LECTURE DEMONSTRATION #2 (TEMPERATURE DEPENDENCE OF *k*)

The Arrhenius expression for the rate constant

$$k = A\, e^{-E_a/RT}$$

is an empirical equation that allows us to systematize kinetic data. Here, R is the Universal gas constant, 8.31451 J mol^{-1} K^{-1}, T is the absolute temperature, E_a is the *activation energy* (units: J mol^{-1}), and A is the *pre-exponential frequency factor*. By running the reaction at several temperatures and fitting the measured rate constants k to the above equation, we can predict k at any temperature. This demonstration should also indicate to you the importance of regulating the temperature carefully during the course of the reaction.

We will use the same reaction as in Demonstration #1:

$$\underset{\text{peroxydisulfate}}{S_2O_8^{2-}} + \underset{\text{thiosulfate}}{2\,S_2O_3^{2-}} \rightarrow \underset{\text{sulfate}}{2\,SO_4^{2-}} + \underset{\text{dithionate}}{S_4O_6^{2-}}$$

We will measure reaction times τ for reaction mixture B (defined in the Demo #1 handout) at three different reaction temperatures: "cold," "warm," and "hot." Each value for τ becomes, first, a rate and then a rate constant. It is the *change in the value of the rate constant* that causes the rates to differ here. In Demo #1, it was the *change in initial concentrations* that governed the rates. From Demo #1, we know that *Rate* = 0.8 m**M**/τ and $k = Rate/[I^-]\,[S_2O_8^{2-}]$. Thus, our working formula, given the initial concentration of iodide and the *average* concentration in reaction mixture B of peroxydisulfate over the time τ is:

$$k = \frac{Rate}{[I^-]\,[S_2O_8^{2-}]} = \frac{0.80\ \text{m}\mathbf{M}}{\tau\,(80\ \text{m}\mathbf{M})\,(39.6\ \text{m}\mathbf{M})} = \frac{0.253\ \mathbf{M}^{-1}}{\tau}$$

Results

	First Demo	Run #1	Run #2	Run #3
T/K	**295**			
τ/s	**72**			
k/ $\mathbf{M}^{-1}$ s^{-1}	$\mathbf{3.4 \times 10^{-3}}$			
$(1/T)$/K^{-1}	$\mathbf{3.39 \times 10^{-3}}$			
ln (k/$\mathbf{M}^{-1}$ s^{-1})	**−5.67**			

The final two rows allow us to plot the data on the graph below in a way that should give a straight line, since we can write the Arrhenius equation as

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

↑ dependent variable ("y") — ↑ intercept — ↑ slope — ↑ dependent variable ("x")

We can find ln A and $-E_a/R$ from the intercept and slope of a straight line through the data: