REB, The Course
Class 26 Learning Activity Solution

An isothermal, steady-state PFR with negligible pressure drop was used to generate kinetics data for liquid-phase reaction (1). In each experiment the temperature (°C), feed concentration of A (M), feed concentration of B (M), and space time (min) were set and the outlet concentration of A (M) was measured. The PFR diameter was 0.3 dm and its length, 10 dm.

In the rate expression, equation (2), the rate coefficient displays Arrhenius temperature dependence. Use the experimental data to estimate the pre-exponential factor and activation energy using (a) a fitting function and (b) a linearized reactor model. Compare the results from the two parameter estimation approaches.

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

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

The experimental data are provided in the file, activity_26_data.csv. The first few data points from that file are shown in Table 1.

Table 1. First 6 of the 30 Isothermal PFR Experiments.

T (°C)	$C_{A,in}$ (M)	$C_{B,in}$ (M)	τ (min)	$C_{A,meas}$ (M)
70	1.0	0.9	2	0.989
70	1.0	0.9	24	0.795
70	1.0	0.9	46	0.678
70	1.0	0.9	68	0.587
70	1.0	0.9	90	0.53
70	1.0	0.9	112	0.472

Assignment Summary

A succinct summary of the information contained in the assignment narrative is presented below. The confidence intervals for the parameter estimates, coefficients of determination, and parity/model/residuals plots were added to the deliverables list because while not specifically requested, they are needed for assessing the accuracy of the reactor model.

<u>Reaction</u>

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

<u>Rate Expression</u>

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

<u>Reactor</u>: Isothermal, steady-state PFR with negligible pressure drop

<u>Given Constants</u>: D = 0.3 dm and L = 10 dm

<u>Given Adjusted Experimental Inputs</u>: $\underline{T}$, $\underline{C}_{A,in}$, $\underline{C}_{B,in}$, and $\underline{\tau}$

<u>Given Experimental Responses</u>: $\underline{C}_{A,meas}$

<u>Parameters to Estimate</u>: k_0 and E

<u>Deliverables</u>: Parameter estimates, coefficients of determination, parity/model/residuals plots, and an assessment of the accuracy of the fitted model.

PFR Model Function

The purpose of the PFR model function is to solve the PFR design equations for the reactor that was used in the experiments. This is done numerically by calling an IVODE solver. Any quantities that are not given and are required for solving the design equations will be passed to it as arguments. If necessary, the PFR function will then make them available to the PFR derivatives function as as global variables because they cannot be passed as arguments. The PFR derivatives function described here also must be written.

<u>PFR Model Equations</u>:

$$\frac{d\dot{n}_A}{dz} = -\frac{\pi D^2}{4} r \tag{3}$$

$$\frac{d\dot{n}_B}{dz} = -\frac{\pi D^2}{4} r \tag{4}$$

$$\frac{d\dot{n}_Y}{dz} = \frac{\pi D^2}{4} r \tag{5}$$

$$\frac{d\dot{n}_Z}{dz} = \frac{\pi D^2}{4} r \tag{6}$$

<u>PFR Model Variables</u>: $\underline{z}$, $\underline{\dot{n}}_A$, $\underline{\dot{n}}_B$, $\underline{\dot{n}}_Y$, and $\underline{\dot{n}}_Z$

<u>Additional Computable Unknowns</u>: r, k, C_A, and C_B

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \tag{7}$$

$$C_i = \frac{\dot{n}_i}{\dot{V}} \qquad i = A \text{ and } B \tag{8}$$

$$\dot{V} = \dot{V}_{in} = \frac{\pi D^2 L}{4\tau} \tag{9}$$

<u>Additional Uncomputable Unknowns</u>: k_0, E, T, and τ

<u>IVODE Solver Inputs</u>:

1. Initial values of the reactor model variables

$$z_{initial} = 0 \tag{10}$$

$$\dot{n}_{i,initial} = \dot{V}_{in} C_{i,in} \quad i = A \text{ and } B \tag{11}$$

$$\dot{n}_{Y,initial} = \dot{n}_{Z,initial} = 0 \tag{12}$$

2. Stopping criterion

$$z_{final} = L \tag{13}$$

3. Derivatives function that
   a. receives z, $\dot{n}_A$, $\dot{n}_B$, $\dot{n}_Y$, and $\dot{n}_Z$ at the start of an integration step
   b. has access to k_0, E, T, and τ as global variables.
   c. calculates the additional unknowns using equations (2), (7), and (8)
   d. evaluates and returns the PFR design equation derivatives using equations (3) - (6).

Linearized PFR Model

The reason for linearizing the PFR 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. Specifically, one of the mole balances is solved analytically. Then the algebraic model equation is rearranged and new variables are defined to convert it to a linear form.

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

$$\frac{d\dot{n}_A}{dz} = -\frac{\pi D^2}{4} r = -\frac{\pi D^2 k}{4} C_A C_B = -\frac{\pi D^2 k}{4} \left(\frac{\dot{n}_A}{\dot{V}_{in}}\right)\left(\frac{\dot{n}_B}{\dot{V}_{in}}\right)$$

$$\dot{n}_A = \dot{n}_{A,in} - \dot{\xi} \quad \Rightarrow \quad \dot{\xi} = \dot{n}_{A,in} - \dot{n}_A$$

$$\dot{n}_B = \dot{n}_{B,in} - \dot{\xi} = \dot{n}_{B,in} - \dot{n}_{A,in} + \dot{n}_A$$

$$\dot{V}_{in} = \frac{V}{\tau} = \frac{\pi D^2 L}{4\tau}$$

$$\frac{d\dot{n}_A}{dz} = -\frac{4k\tau^2}{\pi D^2 L^2}\dot{n}_A\left(\dot{n}_{B,in} - \dot{n}_{A,in} + \dot{n}_A\right)$$

$$\frac{4\tau}{\pi D^2 L}\int_{\dot{n}_{A,in}}^{\dot{n}_A}\frac{d\dot{n}_A}{\dot{n}_A\left(\dot{n}_{B,in} - \dot{n}_{A,in} + \dot{n}_A\right)} = -\frac{k\tau}{L}\int_0^L dz$$

$$\frac{1}{C_{A,in} - C_{B,in}}\ln\frac{C_{A,in}\left(C_{B,in} - C_{A,in} + C_A\right)}{C_{B,in}C_A} = -k\tau \quad \Rightarrow \quad y = mx$$

$$y = \frac{1}{C_{A,in} - C_{B,in}}\ln\frac{C_{A,in}\left(C_{B,in} - C_{A,in} + C_{A,meas}\right)}{C_{B,in}C_{A,meas}} \tag{14}$$

$$x = -\tau \tag{15}$$

$$m = k \tag{16}$$

Deliverables Function

The first purpose of the deliverables function is to use the PFR model function above to estimate the k_0 and E and their confidence intervals, calculate the coefficient of determination, and calculate the predicted responses and experiment residuals for use in parity and residuals functions. This is done numerically by calling a fitting function. To improve the likelihood of numerical convergence, the base-10 log of k_0 is estimated instead of k_0, itself. The predicted responses function described here also must be written.

The second purpose of the deliverables function is to use the linearized PF model above to estimate the k_0 and E, and use them to calculate the coefficient of determination, and the predicted responses and experiment residuals for use in parity and residuals functions. To do so, 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, and an overall coefficient of determination, predicted responses and experiment residuals are calculated.

Deliverables Function

1. Perform the analysis using a fitting function
   a. Define guesses for the parameters

$$\beta = 0.0 \tag{17}$$

$$E = 40.0 \text{ kJ mol}^{-1} \tag{18}$$

   b. Call a numerical fitting function.
      i. Arguments
         1. The experimental data: $\underline{T}$, $\underline{C}_{A,in}$, $\underline{C}_{B,in}$, $\underline{\tau}$, and $\underline{C}_{A,pred}$
         2. The Initial guesses for the parameters from step 1
         3. A predicted responses function as described below
      ii. Returned values
         1. estimates and confidence intervals for β and E
         2. the coefficient of determination, R^2
         3. the predicted responses: $\underline{C}_{A,pred}$
   c. Calculate k_0 and its confidence interval

$$k_0 = 10^{\beta} \tag{19}$$

$$k_{0,CI} = 10^{\beta_{CI}} \tag{20}$$

   d. Calculate the experiment residuals

$$\underline{\epsilon}_{expt} = \underline{C}_{A,meas} - \underline{C}_{A,pred} \tag{21}$$

   e. Generate
      i. a parity plot showing $\underline{C}_{A,pred}$ *vs.* $\underline{C}_{A,pred}$
      ii. residuals plots showing $\underline{\epsilon}_{expt}$ vs. $\underline{T}$, $\underline{C}_{A,in}$, $\underline{C}_{B,in}$, $\underline{\tau}$
2. Perform the analysis using the linearized PFR model
   a. Group the experimental data to form same-temperature data blocks

b. For each data block
   i. calculate x and y, equations (14) and (15)
   ii. call a linear least squares fitting function to fit $y = mx$ to the $x - y$ data
      1. it will return the slope and its uncertainty, the coefficient of determination for that data block, and model-predicted y values
   iii. calculate k and its confidence interval, equations (16) and (22)

$$k_{CI} = m_{CI} \tag{22}$$

c. 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*)
   i. 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
d. Generate an Arrhenius plot
e. Use the resulting Arrhenius parameters and the PFR model function to calculate the linear model predicted responses and experiment residuals using equations (21) and (23)

$$C_{A,pred} = \left.\frac{4\underline{\dot{n}}_A \tau}{\pi D^2 L}\right|_{t=t_{meas}} \tag{23}$$

f. calculate the linear model coefficient of determination

$$C_{A,mean} = \frac{\sum_i C_{A,meas,i}}{n_{expts}} \tag{24}$$

$$ss_{resid} = \sum_i \left(C_{A,meas,i} - C_{A,pred,i}\right)^2 \tag{25}$$

$$ss_{total} = \sum_i \left(C_{A,meas,i} - C_{A,mean}\right)^2 \tag{26}$$

$$R^2 = 1 - \frac{ss_{resid}}{ss_{total}} \tag{27}$$

f. Generate

   i. a linear model parity plot showing $\underline{C}_{A,pred}$ vs. $\underline{C}_{A,meas}$

   ii. linear model residuals plots showing $\underline{\epsilon}_{expt}$ vs. $\underline{T}$, $\underline{C}_{A,0}$, and $\underline{t}_{meas}$

Predicted Responses Function

1. receives the adjusted experimental inputs and guesses for the parameters
2. calculates the pre-exponential factor using equation (19)
3. loops through all of the experiments
   a. calls the PFR model function
   b. calculates the model-predicted response using equation (23)
4. returns the predicted responses for all of the experiments

Implementation of the Calculations

The Python script, activity_26.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. Declare global variables for quantities that cannot be passed to the derivatives function as arguments.
4. Define the PFR model, PFR derivatives, predicted responses, and deliverables functions as described above.
5. Call the deliverables function.

Results and Discussion

The fitting function did not converge quickly when using the parameter guesses in equations (17) and (18). After increasing the guess for β, it did converge, and the results are shown in Table 2. The corresponding parity plot is presented in Figure 1, and the residuals plots in Figure 2. The coefficient of determination is essentially equal to zero, the uncertainty in the pre-exponential factor is between almost 70% but the uncertainty in the activation energy is less than 2%. The data fall very nearly on the parity line and there are no apparent trends in the residuals. These factors all indicate that the PFR model is very accurate, and it captures well the effects of the inputs that were adjusted in the experiments.

Table 2. Parameter Estimation Results from the Fitting Function.

Parameter	Value	95% CI
k_0 (L mol^{-1} min^{-1})	4.16×10^{13}	[2.44×10^{13}, 7.07×10^{13}]
E (kcal mol^{-1})	24.4	[24.0, 24.8]
R^2	0.999	

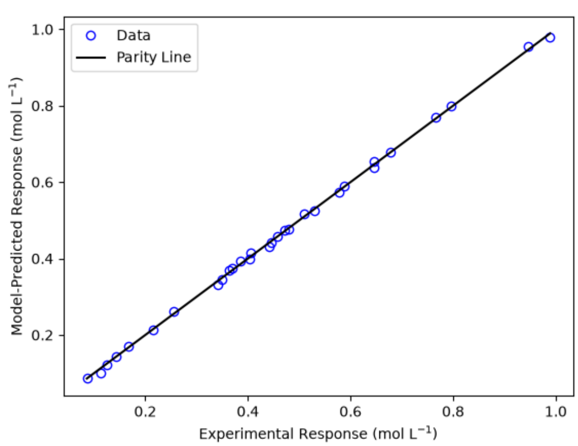

Figure 1. Parity plot for the parameters estimated using a fitting function.

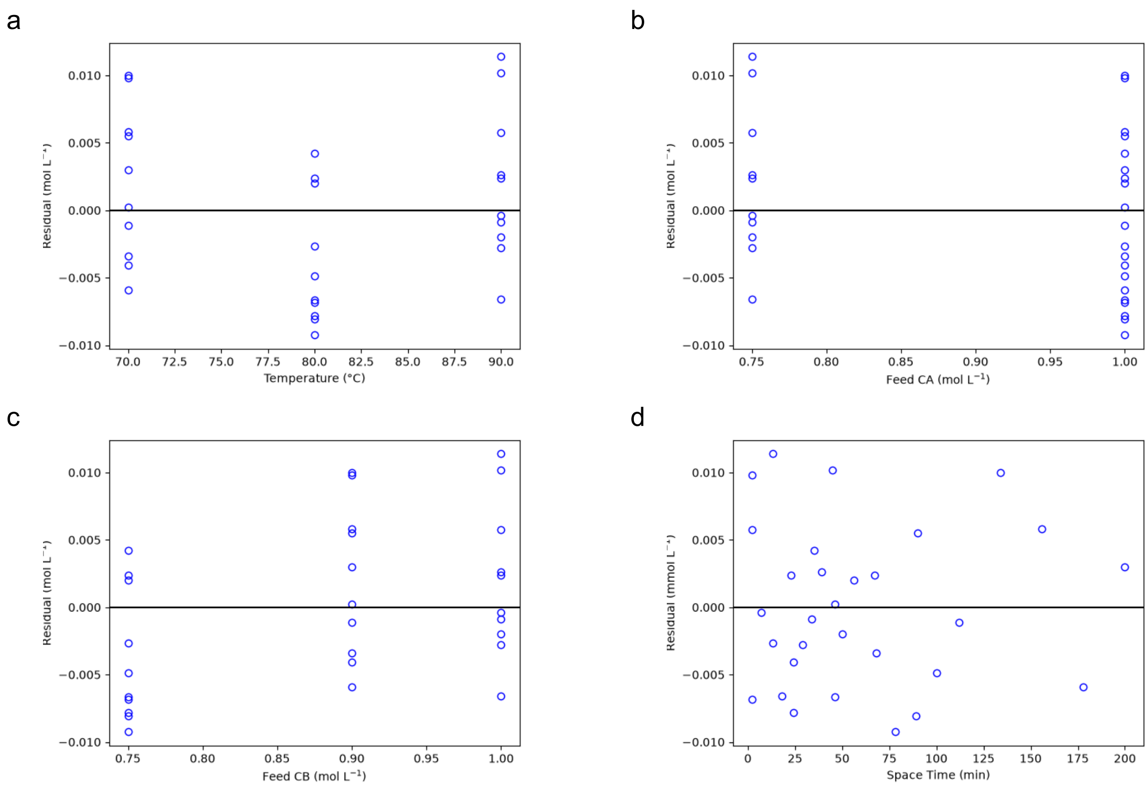

Figure 2. Fitting function residuals plots for a) feed temperature, b) inlet concentration of A, c) inlet concentration of B, and d) space time.

The model plots resulting from fitting the linear PFR model to same-temperature blocks of data are presented in Figure 3, and the estimated rate coefficients and coefficients of determination are presented in Table 3. These fits are also very good as indicated by the coefficients of determination being close to 1, the uncertainties in the rate coefficients being close to the estimated values, the minimal scatter of the data about the lines, and the absence of any trends in the scatter.

The Arrhenius plot resulting from fitting the Arrhenius expression to the data in Table 3 is presented in Figure 4, and the corresponding parameter estimates in Table 4. Confidence intervals are not included because they would be based on the estimated rate coefficients, each of which is based on only part of the data. However, the estimated parameters were used to calculate the predicted responses and experiment residuals for all of the data. From those results the coefficient of determination included in Table 4 was calculated, and the parity and residuals plots in Figures 5 and 6 were generated.

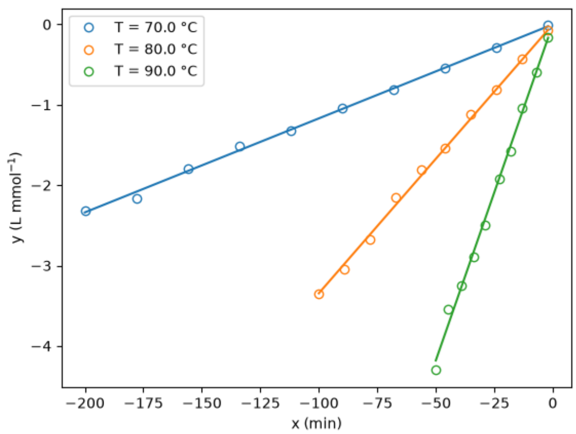

Figure 3. Model plots for the same-temperature data blocks.

Table 3. Parameter Estimates from the Linear Model Plots

T (°C)	k (L mol^{-1} min^{-1})	R^2
70.0	0.0117, 95% CI [0.0117, 0.0115]	0.999
80.0	0.0334, 95% CI [0.0334, 0.0328]	0.999
90.0	0.0836, 95% CI [0.0836, 0.0814]	0.999

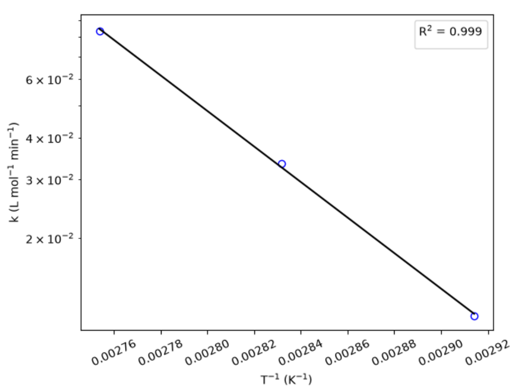

Figure 4. Arrhenius plot for the parameters shown in Table 3

Table 4. Arrhenius Parameters Estimated Using the Linear Model

Parameter	Value
k_0 ($L\ mol^{-1}\ min^{-1}$)	3.90×10^{13}
E ($kcal\ mol^{-1}$)	24.4
R^2	0.999

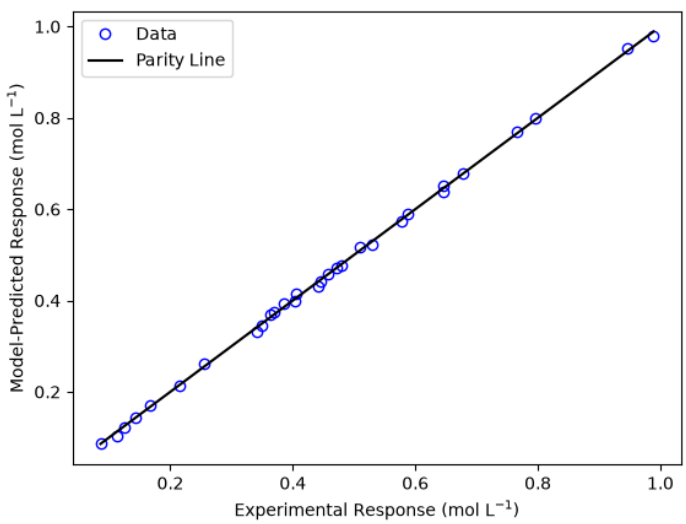

Figure 5. Parity plot for the parameters estimated using the linear model.

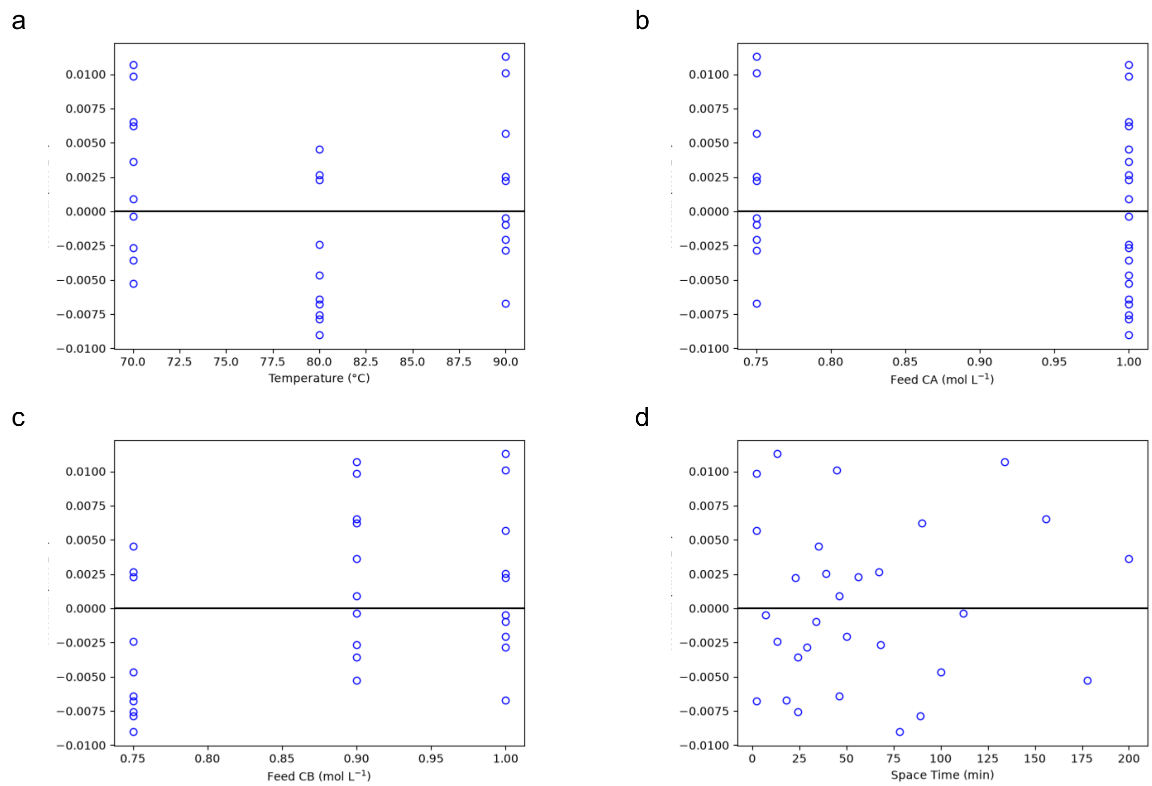

Figure 6. Linear model residuals plots for a) feed temperature, b) inlet concentration of A, c) inlet concentration of B, and d) space time.

The fitting function and linear model parameter estimates are equal to within their uncertainties. Both yielded an accurate model that captures the effects of the adjusted experimental inputs.

Accuracy Assessment

When the pre-exponential factor equals 4.16 x 10^{13} L mol^{-1} min^{-1} and the activation energy equals 24.4 kcal mol^{-1}, the rate expression proposed in equation (2) is very accurate.