Handin 3: Kinetics

1. Show that the integrated rate law for a second-order reaction that is first-order in A and first-order in B for the stoichiometry, 2 A + B → products, is:

$$\frac{1}{2\,[B]_o - [A]_o} \ln\left[\frac{[A]_o([B]_o - \xi)}{[B]_o([A]_o - 2\xi)}\right] = k_2\, t \qquad \text{and} \qquad \xi = [B]_o \frac{\left(1 - e^{(2[B]_o - [A]_o)\, k_2 t}\right)}{\left(1 - \frac{2[B]_o}{[A]_o} e^{(2[B]_o - [A]_o)\, k_2 t}\right)}$$

[Try Chapter 3 Problem 19, first. See the integral table on the inside-back cover of the text.]

2. The rate constants for a first order reaction as a function of temperature are given below.

T (°C)	0.0	10.0	20.0	30.0	40.0
k (s^{-1})	$2.53\text{x}10^{-6}$	$1.11\text{x}10^{-5}$	$4.37\text{x}10^{-5}$	$1.72\text{x}10^{-4}$	$5.54\text{x}10^{-4}$

(a). Use linear least squares curve fitting to find the activation energy and pre-exponential factor.
(b). Use propagation of errors rules to find the uncertainty in the activation energy and pre-exponential factor starting from the uncertainty in the slope and intercept.
(c). Use non-linear curve fitting to the Arrhenius form, $k = A\, e^{-Ea/RT}$, to find the activation energy, pre-exponential factor, and corresponding uncertainties. Use the "Non-linear Least Squares Curve Fitting" applet on the course home page:

www.colby.edu/chemistry/PChem/scripts/lsfitpl.html.

To make the presentation of the data easier in the applet, multiply the rate constants by $1\text{x}10^4$. However, remember to divide the resulting pre-exponential factor by $1\text{x}10^4$ to get the proper order of magnitude. Comment on the meaning of the between-fit-parameters correlation coefficient from the non-linear fit. [Try Chapter 3 Problems 21 and 22, first.]

3. Consider a temperature jump perturbation for a reaction that is first order in the forwards and second order in the reverse direction:

$$A \underset{k_{-2}}{\overset{k_1}{\rightleftarrows}} B + C$$

Starting with A only, show the relaxation time is: $\tau \equiv \dfrac{1}{k_1 + k_{-2}([B]_{eq} + [C]_{eq})}$

[Try Chapter 3 Problems 34-37, first]