REB, The Course
Class 29 Learning Activity Solution

An ideal, 100 cm^3, isothermal BSTR was used to generate kinetics data for reaction (1) at several temperatures. In a typical experiment at any one temperature, reagent A was added to the reactor at that temperature and a pressure of $P_{A,0}$. Then, to begin the reaction, a sufficient amount of reagent B at the same temperature was added instantaneously to bring the total pressure to 6.0 atm. The reaction progress was followed by recording the total pressure once per minute for 24 min after the addition of reagent B. Use the resulting experimental data and an approximate reactor model to make a preliminary assessment the accuracy of the rate expression shown in equation (2).

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

$$r = kP_A\sqrt{P_B} \tag{2}$$

The experimental data are provided in the file, activity_29_data.csv. The first few data points from that file are shown in Table 1.

Table 1. First 6 of the 216 Isothermal BSTR Data.

T (°C)	$P_{A,0}$ (atm)	t_{meas} (min)	P_{meas} (atm)
225.0	2.0	1.0	5.96
225.0	2.0	2.0	5.82
225.0	2.0	3.0	5.81
225.0	2.0	4.0	5.73
225.0	2.0	5.0	5.68
225.0	2.0	6.0	5.58

Assignment Summary

A succinct summary of the information from the assignment narrative is prensented below. The assignment requests a preliminary assessment, so the deliverables only include items that can be calculated using the approximate model.

Reaction

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

Rate Expression

$$r = kP_A\sqrt{P_B} \tag{2}$$

Reactor: Isothermal BSTR

Given Constants: V = 100 cm^3, P = 6 atm.

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

Given Experimental Responses: $\underline{P}_{meas}$

Parameters to Estimate: k_0 and E

Deliverables: Rate coefficient estimates and confidence intervals and model plots for each same-temperature data block, pre-exponential factor and activation energy estimates and confidence intervals and an Arrhenius plot.

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.

<u>Linearized BSTR Model Equation</u>:

$$\frac{dn_A}{dt} \approx \frac{\Delta n_A}{\Delta t} \approx \frac{n_A\Big|_{t=t_i} - n_A\Big|_{t=t_{i-1}}}{t_i - t_{i-1}} = -kV\left(P_A\sqrt{P_B}\right)\Big|_{t=t_i}$$

$$\frac{n_A\Big|_{t=t_i} - n_A\Big|_{t=t_{i-1}}}{t_i - t_{i-1}} = -kV\left(P_A\sqrt{P_B}\right)\Big|_{t=t_i} \quad \Rightarrow \quad y = mx$$

$$y_i = \frac{n_A\Big|_{t=t_i} - n_A\Big|_{t=t_{i-1}}}{t_i - t_{i-1}} \tag{3}$$

$$x_i = -V\left(P_A\sqrt{P_B}\right)\Big|_{t=t_i} \tag{4}$$

$$m = k \tag{5}$$

$$n_{A,0} = \frac{P_{A,0}V}{RT} \tag{6}$$

$$n_{B,0} = \frac{\left(6 - P_{A,0}\right)V}{RT} \tag{7}$$

$$n_{tot} = n_{A,0} + n_{B,0} - \xi \quad \Rightarrow \quad \xi = n_{A,0} + n_{B,0} - \frac{P_{meas}V}{RT} \tag{8}$$

$$n_i = n_{i,0} - \xi \quad i = A \text{ and } B \tag{9}$$

$$P_i = \frac{n_iRT}{V} \quad i = A \text{ and } B \tag{10}$$

Deliverables Function

The purpose of the deliverables function is to use the linearized approximate BSTR 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.

<u>Deliverables Function</u>

1. Group the experimental data to form same-temperature data blocks
2. For each data block
    a. calculate x and y, equations (3), (4), (6) - (10)
    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 (5), and its confidence interval

$$k_{CI} = m_{CI} \tag{11}$$

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, activity_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.

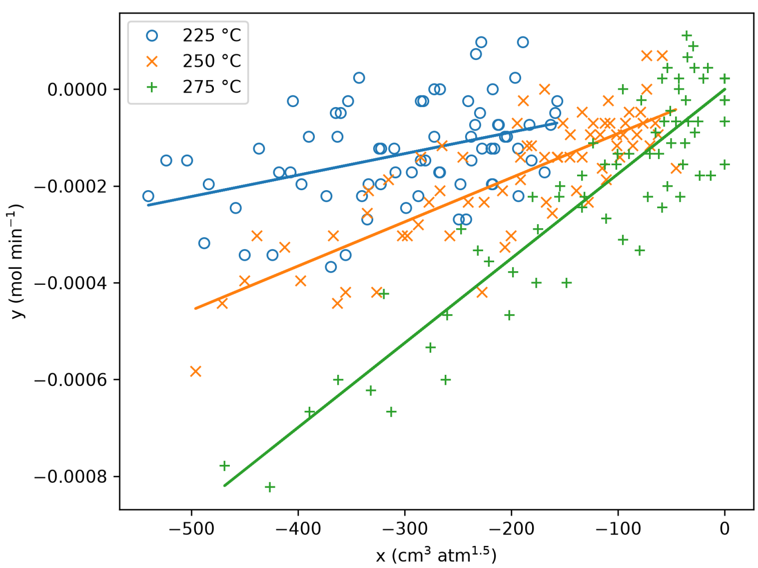

Figure 1. Model plots for the same-temperature data blocks.

Table 2. Model Plot Parameter Estimation Results

T*	k**	95% Confidence Interval**	R^2
225	4.44×10^{-7}	[3.73×10^{-7}, 5.14×10^{-7}]	0.691
250	9.14×10^{-7}	[8.35×10^{-7}, 9.93×10^{-7}]	0.882
275	1.75×10^{-6}	[1.62×10^{-6}, 1.88×10^{-6}]	0.908

* °C

** mol cm^{-3} min^{-1} $atm^{-1.5}$

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 small

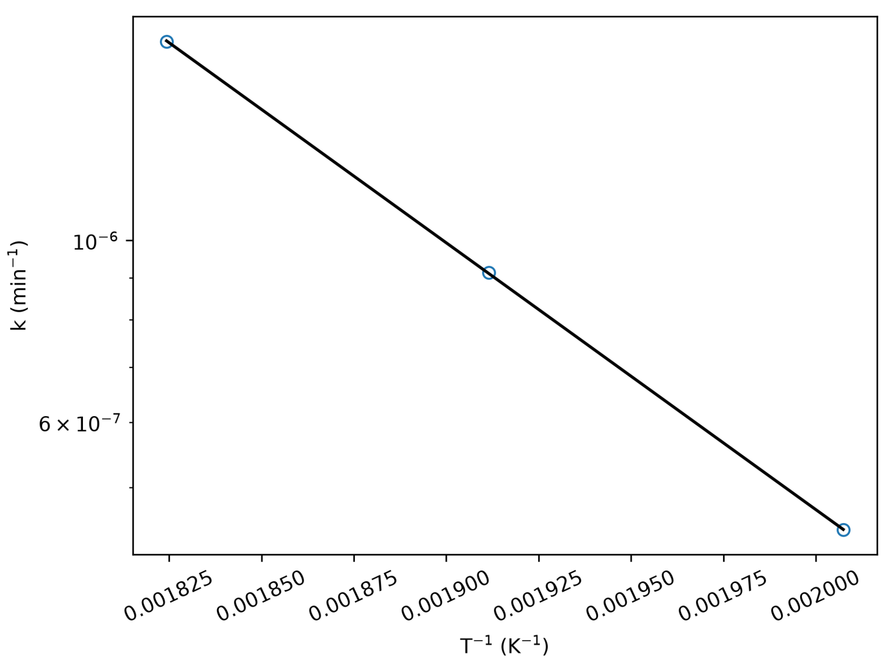

Figure 2. Arrhenius plot of the results from Table 2.

Table 3. Arrhenius Plot Parameter Estimation Results

Parameter	value	95% CI
k_0[1]	1.51	[0.771, 2.95]
E[2]	14.9	[14.2, 15.6]
R^2	1.00	

[1] mol cm^{-3} min^{-1} $atm^{-1.5}$

[2] kcal mol^{-1}

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.

Accuracy Assessment

The approximate model describes the data with reasonable accuracy. An analysis using a fitting function should be performed to obtain better parameter estimates.