REB, The Course
Class 26 Practice Assignment Solution

An isothermal, isobaric, steady-state PFR was used to generate kinetics data for reaction (1). The reactor diameter was 2.5 cm and its length was 1 m. All experiments were performed at atmospheric pressure. The inlet volumetric flow rates of the reagents and the temperature were varied from experiment to experiment, and the ratio of the outlet molar rate of Y to that of A was measured. The equilibrium constant for reaction (1) exhibits Arrhenius temperature dependence with a pre-exponential factor of 2.2 x 10^{23} atm^3 and a heat of reaction of 200 kJ mol^{-1}. Use the experimental data to estimate the pre-exponential factor and activation energy for k in the proposed rate expression, equation (2). Then decide whether the resulting rate expression is sufficiently accurate.

$$A \rightleftarrows Y + 3Z \tag{1}$$

$$r = kP_A\left(1 - \frac{P_Y P_Z^3}{K_1 P_A}\right) \tag{2}$$

The experimental data are provided in the file, practice_26_data.csv. The first few data points from that file are shown in Table 1.

Table 1. First 6 of the 81 Isothermal PFR data.

$\dot{V}_{A,in}$ (cm^3 s^{-1})	$\dot{V}_{Y,in}$ (cm^3 s^{-1})	$\dot{V}_{Z,in}$ (cm^3 s^{-1})	T (°C)	α (mol Y / mol A)
500	0	40000	350	0.063
500	0	50000	350	0.054
500	0	60000	350	0.033
500	250	40000	350	0.648
500	250	50000	350	0.653
500	250	60000	350	0.561

Assignment Summary

A concise summary of the information provided in the assignment narrative follows. The deliverables list includes coefficient of determination, etc. that were not specifically requested in the assignment narrative, but that are needed for assessing the accuracy of the reactor model.

Reaction

$$A \rightleftarrows Y + 3Z \tag{1}$$

Rate Expression

$$r = kP_A\left(1 - \frac{P_Y P_Z^3}{K_1 P_A}\right) \tag{2}$$

Reactor: Steady-state, isothermal, isobaric PFR

Given Constants: D = 2.5 cm, L = 1 m, P = 1 atm, K_0 = 2.2 x 10^{23} atm^{3} and ΔH = 200 kJ mol^{-1}

Given Adjusted Experimental Inputs: $\underline{\dot{V}}_{A,in}$, $\underline{\dot{V}}_{Y,in}$, $\underline{\dot{V}}_{Z,in}$, and $\underline{T}$

Given Experimental Responses: $\underline{\alpha}$

Parameters to Estimate: k_0 and E

Deliverable: Parameter estimates and their confidence intervals, coefficient of determination, parity and 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. The PFR derivatives function described here also must be written.

<u>PFR Model Equations</u>:

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

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

$$\frac{\dot{n}_Z}{dz} = \frac{3\pi D^2}{4} r \tag{5}$$

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

<u>Additional Computable Unknowns</u>: r, k, K, P_A, P_Y, and P_Z

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \tag{6}$$

$$K = K_0 \exp\left(\frac{-\Delta H}{RT}\right) \tag{7}$$

$$P_i = \frac{\dot{n}_i P}{\dot{n}_A + \dot{n}_Y + \dot{n}_Z} \qquad i = A, Y, \text{ and } Z \tag{8}$$

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

IVODE Solver Inputs:

1. Initial values of the reactor model variables

$$z_{initial} = 0 \tag{9}$$

$$\dot{n}_{i,initial} = \frac{P\dot{V}_{i,in}}{RT} \qquad i = A, Y, \text{ and } Z \tag{10}$$

2. Stopping criterion

$$z_f = L \tag{11}$$

3. Derivatives function that
   a. receives the PFR model variables at the start of an integration step
   b. has access to k_0, E, and T as global variables
   c. calculates the additional unknowns using equations (2) and (6) - (8)
   d. evaluates and returns the design equation derivatives using equations (3) - (5)

Deliverables Function

The purpose of the deliverables function is to use the PFR model function above to estimate 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.

Deliverables Function

1. Define guesses for [parameters]

$$\beta_{guess} = 0.0 \tag{12}$$

$$E_{guess} = 40 \text{ kJ mol}^{-1} \tag{13}$$

2. Call a numerical fitting function.

a. Arguments

i. The experimental data: $\underline{\dot{V}}_{A,in}$, $\underline{\dot{V}}_{Y,in}$, $\underline{\dot{V}}_{Z,in}$, $\underline{T}$, and $\underline{\alpha}$

ii. The Initial guesses for the parameters from step 1

iii. A predicted responses function as described below

b. Returned values

i. estimates and confidence intervals for k_0 and E

ii. the coefficient of determination, R^2

iii. the predicted responses: $\underline{\alpha}_{pred}$

3. Calculate k_0 and its confidence interval

$$k_0 = 10^{\beta} \tag{14}$$

$$k_{0,CI} = 10^{\beta_{CI}} \tag{15}$$

4. Calculate the experiment residuals

$$\underline{\epsilon}_{expt} = \underline{\alpha} - \underline{\alpha}_{pred} \tag{16}$$

5. Generate

a. a parity plot showing $\underline{\alpha}_{pred}$ *vs.* $\underline{\alpha}$

b. residuals plots showing $\underline{\epsilon}_{expt}$ *vs.* $\underline{\dot{V}}_{A,in}$, $\underline{\dot{V}}_{Y,in}$, $\underline{\dot{V}}_{Z,in}$, and $\underline{T}$

<u>Predicted Responses Function</u>

1. receives the adjusted experimental inputs and guesses for the parameters
2. calculates the pre-exponential factor using equation (14)
3. loops through all of the experiments

a. calls the PFR model function

b. calculates the model-predicted response

$$\alpha_{pred} = \left.\frac{\underline{\dot{n}}_Y}{\underline{\dot{n}}_A}\right|_{z=L} \tag{17}$$

4. returns the predicted responses for all of the experiments

Implementation of the Calculations

The Python script, practice_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 initially, but after adjusting it to use relative errors instead of absolute ones, it did converge. The results are shown in Table 2. The corresponding parity and residuals plots are shown in Figures 1 and 2.

The model accurately describes the experimental results as indicated by the coefficients of determination being close to 1.0, the uncertainty in the estimated parameters being relatively small compared to their values, the data falling close to the parity plot, and the absence of apparent trends in the residuals plots.

Table 2. Parameter Estimation Results

Parameter	Value	95% CI
k_0 (L mol^{-1} min^{-1})	2.86×10^{20}	[1.50×10^{20}, 5.42×10^{20}]
E (kcal mol^{-1})	292.0	[289.0, 296.0]
R^2	1.0	

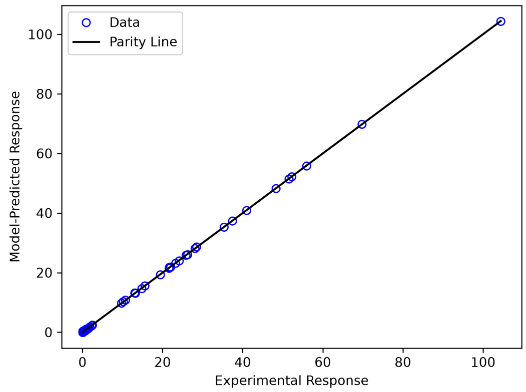

Figure 1. Parity Plot.

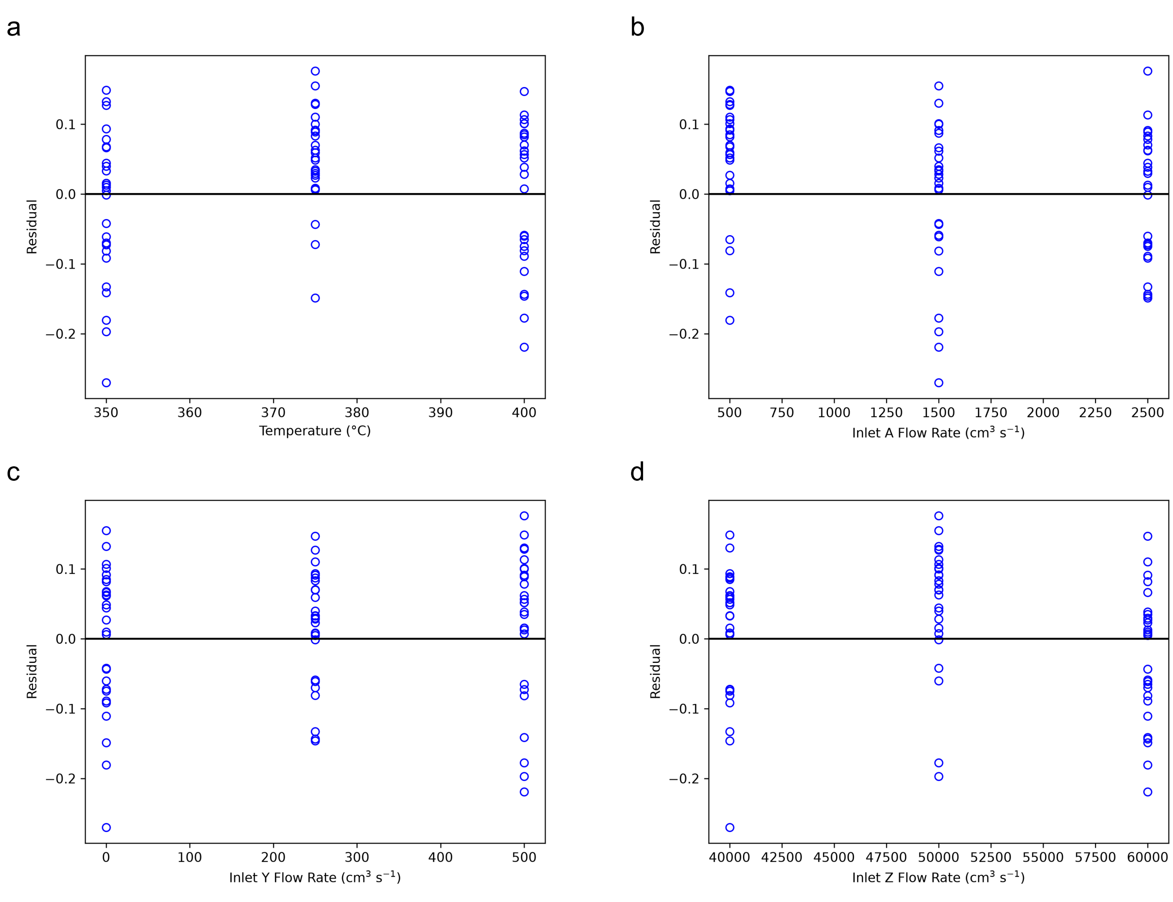

Figure 2. Residuals Plots for a) temperature, b) A feed rate, c) Y feed rate, and d) Z feed rate.

Accuracy Assessment

When used with the parameters shown in Table 2, the reactor model is accurate, which indicates that the proposed rate expression accurately describes the reaction rate.