentrations of OH^- at the moment of mixing, before any reaction with CV^+ has taken place. **Place these values into the table on page N-14 (1.0)**

Run #	$[\text{CV}^+]_i$ (M)	$[\text{OH}^-]_i$ (M)	k' Units: _____	k Units: _____
1				
2				
3				

5. Using the ratio method described on pages M-5 and M-6, determine the partial order of the reaction with respect to the hydroxide ion. To do this, perform the calculation three times: compare Run 1 to Run 2, compare Run 1 to Run 3, and compare Run 2 to Run 3. Determine the average of your three results, and round it to the nearest integer. **(1.0)**
6. Calculate the value of k for each run and **add these values to the table at the top of this page** and indicate the units for k . Show your calculations for Run 1. Determine the *average* overall rate constant k . **(1.0)**

7. If the stock concentration of the crystal violet in this experiment was 1.00×10^{-5} mol/L, instead of 2.50×10^{-5} mol/L, explain how this change would affect:
 - a. the initial reaction rate. **(0.5)**
 - b. the overall rate constant (k). **(0.5)**
8. Explain why the reaction temperature was measured for each run in Experiment M. **(0.5)**
9. Using the values from Run 1 of Experiment M, determine the value for $[\text{OH}^-]$ at $t=120$ s. What percentage of the initial amount of hydroxide is consumed during the 120 seconds? Is this consistent with our treatment of the run as pseudo-first order? (Hint. What amount of $[\text{CV}^+]$ is consumed during this time?) **(1.5)**

10. If you performed another run in which $[\text{OH}^-]_i$ was identical to $[\text{CV}^+]_i$, would a plot of $\ln[\text{CV}^+]$ versus time reveal a straight-line relationship? Would any of the three types of integrated rate-law plot reveal a linear relationship? Explain your answers. **(1.0)**

Part II: Activation Energy Calculations

For the calculations in Part II use the data from Experiment N, unless instructed otherwise

Run #	Volume of CV^+ (mL)	Volume of 0.0100 M NaOH (mL)	Temperature ($^{\circ}\text{C}$)			k' (s^{-1})	k ($\text{M}^{-1}\text{s}^{-1}$)
			Initial	Final	Average		
Run 1	3.00	3.00					
Run 2	3.00	3.00					
Run 3	3.00	3.00					
Run 4	3.00	3.00					

1. Show your calculation for the initial molarity of OH^- for the Experiment N kinetics runs in the space below. Note: This refers to the concentration of the OH^- at the point of mixing (*i.e.* before reaction: account for dilution!). **(0.5)**
2. Based on the order of reaction with respect to CV^+ , as determined in Experiment M, prepare (for each of the four runs) the appropriate integrated rate law plot and determine k' and k for each run. For best results, use only the data points from 60s to 120s inclusive for each run. Do not attach these plots to your lab report: simply **report the experimental values for k' and k in the above table, and include the corresponding temperature values from Observation Sheet N-11.** **(1.5)**

Complete the following table relating the temperature to reaction rate. **(1.0)**

Run	Temperature		1/T (K ⁻¹)	k (M ⁻¹ s ⁻¹)	ln(k)
	(°C)	(K)			
1					
2					
3					
4					
Exp M Run 1					

- Plot $\ln(k)$ vs. $1/T$ (K⁻¹) using Google Sheets or some other computer spreadsheet software. Your graph should include a best-fit line from software-calculated linear regression analysis. Include the data from Exp M Run 1 as a data point as well. Attach the plot to your lab report. **(1.0)**
- In the space below, write the linear equation (of the form $y = mx + b$) for the best-fit line for the data plotted above. Be sure to include units, even if they are absent in the equation as it appears in your software. Clearly identify and label both the slope and the y-intercept portions of this equation. **(1.0)**
- Using the value of the slope of the best fit line, calculate the activation energy (E_a) for the reaction of CV⁺ and OH⁻. **(1.5)**

