Lightstick Kinetics

NAME:____PERIOD:___________

Prelab

1. The following data was collected for the first order reaction:

$$2\ N_2O_{5\ (g)} \rightarrow 2\ N_2O_{4\ (g)} + O_{2\ (g)}$$

Determine graphically the energy of activation for the reaction. Show your calculations.

Temperature (°C)	Rate constant k (sec^{-1})	ln k	Temperature (K)	1/Temperature (K^{-1})
0.0	7.87×10^3			
25.0	3.46×10^5			
45.0	4.98×10^6			
65.0	4.87×10^7			

Slope of the regression line	
Y intercept	
Correlation factor	
E_a (kJ/mol)	

2. Calculate the rate constant at 35.0 °C. Show your calculations.

3. At what temperature (°C) will the rate constant be 8.00×10^6 sec^{-1}? Show your calculations.

Lightstick Kinetics

The rate of a chemical reaction is generally expressed by the rate law:

$$\text{Rate} = k\,[A]^{\alpha}\,[B]^{\beta}$$

where [A] and [B] are the concentrations of the reactants in mol/L, α and β are experimentally determined exponents in the rate equation, and k is the experimentally determined rate constant which is reaction and temperature dependent.

Temperature exerts a significant effect on the rate of a chemical reaction. Increasing the temperature increases the average speed of the molecules thereby increasing the collision rate between the reacting molecules. Increasing the temperature also increases the fraction of the reacting molecules with energy greater than the energy of activation. The relationship between the rate constant, **k** , and temperature is expressed by the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}}$$

A is the pre-exponential factor which includes the collision frequency and the fraction of molecules that collide with the correct orientation. $\mathbf{E_a}$ is the energy of activation, the minimum energy the colliding molecules must possess to have a successful reaction. **R** is the ideal gas constant in energy units, 8.1344 J/mol K. **T** is the temperature in Kelvin. The exponential term

$$e^{-\frac{E_a}{RT}}$$

gives the fraction of the reacting molecules with energy greater than the energy of activation. As E_a increases, the exponent becomes more negative and the fraction of the reacting molecules with energy greater than the energy of activation decreases, the rate constant becomes smaller, and the rate of reaction decreases. As T increases, the exponent becomes less negative and the fraction of the reacting molecules with energy greater than the energy of activation increases, the rate constant becomes larger, and the rate of reaction increases. Taking the natural logrithm of both sides of the Arrhenius equation gives

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

A graph of ln k versus 1/T with the temperature in Kelvin gives a straight line with a slope of $-E_a/R$. The value of E_a is determined from the slope of the line.

In this experiment, the energy of activation for the light-producing reaction in a lightstick will be determined by monitoring the light intensity of the lightstick as a function of temperature. The light-producing reaction follows first order kinetics, where [X] is the reactant concentration.

$$\text{Rate} = k\,[X]$$

Substituting from the Arrhenius equation gives:

$$Rate = A[X]e^{-\frac{E_a}{RT}}$$

The light intensity, **I**, at a fixed point from the lightstick should be proportional to rate of the chemiluminescence reaction. Providing a proportionality constant, c , gives the equation:

$$\text{Rate} = cI$$

Substituting for the rate in the previous equation:

$$cI = A[X]e^{-\frac{E_a}{RT}}$$

Dividing both sides of the equation by c gives:

$$I = \frac{A[X]}{c}e^{-\frac{E_a}{RT}}$$

Taking the natural logarithm of both sides of the equation gives:

$$\ln I = \left[-\frac{E_a}{R}\right]\frac{1}{T} + \ln\frac{A[X]}{c}$$

A graph of ln I versus 1/T with the temperature in Kelvin gives a straight line with a slope of $-E_a/R$. The value of E_a is determined from the slope of the linear regression line.

The light intensity is measured using a Vernier light sensor and the temperature is measured using a standard Vernier metal temperature probe. The reaction tube and the two probes are supported in a wooden block. The arrangement of the equipment is shown in Figure 1.

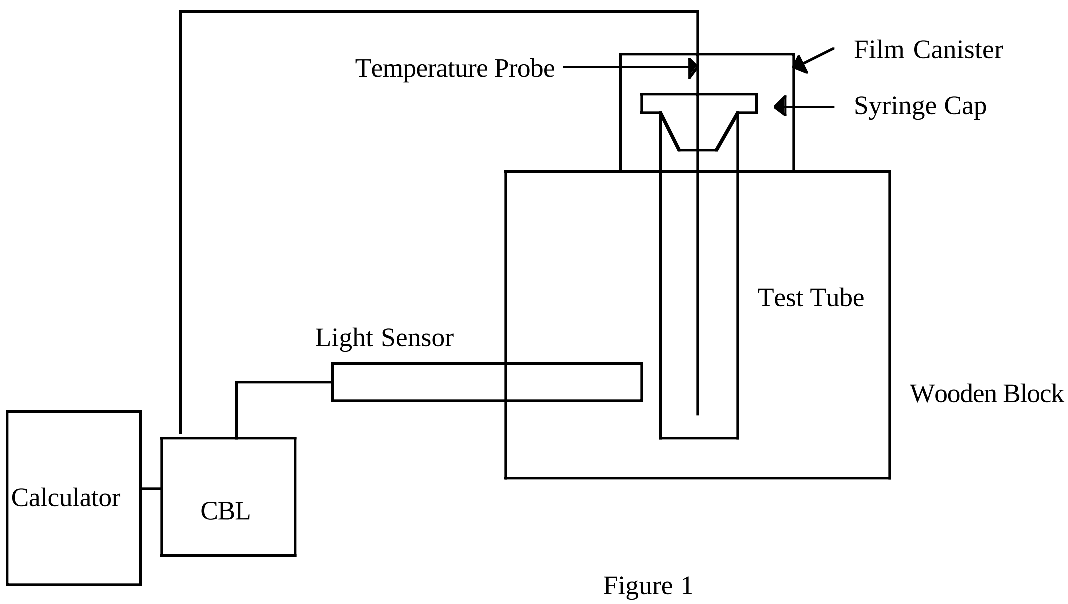


Figure 1

Procedure:

Part 1: Setup of the CBL and Calculator

1. Connect the CBL unit to the TI-82/83 calculator with the unit-to-unit link cable using the I/O ports located on the bottom edge of each unit. Press the cable ends in firmly.

2. Connect a CBL DIN adapter to the end of the Vernier Light Sensor (if it has the round 5-pin plug) and plug the adapter into channel 1, CH 1, on the CBL unit. Set the switch on the probe to 0-600 Lux.

3. Connect a CBL DIN adapter to the end of the Vernier standard metal temperature probe (if it has the round 5-pin plug) and plug the adapter into channel 2, CH 2, on the CBL unit.

4. Plug the CBL voltage adapter into the bottom of the CBL.

5. Turn on the CBL unit and calculator. The CBL system is now ready to receive commands from the calculator.

Part 2: Calibration of the Light Sensor and Temperature Probe

Make sure the CBL unit and the calculator are turned on.

1. Press **[PRGM]** on the TI-82/83. Using the arrow keys, highlight the program CHEMBIO. Press **[ENTER].**

2. (Display should read "prgmCHEMBIO") Press **[ENTER]**.

3. (Display should read "VERNIER SOFTWARE...") Press **[ENTER]**.

4. Select **"SET UP PROBES"** by using the arrow keys to highlight this choice. Press **[ENTER]**. If you get the ***Link Error*** message check all link connections and make sure the CBL is turned on. Press **[ENTER]**.

5. The display should read "Enter number of probes." You are using two probes, therefore press **[2]** and **[ENTER]**. The CBL display should show three dashes.

6. You are using the light sensor therefore, select **More Probes**. Press **[ENTER]**. Select **Light**. Press **[ENTER]**.

7. You should have your probe connected in channel one, CH 1, therefore, press **1** and **[ENTER]**.

8. The display should now show a Calibration Menu. You want to select **"Used Stored"** and press **[ENTER]**. The calculator will show the message "Be sure to set switch on probe. CBL shows only 3 sig. figures ex. 1134 → 113. Collected data shows all digits". Press **[ENTER].**

10. Select **0-600 Lux**. Press **[ENTER]**.

11. You should be back at the Select Probe menu. Select the second probe, **Temperature.** Press **[ENTER]**.

12. You should have your probe connected in channel two, CH 2, therefore, press **2** and press **[ENTER]**.

13. The display should now show a Calibration Menu. You want to select **Perform New"** by using the arrow keys to highlight this choice then press **[ENTER]**. The message "Use [CH View] Button on CBL to Monitor Voltage, when Stable Push CBL [Trigger]" will appear.

14. Press the [CH View] Button to select CH 2. A CH2 will be flashing in the upper left corner of the calculator to indicate that you are viewing the probe in channel 2. A 1 will

appear in the upper right corner of the calculator to indicate that you are doing the first point of a two point calibration. A voltage reading will appear on the CBL.

15. Place the temperature probe and a thermometer in a boiling water bath (or a room temperature bath if you choose). When the reading on the CBL unit is stable, press **[TRIGGER]** on the CBL. Read the temperature from the thermometer and enter it into the calculator as the reference value and press **[ENTER]**.

16. Place the temperature probe and a thermometer in a ice water bath. A 2 will appear in the upper right corner of the calculator to indicate that you are doing the second point of a two point calibration. When the reading on the CBL unit is stable, press **[TRIGGER]** on the CBL. Read the temperature from the thermometer and enter it into the calculator as the reference value and press **[ENTER]**. The calculator display should show the intercept and slope values of the calibration procedure for the temperature probe.

17. Press **[ENTER]** to return to the Main Menu.

Part 3: Sample Preparation and Data Collection:

Wear gloves and lab aprons during the sample preparation to protect your hands and clothes. The dye in the lightstick will stain. Safety glasses must be worn.

1. Place 200 ml of water in a 400 ml beaker and heat the water to about 45^{o}C on a hotplate.

2. Snap the lightstick. The light intensity decreases rather quickly but then stays fairly constant. The are two pathways for the production of light. The short term pathway is finished in 5-10 min while the long term pathway lasts the entire lifetime of the lightstick. Wait at least 10 min after the lightstick is snapped before starting the data collection. While you are waiting, complete steps 3-12.

3. **Carefully** cut off the top of the lightstick with a set of shears. Your instructor may want to do this for you.

4. Use a long stem Pasteur pipet to transfer the contents of the lightstick to a 18x150 mm test tube.

5. Place the test tube in the water bath and allow it to reach temperature equilibrium. Stir the solution to be sure the temperature is constant.

6. Insert the temperature probe through the bottom of the film canister and the top of the syringe cap.

7. Set up the calculator and CBL for data collection.
a. Select **COLLECT DATA** from the **MAIN MENU**.Press **[ENTER]**.
b. Select **TIME GRAPH** from the **DATA COLLECTION** menu. Press **[ENTER]**.
c. Enter "**30**" as the time between samples, in seconds. Press **[ENTER]**.
d. Enter "**20**" as the number of samples. Press **[ENTER]**.
e. A screen will appear listing the sample time, number of samples, and the length of the experiment. Press **[ENTER]**.
f. Select **Use Time Set Up**. Press **[ENTER]**.

8. The calculator will display “press **[ENTER]** to begin collecting data”. **DO NOT PRESS [ENTER] at this time.** Proceed with the sample preparation below.

9. When the lightstick solution has reached equilibrium with the water bath temperature, remove the test tube from the water bath and dry the outside of the tube.

10. Place the temperature probe in the solution. Use the syringe cap to hold the probe in the center of the liquid and to stopper the test tube.

11. Place the test tube in the wooden block and cover the top of the tube with the film canister.

12. Insert the light probe into the side of the wooden block until it touches the side of the test tube.

13. **Be sure the CBL is ON.** Press **[ENTER]** on the calculator to start collecting data.

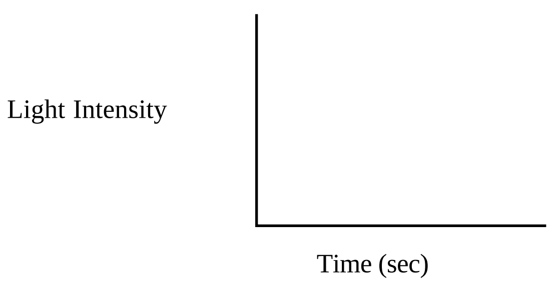
14. The calculator will display “ Performing Experiment- Select Retrieve Data from CBL from the Next Screen when the CBL Shows Done”. Be sure data is being displayed on the CBL. If it shows three dashes continually then no data is being collected or stored and the run needs to be restarted.

15. The [CHVIEW] button can be used to monitor the data as it is being taken. Pressing the [CHVIEW] will toggle back and forth from CH1 to CH2 indicated by the flashing channel number. The light intensity is CH1 and the temperature is CH2.

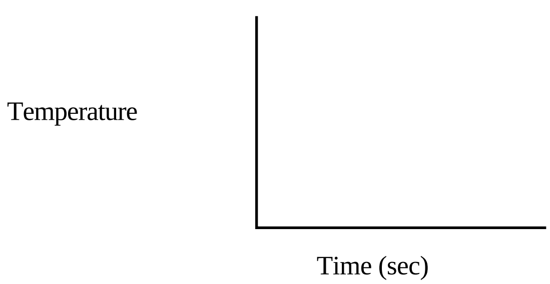
16. When the CBL show DONE, select **Retrieve Data**. Press **[ENTER].** The calculator displays “ Be Sure CBL shows DONE”. Press **[ENTER]**.

17. The calculator displays “ Time in L1, Data in L2 and L3”. Press **[ENTER]**.

18. The light intensity versus time graph appears. Sketch the graph below and then press **[ENTER]**.



19. The temperature versus time graph appears. Sketch the graph below and then press **[ENTER]**.



20. Select **No** for repeating the experiment. Press **[ENTER]**.

21. Select **Quit** from the Main Menu. Press **[ENTER]**.

22. Press **[MODE].** Select **Normal**. Press **[ENTER]**. Select **Float**. Press **[ENTER]**.

23. Press **[STAT]. EDIT** will be highlighted. Press **[ENTER]**. Time will be in L1, Light Intensity will be in L2, and Temperature will be in L3. Record the time to the nearest second, the light intensity to the nearest whole number, and the temperature to the nearest 0.1^{o}C in the data table.

24. Use the arrow keys move the cursor to the <u>column heading</u> L4. Press **[CLEAR].** Press **[ENTER]**. This should clear any data in L4.

25. Move the cursor to the column heading L4. Press **[ln] [L2] [ENTER]**. The values for the natural logrithm (ln) of the light intensity should appear in L4. Record these values in the data table to the nearest 0.01.

26. Use the arrow keys move the cursor to the <u>column heading</u> L5. Press **[CLEAR].** Press **[ENTER]**. This should clear any data in L5.

27. Move the cursor to the column heading L5. Press **[L3] [+] [273] [ENTER]**. The values for temperature in Kelvin should appear in L5. Record these values in the data table to the nearest 0.1 K.

28. Use the arrow keys move the cursor to the <u>column heading</u> L6. Press **[CLEAR].** Press **[ENTER]**. This should clear any data in L6.

25. Move the cursor to the column heading L6. Press **[L5] [x^{-1}] [ENTER]**. The values for the reciprocal of the temperature in Kelvin should appear in L6. Record these values in the data table.

Part 4: Calculator Graphing

1. Graph the light intensity versus temperature using the following instructions.

a. To clear any previous regression equation and curve, press **[Y=]** and **[CLEAR].** Press **[QUIT]**, then press **[CLEAR]** to clear the calculator screen.

b. To plot a graph of light intensity vs. temperature, press **[STAT PLOT],** then select **Plot1**. Press **[ENTER].** Use the arrow keys to position the cursor on each of the following Plot1 settings. Press **[ENTER]** to select any of the settings you change: Plot1 = On, Type = Scatter (1st type), Xlist = L3 Ylist = L2 and Mark = square. On the TI-83 the list numbers have to be typed in for the Xlist and Ylist.

c. Press **[GRAPH]** , then **[ZOOM]**, select **ZoomStat** and press **[ENTER].**

2. Sketch your graph below.

Light Intensity

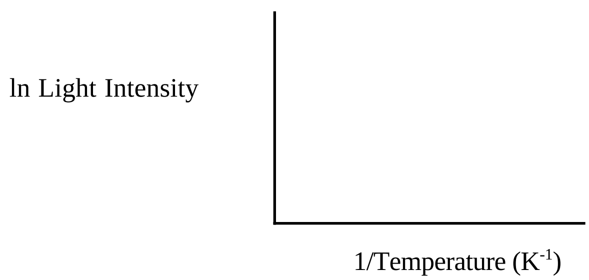
Temperature (C^{o})

3. Plot a graph of the natural logrithm of the light intensity versus 1/T in Kelvin using the following instructions.
a. To clear any previous regression equation and curve, press **[Y=]** and **[CLEAR].** Press **[QUIT]**, then press **[CLEAR]** to clear the calculator screen.

b. To plot a graph of ln light intensity vs. temperature, press **[STAT PLOT],** then select **Plot1**. Press **[ENTER].** Use the arrow keys to position the cursor on each of the following Plot1 settings. Press **[ENTER]** to select any of the settings you change: Plot1 = On, Type = Scatter (1st type), Xlist = L6 Ylist = L4 and Mark = square. On the TI-83 the list numbers have to be typed in for the Xlist and Ylist.

c. Press **[GRAPH]** , then **[ZOOM]**, select **ZoomStat** and press **[ENTER].**

4. Sketch the graph below



5. If there is an apparent linear relationship between the natural logrithm of the light intensity and 1/T, find the slope and the y-intercept of the line that best fits this linear relationship by the following steps.

a. Press **[STAT]**

b. Arrow right to **CALC.**

c. Select **LinReg (ax+b)** Press **[ENTER].**

d. Press **[L6] [,] [L4].** Press **[ENTER].**

6. The results of the least-squares fit (linear regression) appear on the (LinReg) screen:

a = slope of the line b = y-intercept of the line
r = correlation coefficient (a measure of how well this line fits the data).
The closer the value is to 1.00, the better the data fits a straight line.) Record these values in the Data Table. On the TI-83 If the r value does not appear on the screen, press **[CATALOG]**. Arrow down to **Diagnostic On** and press **[ENTER]** twice. The screen should show Diagnostic On and Done. Run the linear regression analysis again.

7. To display the best-fit line on the graph:

a. Press **[Y=]**

b. Press **[ENTER]** to select Y1.

c. Press **[CLEAR]** to delete any unwanted function.

d. Press **[VARS]**

e. Select **Statistics**. Press **[ENTER].**

f. Arrow right to **EQ** since we want an equation.

g. Press **RegEQ** and press **[ENTER].** The regression equation appears in the Y1 slot.

h. Press **[GRAPH]** and both the data and the line will be plotted.

8. Use the slope of the linear regression line to calculate the value of E_a. The value will be in J/mol . Record the value in kJ/mol.

Part 5: Graphical Analysis

1. Use Graphical Analysis to plot a graph of ln light intensity versus 1/temperature in K^{-1}. This graph should have labeled axes with units.

2. Type in the data from your data table, calculator lists, or import L4 and L6 using the TI-Graph Link cable.

3. Be sure to cut off the connecting line option under the Graph menu.

4. Show the linear regression line through your data with the slope, y-intercept, and correlation factor.

5. Use **Regression** line under the Analyze menu (not the Auto Fit). Attach your graph to the report.

6. Expand the graph so it fills the screen. Print only the graph and print the graph down the page

This experiment is adapted from Lightstick Magic by Thomas H. Bindel, *J. Chem. Educ.*, 1996, **73**, p.356-358.

Lightstick Kinetics

Name: ____ Period:_________

Lab Partner: ____________________________________ Date: __________

Data Table

Attach the graphs to the lab report.

Light Intensity (lux)	Ln (Light Intensity)	Temperature (°C)	Temperature (K)	1/Temperature (K^{-1})

Slope of the regression line	
Y-intercept	
Correlation factor	
Experimental value for E_a	kJ/ mol
Accepted value for E_a	kJ/mol
Percent error	

Calculations:

Questions:

1. How did the light intensity vary with temperature? Explain why this happens.

Lightstick Kinetics

Setup Sheet

10 CBL units with AC adapters
10 TI-82 or TI-83 calculators with CHEMBIO programs
10 Calculator to CBL link cables
20 DIN adapters
10 Vernier Light Sensors
10 Vernier metal temperature probes
10 Boxes Kimwipes
10 Drilled wood blocks
10 18x150 mm test tubes
10 Long stem Pasteur pipets with dropper bulbs
10 Stirring rods
10 Test tube holders
10 Thermometers
10 Test tube racks
10 250 ml beakers
10 Hotplates or stirring hotplates with magnetic stir bar

Light sticks
Shears

TI-Graph Link cables

Lightstick Kinetics

Instructor's Notes

1. The wooden block was 5 "in." x 5 "in." x 1.5 "in." thick. A 3/4 in diameter hole 4.5 "in." deep is drilled in the center of the top of the "1.5 in." edge. A 5/8 "in." diameter hole "3 in." deep is drilled 1.5 "in." up from the bottom of the adjacent 1.5 "in." edge. The 3/4 "in." diameter hole fits a 18x150 mm test tube. The 5/8 "in." diameter hole fits the light probe. Drill a 9/32 "in." hole in the center of the bottom of the film canister and in the center of the syringe cap to accommodate the temperature probe.

2. Depending on the size of the lightstick, there may be enough contents from one lightstick for 2 student groups. Only about 5ml are seen by the light sensor. It can save a lot of time in lab if the temperature probes are calibrated ahead of time. As long as the Perform New option is not used, this calibration is stored in the CBL. **It would be useful to write down the slope and intercept of the calibration line so they can be manually entered if necessary.**

3. Do not heat the test tube above 70°C. If the sample is allowed to cool too close to room temperature before starting data collection, the temperature may vary erratically. When the student views the temperature versus time and the light intensity versus time graphs and they are not smooth curves, they should repeat the run. A higher starting temperature will give better data.

4. Using the same brand of lightsticks for all the students will make the lab easier to run. Run the experiment yourself ahead of time to see what light intensity that brand produces. It may be necessary to use the 0-6000 lux setting on the light probe if the lightstick is very bright and produces light intensities over 600 lux. If there is a set of level points at the beginning of the ln I versus 1/T graph, eliminate these points from the lists. This is probably due to too high an initial light intensity. If you collect data for too long a time, the temperature will become constant and the graph will drop at the end. These points may be eliminated or use a different time range.

5. Sample data was collected using green Coleman Illumisticks™.

Slope of the regression line	-13266
Y-intercept	49.1
Correlation factor	-0.999
Experimental value for E_a	108 kJ/ mol
Accepted value for E_a	kJ/mol
Percent error	

6. Answers to prelab questions:
1.

Temperature (°C)	Rate constant k (sec^{-1})	ln k	Temperature (K)	1/Temperature (K^{-1})
0.0	7.87×10^3	8.97	273.0	3.663×10^{-3}
25.0	3.46×10^5	12.8	298.0	3.356×10^{-3}
45.0	4.98×10^6	15.4	318	3.145×10^{-3}
65.0	4.87×10^7	17.7	338	2.959×10^{-3}

Slope of the regression line	-12413
Y intercept	54.4
Correlation factor	1.0
E_a (kJ/mol)	10.1

2. 1.38×10^6 sec^{-1}
3. 322 K (49.0°C)