

### 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,  $2 A + B \rightarrow \text{products}$ , is:

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

[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.

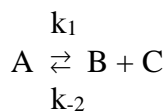
T (°C)	0.0	10.0	20.0	30.0	40.0
k (s <sup>-1</sup> )	2.53x10 <sup>-6</sup>	1.11x10 <sup>-5</sup>	4.37x10 <sup>-5</sup>	1.72x10 <sup>-4</sup>	5.54x10 <sup>-4</sup>

- Use linear least squares curve fitting to find the activation energy and pre-exponential factor.
- 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.
- Use non-linear curve fitting to the Arrhenius form,  $k = A e^{-E_a/RT}$ , 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/lffitpl.html](http://www.colby.edu/chemistry/PChem/scripts/lffitpl.html).

To make the presentation of the data easier in the applet, multiply the rate constants by  $1 \times 10^4$ . However, remember to divide the resulting pre-exponential factor by  $1 \times 10^4$  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:



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

[Try Chapter 3 Problems 34-37, first]