REB, The Course
Class 27 Practice Assignment Solution

A 1 L, isothermal BSTR was used to generate kinetics data for the liquid-phase reaction, equation (1). In each experiment the temperature, initial concentration of A and initial concentration of B were set, after which the concentration of A was measured at several reaction times. Use those data and a linear BSTR model to estimate the pre-exponential factor and activation energy for the rate coefficient in equation (2), and assess the accuracy of the resulting rate expression.

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

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

The experimental data are provided in the file, practice_27_data.csv. The first few data points from that file are shown in Table 1.

Table 1. First 6 of the 180 Experimental Data

Experiment	T (°C)	$C_{A,0}$ (M)	$C_{B,0}$ (M)	t_{meas} (min)	$C_{A,meas}$ (M)
1	160	1.0	1.0	20.0	0.93
1	160	1.0	1.0	40.0	1.02
1	160	1.0	1.0	60.0	0.97
1	160	1.0	1.0	80.0	0.87
1	160	1.0	1.0	100.0	0.83
2	170	1.0	1.0	20.0	0.79

Assignment Summary

The information provide in the assignment narrative is summarized below. The list of deliverables includes items necessary for assessing the accuracy of the model, and not just the items specifically requested.

Reaction

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

Rate Expression

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

Reactor: Isothermal BSTR

Given Constants: V = 1L

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

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

Parameters to Estimate: k_0 and E

Deliverable: Parameter estimates and confidence intervals, coefficients of determination, parity and residuals plots, and an assessment of the accuracy of the fitted model.

Linearized BSTR Model

The reason for linearizing the BSTR model function is to allow parameter estimation using linear least squares. The design equations, which are IVODEs, must first be solved analytically, which results in an algebraic model equation. Then the algebraic model equation is rearranged and new variables are defined to convert it to a linear form.

Linearized BSTR Model Equation:

$$\frac{dn_A}{dt} = -Vr = -kVC_A C_B = -\frac{kn_A n_B}{V}$$

$$\frac{dn_A}{n_A n_B} - \frac{k}{V} dt$$

$$n_B = n_{B,0} - \xi$$

$$\xi = n_{A,0} - n_A \quad \Rightarrow \quad n_B = n_{B,0} - n_{A,0} + n_A$$

$$\int_{n_{A,0}}^{n_A} \frac{dn_A}{n_A \left(n_{B,0} - n_{A,0} + n_A\right)} = -\frac{k}{V} \int_0^t dt$$

$$n_{A,0} = n_{B,0} \quad \Rightarrow \quad \frac{1}{n_{A,0}} - \frac{1}{n_A} = -\frac{kt}{V}$$

$$\Rightarrow \quad \frac{1}{C_{A,0}} - \frac{1}{C_A} = -kt$$

$$\Rightarrow \quad y = mx$$

$$n_{A,0} \neq n_{B,0} \quad \Rightarrow \quad \frac{1}{n_{A,0} - n_{B,0}} \ln \frac{n_{A,0}\left(n_{B,0} - n_{A,0} + n_A\right)}{n_{B,0} n_A} = -\frac{kt}{V}$$

$$\Rightarrow \quad \frac{1}{C_{A,0} - C_{B,0}} \ln \frac{C_{A,0}\left(C_{B,0} - C_{A,0} + C_A\right)}{C_{B,0} C_A} = -kt$$

$$\Rightarrow \quad y = mx$$

<u>Linearized BSTR Model Equation</u> (for each same-temperature data block):

$$y = mx \tag{3}$$

$$C_{A,0} = C_{B,0} \qquad y = \frac{1}{C_{A,0}} - \frac{1}{C_{A,meas}}$$

$$C_{A,0} \neq C_{B,0} \qquad y = \frac{1}{C_{A,0} - C_{B,0}} \ln \frac{C_{A,0}\left(C_{B,0} - C_{A,0} + C_{A,meas}\right)}{C_{B,0} C_{A,meas}} \tag{4}$$

$$x = -t_{meas} \tag{5}$$

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

Deliverables Function

The purpose of the deliverables function is to use the linearized BSTR model above to estimate the k, along with quantities that are needed for assessing the model's accuracy. Generally, the data are 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, which yields the pre-exponential factor and activation energy and their confidence intervals. An overall coefficient of determination, predicted responses and experiment residuals are calculated, and a parity and residuals plots are generated.

<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) through (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, and the coefficient of determination for the Arrhenius expression
4. Calculate the predicted rate coefficients and generate an Arrhenius plot
5. Calculate the experiment residuals and overall coefficient of determination using the full data set

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \tag{8}$$

$$C_{A,0} = C_{B,0}$$

$$\begin{aligned} &\Rightarrow \quad \frac{1}{C_{A,0}} - \frac{1}{C_{A,pred}} = kx \\ &\Rightarrow \quad C_{A,pred} = \left(\frac{1}{C_{A,0}} - kx\right)^{-1} \end{aligned} \tag{9a}$$

$$C_{A,0} \neq C_{B,0}$$

$$\begin{aligned} &\Rightarrow \quad \frac{1}{C_{A,0} - C_{B,0}} \ln \frac{C_{A,0}\left(C_{B,0} - C_{A,0} + C_{A,pred}\right)}{C_{B,0} C_{A,pred}} = kx \\ &\Rightarrow \quad C_{A,pred} = \frac{C_{A,0} - C_{B,0}}{1 - \frac{C_{B,0}}{C_{A,0}} e^{(C_{A,0} - C_{B,0})kx}} \end{aligned} \tag{9b}$$

$$\underline{\epsilon}_{expt} = \underline{C}_{A,meas} - \underline{C}_{A,pred} \tag{10}$$

$$C_{A,mean} = \frac{\sum_i C_{A,meas,i}}{n_{expts}}$$

$$ss_{resid} = \sum_i \left(C_{A,meas,i} - C_{A,pred,i}\right)^2$$

$$ss_{total} = \sum_i \left(C_{A,meas,i} - C_{A,mean}\right)^2$$

$$R^2 = 1 - \frac{ss_{resid}}{ss_{total}}$$

6. Generate
    a. a parity plot showing $\underline{C}_{A,pred}$ *vs.* $\underline{C}_{A,meas}$
    b. residuals plots showing $\underline{\epsilon}_{expt}$ *vs.* $\underline{T}$, $\underline{C}_{A,0}$, $\underline{C}_{B,0}$, and $\underline{t}_{meas}$

Implementation of the Calculations

The Python script, practice_27.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 data were separated into same-temperature data blocks, each of which was analyzed separately. The resulting model plots are shown in Figure 1, and the corresponding rate coefficient estimates and coefficients of determination are presented in Table 2. There is a fair amount of scatter in the model plots, particularly at the highest temperature. This is confirmed by the coefficients of determination where the lowest and highest temperatures have values close to 0.9. The confidence intervals are relatively narrow.

The Arrhenius expression was fit to the data in Table 2. The results are shown in Table 3 and Figure 2. As is often the case, the uncertainty in the pre-exponential factor is large, but all other indicators reflect a very accurate model. There is virtually no scatter in the Arrhenius plot, the coefficient of determination is essentially equal to 1, and the uncertainty in the activation energy is acceptable. However, it is important to note that the uncertainties in the Arrhenius parameters are not derived directly from the data, but from the estimated rate coefficients in Table 2, each of which is derived from only a fraction of the data.

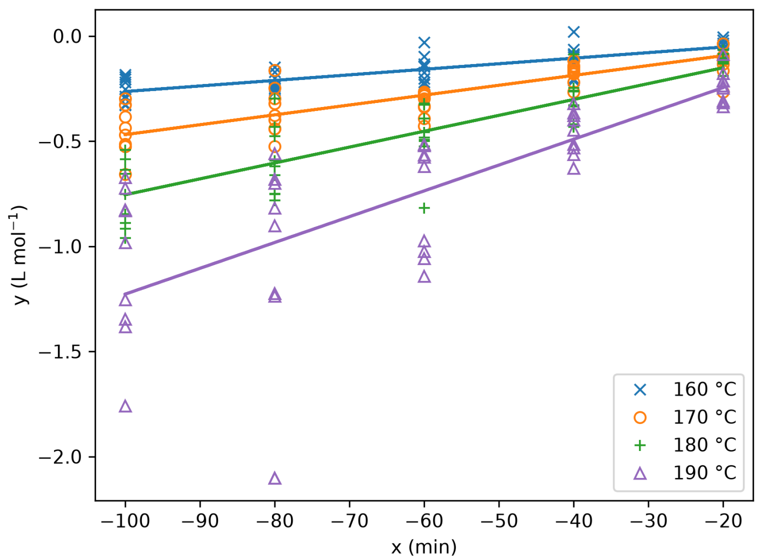

Figure 1. Model Plots for Same-Temperature Data Blocks.

Table 2. Model Plot Parameter Estimates

T (°C)	k (L mol^{-1} min^{-1})	95% Confidence Interval	R^2
160	0.00264	[0.00241, 0.00288]	0.919
170	0.00469	[0.00432, 0.00507]	0.935
180	0.00755	[0.00698, 0.00812]	0.942
190	0.0123	[0.0108, 0.0138]	0.857

The Arrhenius parameters in Table 3 were used to calculate model-predicted concentrations of A for each experiment. The results were then used to generate the model plot in Figure 3. The scattering of the data in that plot is acceptable, and the coefficient of determination is equal to 0.984. The residuals plots shown in Figure 4 do not show any significant trends in the residuals with respect to the adjusted experimental inputs. It might be argued that there is a very slight increase in the residuals as the temperature increases, but if there is a trend, it is not significant.

Table 3. Arrhenius Expression Parameter Estimates

Parameter	Value	95% Confidence Interval
k_0 (L mol^{-1} min^{-1})	4.55×10^7	[6.58×10^6, 3.15×10^8]
E (kcal mol^{-1})	20.3	[18.6, 22.0]
R^2	0.999	

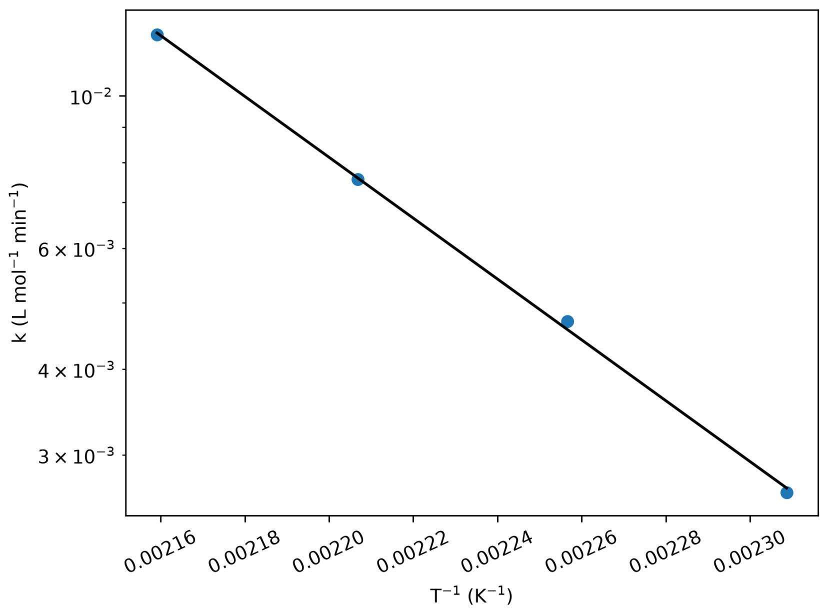

Figure 2. Arrhenius Plot for the Estimated Rate Coefficients in Table 2.

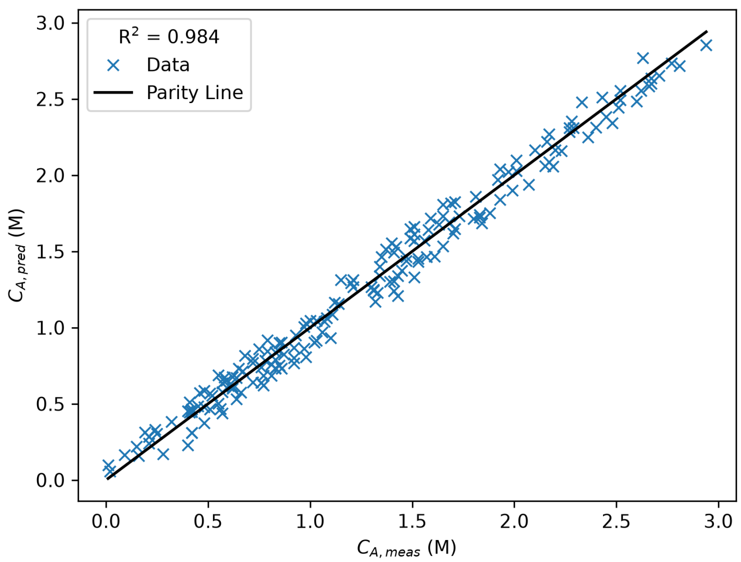

Figure 3. Parity Plot Generated Using the Arrhenius Parameters in Table 3.

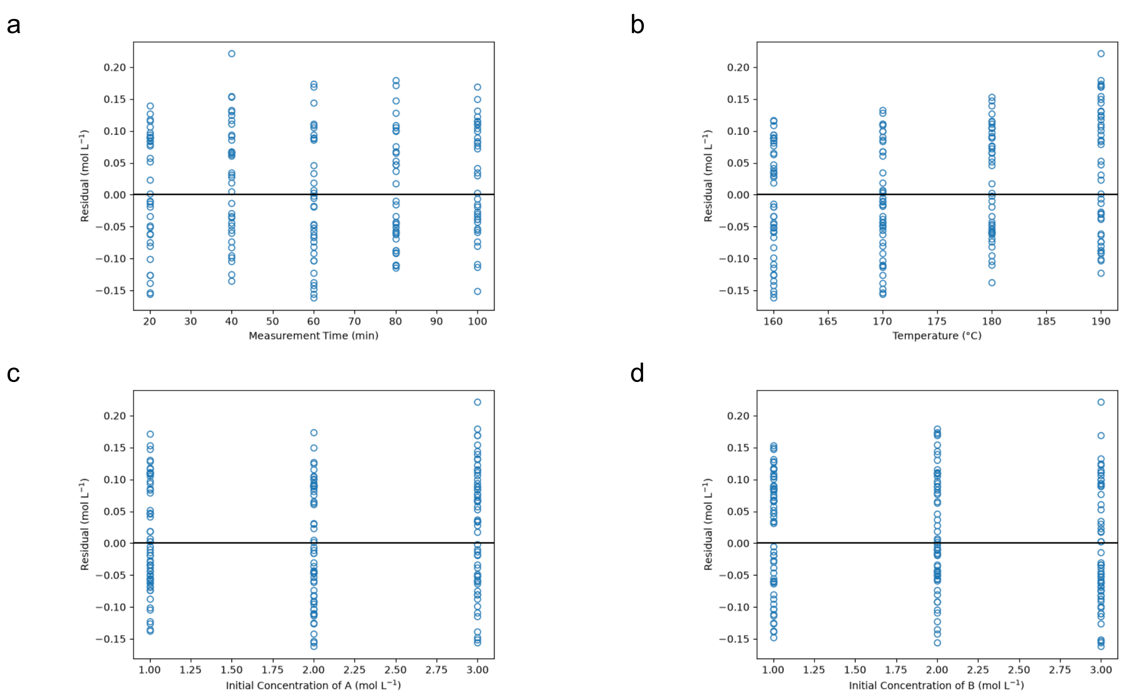

Figure 4. Residuals plots for a) the measurement time, b) the temperature, c) the initial concentration of A, and d) the initial concentration of B generated using the Arrhenius parameters in Table 3.

Accuracy Assessment

When used with the parameters shown in Table 2, the reactor model is acceptably accurate, which indicates that the proposed rate expression offers a reasonable description of the reaction rate.