# REB, The Course
# Class 29 Practice Assignment Solution

Liquid-phase reaction (1) was studied in a batch reactor as the first step in generating a rate expression. Three experiments were performed. In experiment 1, the temperature was 70 °C, the initial concentration of A was 1 M and the initial concentration of B was 0.9 M. In experiment 2, the temperature was 80 °C, the initial concentration of A was 1 M and the initial concentration of B was 0.75 M. In experiment 3, the temperature was 90 °C, the initial concentration of A was 0.75 M and the initial concentration of B was 1 M. The concentration of Y was measured at several elapsed times. The resulting data are provided in Table 1. Using these data and an approximate BSTR model, find preliminary values for the pre-exponential factor and the activation energy for the second-order rate expression shown in equation (2) and recommend how to proceed.

$$A + B \rightarrow Y + Z \tag{1}$$

$$r = kC_AC_B \tag{2}$$

The experimental data are provided in the file, practice_29_data.csv. The first few data points from that file are shown in Table 1.

Table 1. First 6 Data from each of the 3 Isothermal BSTR Experiments.

| Experiment 1 | | Experiment 2 | | Experiment 3 | |
|---|---|---|---|---|---|
| $t_{meas}$ | $C_{Y,meas}$ | $t_{meas}$ | $C_{Y,meas}$ | $t_{meas}$ | $C_{Y,meas}$ |
| 0.2 | 0.014 | 0.1 | 0.015 | 0.02 | 0.009 |
| 1.3 | 0.067 | 0.3 | 0.038 | 0.08 | 0.045 |
| 2.4 | 0.083 | 0.6 | 0.088 | 0.14 | 0.085 |
| 3.7 | 0.149 | 0.9 | 0.13 | 0.22 | 0.121 |
| 5.2 | 0.189 | 1.2 | 0.159 | 0.3 | 0.149 |
| 6.8 | 0.222 | 1.5 | 0.199 | 0.38 | 0.191 |

Time in minutes, concentration in moles per liter

## *Assignment Summary*

The information provided in the assignment narrative is summarized below. No extensive quantities were provided, so a basis was chosen. The deliverables only include items that can be generated when using an approximate model.

Reaction

$$A + B \rightarrow Y + Z \tag{1}$$

Rate Expression

$$r = kC_A C_B \tag{2}$$

Reactor: Isothermal BSTR

Given Adjusted Experimental Inputs: $\underline{T}$, $\underline{C}_{A,0}$, $\underline{C}_{B,0}$, $\underline{t}_{meas}$

Given Experimental Responses: $\underline{C}_{Y,meas}$

Parameters to Estimate: $k_0$ and $E$

Basis: $V$ = 1 L

Deliverables: Parameter estimates and uncertainties, coefficients of determination, model and Arrhenius plots, and a recommendation for how to proceed..

## *Approximate BSTR Model*

The reason for approximating the derivative in the BSTR model function is to eliminate the need to solve the design equations analytically. The approximate BSTR model is an algebraic equation and allows parameter estimation using linear least squares. That approximate, algebraic model equation is rearranged and new variables are defined to convert it to a linear form. The data are then separated into same-temperature blocks, and the linear approximate model is fit to the data in each block.

This yields rate coefficient estimates for each data block temperature. To complete the analysis, the Arrhenius expression is fit to those data.

Linearized BSTR Model Equation:

$$\frac{dn_Y}{dt} \approx \frac{\Delta n_Y}{\Delta t} \approx \frac{n_Y\Big|_{t=t_i} - n_Y\Big|_{t=t_{i-1}}}{t_i - t_{i-1}} = kV\left(C_A C_B\right)\Big|_{t=t_i}$$

$$\frac{C_Y\Big|_{t=t_i} - C_Y\Big|_{t=t_{i-1}}}{t_i - t_{i-1}} = k\left(C_A C_B\right)\Big|_{t=t_i} \quad \Rightarrow \quad y = mx$$

$$C_i = C_{i,0} - C_Y \quad i = A \text{ and } B \tag{3}$$

$$y_i = \frac{C_Y\Big|_{t=t_i} - C_Y\Big|_{t=t_{i-1}}}{t_i - t_{i-1}} \tag{4}$$

$$x_i = \left(C_A C_B\right)\Big|_{t=t_i} \tag{5}$$

$$m = k \tag{6}$$

***Deliverables Function***

The purpose of the deliverables function is to use the linearized approximate ?R model above to estimate the [parameters], along with quantities that are needed for assessing the model's accuracy.  Generally, the data are then separated into same-temperature blocks, and the linear model is fit to the data in each block. This yields rate coefficient estimates for each data block temperature. The Arrhenius expression is fit to those data, and an overall coefficient of determination, predicted responses and experiment residuals are calculated.

Deliverables Function

1. Group the experimental data to form same-temperature data blocks
2. For each data block
   a. calculate $x$ and $y$, equations (4) and (5)
   b. call a linear least squares fitting function to fit $y = mx$ to the $x - y$ data
      i. it will return the slope and its uncertainty, the coefficient of determination for that data block, and model-predicted $y$ values
   c. calculate $k$, equation (6) and its confidence interval

$$k_{CI} = m_{CI} \tag{7}$$

3. Call a linear least squares fitting function to fit the Arrhenius expression to the $T - k$ data from step 2 (see Example 3.6.3 in *REB, The Book*)
   a. it will return estimates and confidence intervals for $k_0$ and $E$, the coefficient of determination for the Arrhenius expression, and model-predicted $k$ values
4. Generate an Arrhenius plot

### *Implementation of the Calculations*

The Python script, practice_29.py, that was written to perform the calculations accompanies this solution. It is structured as follows.

1. Import necessary libraries.
2. Make the given constants, adjusted experimental inputs, and measured responses available wherever they are needed.
3. Define the deliverables function as described above.
4. Call the deliverables function.

### *Results and Discussion*

The model plots for the three same-temperature data blocks are shown in Figure 1, and the parameter estimation results are listed in Table 2. There is a great deal of scatter in the model plots, but that often occurs when using finite differences to estimate the derivative. Despite the scatter and the low coefficients of determination, the uncertainties are not large.

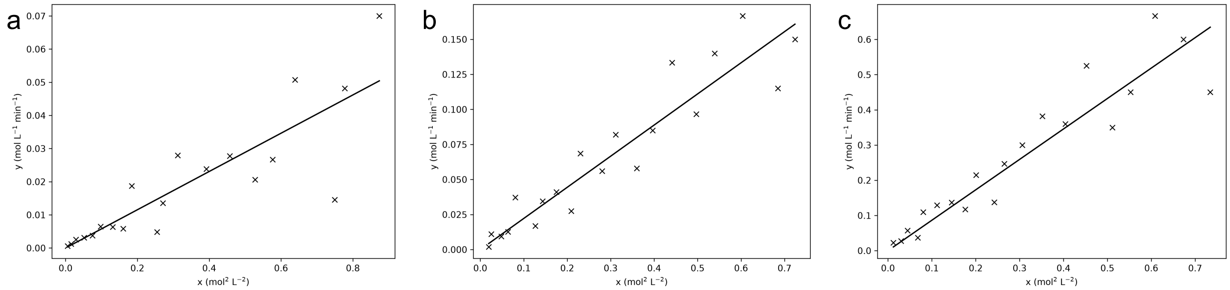


*Figure 1. Model plots for experiments a) 1, b) 2, and c) 3.*

Table 2. Model Plot Parameter Estimation Results

| T* | k** | 95% Confidence Interval** | $R^2$ |
|---|---|---|---|
| 70 | $5.77 \times 10^{-2}$ | [$4.70 \times 10^{-2}$, $6.85 \times 10^{-2}$] | 0.869 |
| 80 | $2.22 \times 10^{-1}$ | [$1.99 \times 10^{-1}$, $2.45 \times 10^{-1}$] | 0.955 |
| 90 | $8.64 \times 10^{-1}$ | [$7.73 \times 10^{-1}$, $9.56 \times 10^{-1}$] | 0.953 |

* °C

** L $mol^{-1}$ $min^{-1}$

The $k$ vs. $T$ results in Table 2 were used to generate the Arrhenius plot shown in Figure 2. The parameter estimation results are shown in Table 3. Given the scatter in the model plots, it is surprising to see that the data fall almost exactly on the line in the Arrhenius plot. The uncertainties in the estimated values are quite large, though.

The estimates, confidence intervals, and coefficients of determination in the tables are not derived from the complete data set. An overall coefficient of determination and overall parity and residuals plots could be generated, but doing so would require solving the design equations. That defeats the purpose of using an approximate model.

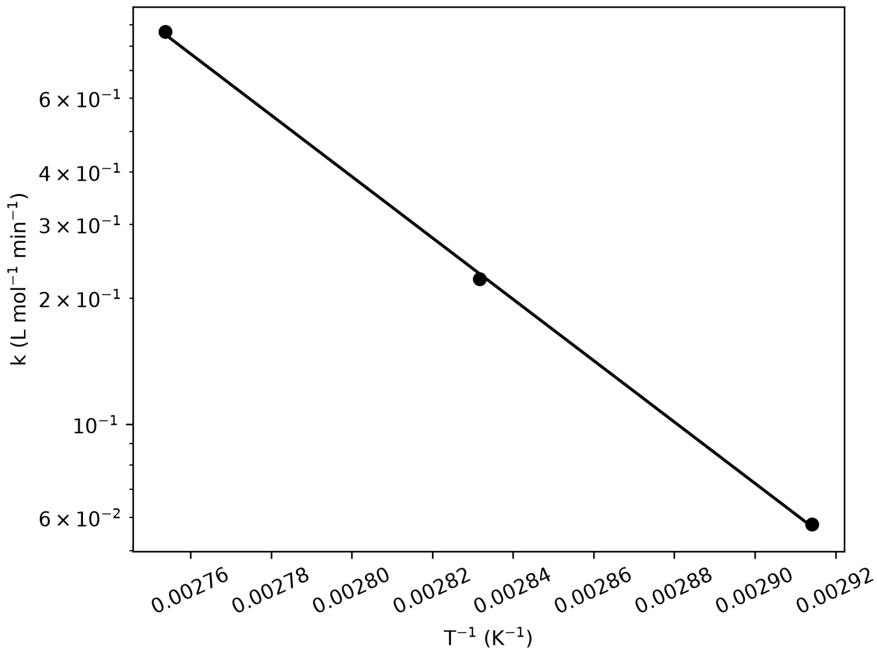


*Figure 2. Arrhenius plot of the results from Table 2.*

Table 3. Arrhenius Plot Parameter Estimation Results

| Parameter | value | 95% CI |
|---|---|---|
| $k_0$* | $1.23 \times 10^{20}$ | [$1.37 \times 10^{15}$, $1.10 \times 10^{25}$] |
| E** | 33.5 | [25.5, 41.5] |
| $R^2$ | 1.00 | |

* $L\ mol^{-1}\ min^{-1}$

** $kcal\ mol^{-1}$

### ***Accuracy Assessment***

The proposed rate expression may be accurate, but additional experiments should be performed and the data should be analyzed using a fitting function to get the best assessment of the model's accuracy.