

LIGHTSTICK KINETICS

From *Advancing Science*, Gettysburg College

INTRODUCTION: General background on rate, activation energy, absolute temperature, and graphing.

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

$$\text{Rate} = k[\text{A}]^a[\text{B}]^b$$

- [A] and [B] are the concentrations of the reactants in mol/L
- a and b are experimentally determined exponents in the rate equation
- k is the experimentally determined rate constant that is reaction- and temperature-dependent

TEMPERATURE EFFECTS: 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
- increases the fraction of the reacting molecules with energy greater than the energy of activation.

ARRHENIUS: The relationship between the rate constant, k, and the temperature, T, is expressed by the Arrhenius equation:

$$k = Ae^{-E_a/RT}$$

- A is the pre-exponential factor—related to the collision frequency and the fraction of molecules that collide with the correct orientation
- 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 $e^{-E_a/RT}$ expresses 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. Therefore, as E_a increases, 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, resulting in the rate constant becoming larger and the rate of reaction increasing

ACTIVATION ENERGY FROM A SLOPE: Taking the natural logarithm of both sides of the Arrhenius equation gives

$$\begin{array}{rcl} \ln k & = & (-E_a/R) (1/T) + \ln A \\ y & = & m \quad x \quad + \quad b \end{array}$$

Notice how it can be viewed with some creativity as being the equation of a straight line with dependent variable $\ln k$ (a.k.a. “y”) and independent variable $1/T$ (a.k.a. “x”)

Graphing $\ln k$ verses $1/T$ (remember, T in Kelvin) gives a straight line with a slope of $-E_a/R$. The value of activation energy— E_a —is the slope of this line.

Applying our knowledge of the rate and temperature relationship to lightsticks to find ACTIVATION ENERGY

- The energy of activation for the long-term, 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. (“first order” meaning that there is only one reactant affecting the reaction rate)

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

- The Arrhenius equation gives us an expression for k , which we substitute:

$$\text{Rate} = A \cdot e^{-E_a/RT} \cdot [X] \quad \text{usually written} \rightarrow \quad \text{Rate} = A \cdot [X] \cdot e^{-E_a/RT}$$

- **ILLUMINATION—A MEASURE OF REACTION RATE:** The illumination, I , at a fixed point from the lightstick should be proportional to the rate of the chemiluminescence reaction. Providing a proportionality constant, c , gives another equation for **Rate**:

$$\text{Rate} = c \cdot I$$

- Setting the two expressions for Rate equal to each other does this:

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

- Dividing both sides of the equation by c isolates the illumination:

$$I = (A \cdot [X]e^{-E_a/RT}) / c$$

- **SLOPE, AGAIN:** Taking the natural logarithm of both sides of the equation simplifying gives us reason to graph **$\ln(I)$** vs **$1/T$** :

$$\begin{array}{rcl} \ln I & = & (-E_a/R) \cdot (1/T) + \ln(A \cdot [X] / c) \\ y & = & m \cdot x + b \end{array}$$

A graph of $\ln(I)$ verses $1/T$ (T in Kelvins) ideally should give a straight line with a slope being $-E_a/R$. The value of E_a is determined from the slope of the linear regression line. (*multiply by $-R \rightarrow -8.1344 \text{ J/mol}\cdot\text{K}$*)

Illumination is usually symbolized as E . We use “ I ” so as not to confuse illumination with activation energy, E_a .

LAB PURPOSE

The purpose of this experiment is to study the reaction rate of a chemical reaction (by monitoring illumination of a light sensor) as it varies with temperature (by monitoring a temperature sensor) and determine the energy of activation of the chemiluminescent (light-producing) reaction utilized within lightsticks (by mathematical/graphical analysis of illumination and temperature data).

EQUIPMENT/MATERIALS

- Laptop computer with Logger *Pro*
- LabPro with AC adapter
- LabPro USB computer cable
- Vernier Light Sensor
- Vernier Temperature Probe
- Water bath (50°C)
- 18x150 mm test tube (approx.)
- Light sticks (2?)
- Pre-drilled film canister
- Pre-drilled wood block
- Scissors
- Disposable Pipette
- Disposable gloves

SAFETY

- Always wear an **apron** and **goggles** in the lab
- **Gloves** should be worn because the dye in the lightstick will stain

PROCEDURE

- **Prepare the sensors for data collection**

1. Connect the light sensor to CH-1 of the LabPro
2. Connect the temperature probe to CH-2 of the LabPro
3. Connect the LabPro to the computer using the USB cable provided
4. Plug in the LabPro and wait for its happy “I’m on!” song.

Be sure the light sensor range switch is set at 0-600 lux.

- **Prepare the computer software to record and analyze data**

1. **Ensure that the LoggerPro 3.3 software is running on the computer**
2. **Set up the data collection table**

- **First, you should see:** If your connections are properly done, the LoggerPro software will (should?) start up with a 3-column data table: Time, Illumination, and Temperature

(NOTE: Columns “x” and “y” may appear briefly until sensors are recognized)

- **You will need to add these columns to the table**

1. “Logarithm of Illumination” – $\ln(I)$
2. “Abs Temp” – (T_{ab})
3. “1/(Abs Temp)” – $1/T_{ab}$

See the instruction box at the end of the lab to learn how to add columns.

- 3. **Set up the graph of $\ln(\text{illumination})$ vs. $1/(\text{abs temp})$**

- Delete one of the default graphs that should be on the computer screen (if you have the LabPro and sensors installed properly).
(*Note: clicking once on a graph activates it; then pressing <Delete> zaps it.*)
- In the remaining graph window, set up the axes’ labels and scales
 - mouse-over the vertical (y-) axis **label** and *left*-click; the list of data column names will appear—select/click on “Log of Illumination”
 - mouse-over the horizontal (x-) axis **label** and *left*-click; the list of data column names will appear—click on “1/(abs temp)”
 - mouse-over the graph (just about anywhere) and *right*-click, then select “Autoscale” from the dropdown list
(Alternatively, you may select “Graph options...”, then the “Axes Options” tab, and set scaling to “Autoscale” for each axis)

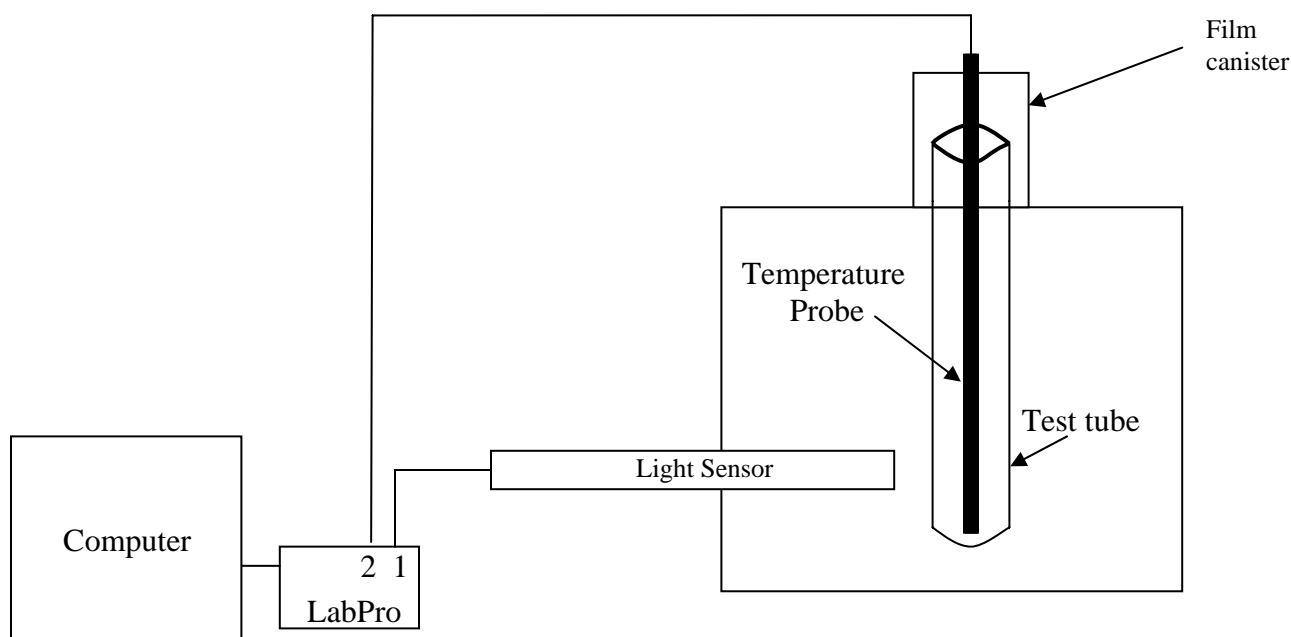
- 4. **Set up the data collection timing parameters**

- Click on the toolbar icon that looks like a clock on a graph (a slow mouse-over displays “Data Collection”)
- Ensure that the *Collection* page shows the following then click *Done*:
 - Set “Mode” to **Time Based**
 - Set “Length” to **600 seconds**
 - Set “Seconds per sample” to **30**

Careful here →

(*The “samples/second” value will self-adjust to match.*)

- **Prepare the apparatus** (note that the centered hole in the block is at the top)



PREPARE THE APPARATUS

1. Prepare a 50°C water bath
2. Activate the lightstick:
 - a. Snap the lightstick's internal glass vial, and shake well
 - b. Wait 10 minutes for the short-term light-emitting reaction to finish so only the light from the long-term reaction is being measured
 - c. Continue with the next few steps while you wait
3. Set up the experiment-specific apparatus as much as possible at this time to match Figure 1, using the pre-drilled wooden block and other items shown
 - a. Insert the temperature probe through the hole in the film canister
[and then into the test tube]
 - b. Place the light sensor into the horizontal hole of the wood block.
4. Following your 10-minute wait, cut off the top of the lightstick with a pair of scissors and transfer approximately 5 ml of the contents into the test tube using a pipette
5. Place the test tube with contents, including the temperature probe, in the water bath until the meter reads 50° C. (Alternate plan—Use a standard lab thermometer instead of the Vernier Temperature Probe for this reading if your instructor directs you to do so.)
6. Remove the test tube assembly from the water bath, drying the outside surface

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7. Insert the test tube and light sensor assembly into the top hole in the wood block, making sure that the film canister shields the test tube from any incoming light

- **Collect reaction rate and temperature data**

1. Click on the Green “collect” button on the toolbar
2. Pay attention to the data as it’s being collected to make sure that it makes sense—indicating that your equipment setup is probably correct

DATA ANALYSIS:

- *Find the linear equation that best matches your data*

1. Click on the data point in the upper left of the graph window, hold down the mouse button and drag to the data point in the lower right of the graph window, and then release the mouse button.
2. Follow the menu bar drop-down path: Analyze – Linear Fit
 - a. A regression box containing slope (M), intercept (B), and a correlation value (COR) will appear on your graph
3. If you are connected to a printer, you have several options for printing
 - a. Data table and graph together (can view in *Print Preview*)
 - b. Data table alone
 - c. Graph alone

DATA ANALYSIS

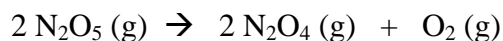
- *Determine the Activation Energy*

1. According to our substituted Arrhenius equation:
 - a. the slope should be equal to $-E_a/R$
 - b. where R has a value of 8.3144 J/mole•K
 - c. thus allowing us to calculate the value of E_a in both **J/mole** and **kJ/mole**.
2. Using the actual value in **kJ/mole**, your percent error should be calculated.

Lightstick Kinetics Pre-lab

Name _____
Name _____
Pd/Course _____
Date _____

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



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 X 10 ³			
25.0	3.46 X 10 ⁵			
45.0	4.98 X 10 ⁶			
65.0	4.87 X 10 ⁷			

Slope of the regression line (m)	
Y intercept (b)	
Correlation factor (cor)	
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 X 10⁶ sec⁻¹? Show your calculations.

Light Stick Kinetics Data Sheet

Name _____
Name _____
Pd/Course _____
Date _____

Attach your graphs and data tables, formatting your report as instructed by your teacher.

Slope of the regression line (m)	
Y-intercept (b)	
Correlation factor (cor)	
Experimental value for E_a (kJ/mol)	
Accepted value for E_a (kJ/mol)	
Percent Error	

CALCULATIONS: (include a sample of each type of calculation performed by LoggerPro)

QUESTION:

1. How did the light intensity vary with temperature? Why does this happen?