Overview: Copper Doped Zinc Sulfide (ZnS:Cu) is a semi-conductor that exhibits the property of phosphorescence. It is commonly used in manufacturing Glow-in-the-Dark toys. Absorption of UV and visible light causes excitation of electrons resulting in non-equilibrium electrons and holes in the solid matrix. Relaxation occurs through phosphorescence. The rate of phosphorescence depends on the concentrations of both excited electrons (p) and holes (n). Since $p \approx n$ upon excitation of these ZnS:Cu semiconductors, the kinetics of phosphorescence approximates second-order behavior.

Task 1: Measure the decay of phosphorescence for a piece of a Glow-in-the-Dark Toy at various (10-15) temperatures, ranging from 0-80 °C. Also try using an acetone bath of dry ice to obtain a point at -80 °C. The key to the experiment is coordinating the equilibration in a temperature bath, excitation with a high intensity fluorescent lamp, and the measurement of the phosphorescence in a rapid, reproducible sequence of events.

Task 2: Repeat with a different Glow-in-the-Dark toy.

Data Analysis: Derive the first order rate law, assuming that the rate of phosphorescence depends only of the population of excited electrons.

$$\frac{-dp}{dt} = kp$$

$$\ln(p) - \ln(p_0) = -kt$$

Derive the second order rate law, assuming the rate of phosphorescence depends on the concentrations of both excited electrons (p) and holes (n), and $p \approx n$.

$$\frac{-dp}{dt} = kp n = kp^2$$

$$\frac{1}{p} - \frac{1}{p_0} = -kt$$

Assume the intensity of the phosphorescence is directly proportional to $p$. Plot the data acquired at room temperature, according to the derived first order law and second. Which one fits better?

Use the rate law that fits better to plot the data at the rest of the temperatures. The slopes of the line are proportional to the rate constants. Thus, they are relative rate constants.
The Arrhenius equation relates the rate of a reaction to temperature. It can be used to obtain activation energies for the reactions being studied. The activation energy is an energy barrier that must be overcome to initiate the reaction (in the case relaxation by phosphorescence).

\[ k = Ae^{-\frac{E_a}{RT}} \]

\[ \ln(k) - \ln(A) = -\frac{E_a}{RT} \]

A plot of the relative rate constants as a function of 1/T, gives a linear relationship with a slope of \(-\frac{E_a}{R}\).

**ERROR ANALYSIS**

Use Excel to obtain the 95 % CL for each of the slopes. Report the relative rate constants at each of the temperatures in a table. Place error bars on the Arrhenius plot that correspond to these errors in the relative rate constants. Using the error in the slope of the Arrhenius plot calculate the error in the activation energy corresponding to the 95 % CL. Comment on the limitations of the experiment.