REB, The Course
Class 28 Learning Activity Solution

Kinetics data for reaction (1) were generated in a steady-state, isothermal PFR operating at 1 atm pressure. Only one temperature was studied. The same amount of catalyst, 3.0 g, was present in the reactor, forming a small packed bed. The apparent density of the catalyst bed was constant, and pressure drop across the catalyst bed was negligible. The inlet volumetric flow rate was also the same in all experiments and equal to 0.85 L_{STP} min^{-1} at standard temperature and pressure. The inlet mole fractions of A, B, Y, and Z were varied in the experiments and the partial pressure of A at the reactor outlet was recorded. Use the resulting data to assess the accuracy of the mechanistic rate expression shown in equation (2). The equilibrium constant, K, in equation (2) can be calculated from available thermodynamic data. At the temperature of the experiments, 400 °C, the value of K is 12.2.

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

$$r = \frac{kP_AP_B}{1 + K_AP_A + K_BP_B + K_YP_Y + K_ZP_Z}\left(1 - \frac{P_YP_Z}{K_1P_AP_B}\right) \tag{2}$$

The experimental data are provided in the file, activity_28_data.csv. The first few data points from that file are shown in Table 1.

Table 1. First 6 of the 45 Isothermal, Steady-State PFR Experiments.

y_A	y_B	y_Y	y_Z	$P_{A,out}$ [1]
0.3	0.231	0.155	0.314	0.256
0.3	0.231	0.234	0.234	0.267
0.3	0.231	0.31	0.159	0.265
0.3	0.35	0.115	0.234	0.242
0.3	0.35	0.175	0.175	0.245
0.3	0.35	0.231	0.119	0.249

[1] atm.

Assignment Summary

A concise summary of the information provided in the assignment narrative is given below. The deliverables list includes items that were not specifically requested in the assignment narrative, but that are needed for assessing the accuracy of the reactor model.

<u>Reaction</u>

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

<u>Rate Expression</u>

$$r = \frac{kP_AP_B}{1 + K_AP_A + K_BP_B + K_YP_Y + K_ZP_Z}\left(1 - \frac{P_YP_Z}{K_1P_AP_B}\right) \tag{2}$$

<u>Reactor</u>: Steady-state, isothermal, isobaric PFR

<u>Given Constants</u>: P = 1 atm, m_{cat} = 3.0 g, $\dot{V}_{in}$ = 0.85 L$_{\text{STP}}$ min^{-1}, T = 400 °C, K = 12.2

<u>Given Adjusted Experimental Inputs</u>: $\underline{y}_{A,in}$, $\underline{y}_{B,in}$, $\underline{y}_{Y,in}$, and $\underline{y}_{Z,in}$

Given Experimental Responses: $\underline{P}_{A,out}$

Parameters to Estimate: k, K_A, K_B, K_Y, and K_Z

Deliverables: Parameter estimates and uncertainties, 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.

PFR Model Equations:

$$\frac{d\dot{n}_A}{dm} = -r \tag{3}$$

$$\frac{d\dot{n}_B}{dm} = -r \tag{4}$$

$$\frac{d\dot{n}_Y}{dm} = r \tag{5}$$

$$\frac{d\dot{n}_Z}{dm} = r \tag{6}$$

PFR Model Variables: $\underline{m}$, $\underline{\dot{n}}_A$, $\underline{\dot{n}}_B$, $\underline{\dot{n}}_Y$, and $\underline{\dot{n}}_Z$

Additional Computable Unknowns: r, P_A, P_B, P_Y, and P_Z

$$P_i = \frac{\dot{n}_i}{\dot{n}_A + \dot{n}_B + \dot{n}_Y + \dot{n}_Z} P \quad i = A, B, Y, \text{ and } Z \tag{7}$$

<u>Additional Uncomputable Unknowns</u>: k, K_A, K_B, K_Y, and K_Z

<u>IVODE Solver Inputs</u>:

1. Initial values of the reactor model variables

$$m_{initial} = 0 \tag{8}$$

$$\dot{n}_{total,in} = \frac{\dot{V}}{\hat{V}} \tag{9}$$

$$\dot{n}_{A,in} = y_{A,in}\dot{n}_{total,in} \tag{10}$$

$$\dot{n}_{B,in} = y_{B,in}\dot{n}_{total,in} \tag{11}$$

$$\dot{n}_{Y,in} = y_{Y,in}\dot{n}_{total,in} \tag{12}$$

$$\dot{n}_{Z,in} = y_{Z,in}\dot{n}_{total,in} \tag{13}$$

2. Stopping criterion

$$m_{final} = m_{cat} \tag{14}$$

3. Derivatives function that
   a. receives the PFR model variables at the start of in integration step
   b. has access to k, K_A, K_B, K_Y, and K_Z as global variables
   c. calculates the additional unknowns using equations (2) and (7)
   d. evaluates and returns the PFR design equation derivatives using equations (3) through (6)

Deliverables Function

The purpose of the deliverables function is to use the PFR model function above to estimate the parameters 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 logs of k, K_A, K_B, K_Y, and K_Z are estimated instead of the pre-exponential factors, themselves. The predicted responses function described here also must be written.

<u>Deliverables Function</u>

1. Define guesses for [parameters]

$$\beta_{i,guess} = 0 \quad i = k, A, B, Y, \text{ and } Z \tag{15}$$

2. Call a numerical fitting function.
   a. Arguments
      i. The experimental data: $\underline{y}_{A,in}$, $\underline{y}_{B,in}$, $\underline{y}_{Y,in}$, $\underline{y}_{Z,in}$, and $\underline{P}_{A,out}$
      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 the parameters
      ii. the coefficient of determination, R^2
      iii. the predicted responses: $\underline{P}_{A,out,pred}$
3. Calculate the pre-exponential factors and their confidence intervals

$$k = 10^{\beta_k} \tag{16}$$

$$K_i = 10^{\beta_i} \quad i = A, B, Y, \text{ and } Z \tag{17}$$

$$k_{CI} = 10^{\beta_{k,CI}} \tag{18}$$

$$K_{i,CI} = 10^{\beta_{i,CI}} \quad i = A, B, Y, \text{ and } Z \tag{19}$$

4. Calculate the experiment residuals

$$\underline{\epsilon}_{expt} = \underline{P}_{A,out} - \underline{P}_{A,out,pred} \tag{20}$$

5. Generate

a. a parity plot showing $\underline{P}_{A,out,pred}$ vs. $\underline{P}_{A,out}$

b. residuals plots showing $\underline{\epsilon}_{expt}$ vs. $\underline{y}_{A,in}$, $\underline{y}_{B,in}$, $\underline{y}_{Y,in}$, and $\underline{y}_{Z,in}$

<u>Predicted Responses Function</u>

1. receives the adjusted experimental inputs and guesses for the parameters
2. calculates the rate expression parameters using equations (16) and (17)
3. loops through all of the experiments
    a. calls the PFR model function
    b. calculates the model-predicted response

$$P_{A,out,pred} = \left. \frac{\underline{\dot{n}}_A P}{\underline{\dot{n}}_A + \underline{\dot{n}}_B + \underline{\dot{n}}_Y + \underline{\dot{n}}_Z} \right|_{\underline{m}=m_{cat}} \tag{21}$$

4. returns the predicted responses for all of the experiments

Implementation of the Calculations

The Python script, activity_28.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

Using the parameter guesses in equations (16) and (17), the fitting function converged to a solution that significantly under-predicted the outlet partial pressure of A. After changing the parameter guesses to decrease the reaction rate, the fitting function converged to the solution shown in Table 2a. Since the uncertainties were so large, the parameter guess was changed again, yielding the solution shown in Table 2b.

Table 2. Parameter Estimation Results from Two Different Initial Guesses

a

Parameter	Value	95% CI
k*	2.06×10^5	[0.0, ∞]
K_A**	0.015	[0.0, ∞]
K_B**	5.70×10^7	[0.0, ∞]
K_Y**	3.80×10^7	[0.0, ∞]
K_Z**	0.15	[0.0, ∞]
R^2	0.997	

* mol g^{-1} min^{-1} atm^{-2}

** atm^{-1}

b

Parameter	Value	95% CI
k*	7.91×10^5	[0.0, ∞]
K_A**	0.0053	[0.0, ∞]
K_B**	2.20×10^8	[0.0, ∞]
K_Y**	1.50×10^8	[0.0, ∞]
K_Z**	0.09	[0.0, ∞]
R^2	0.997	

* mol g^{-1} min^{-1} atm^{-2}

** atm^{-1}

While the coefficients of determination are both close to 1.0, the uncertainties are unacceptable. The two models are of comparable accuracy even though the individual parameter values are different. This could indicate that additional data are needed in order to resolve the individual parameters or that some of the parameter values are coupled.

If some of the parameter estimates are coupled, a rate expression with fewer parameters might describe the results equally well. Here it appears that the only significant terms in the denominator are those involving the partial pressures of B and Y because the estimated values of K_B and K_Y are much greater than K_A, K_Z or 1.0. To see whether this is true, the rate expression shown in equation (22) was used in place of equation (2). The results are shown in Table 3.

$$r = \frac{k' P_A P_B}{K'_B P_B + P_Y}\left(1 - \frac{P_Y P_Z}{K_1 P_A P_B}\right) \qquad (22)$$

Table 3. Parameter Estimates for the Rate Expression Shown in Equation (22).

Parameter	Value	95% CI
k*	0.0054	[0.00426, 0.00683]
K_B**	1.5	[1.1, 2.1]
R^2	0.997	

* mol g^{-1} min^{-1} atm^{-2}

** atm^{-1}

The coefficient of determination for the simplified rate expression is equal to those for the full rate expression. Here, however, the confidence intervals are acceptable. The corresponding parity plot is shown in Figure 1, and the residuals plots in Figure 2. The data all lie close to the parity line, and there aren't any obvious trends in the deviations in the residuals plots.

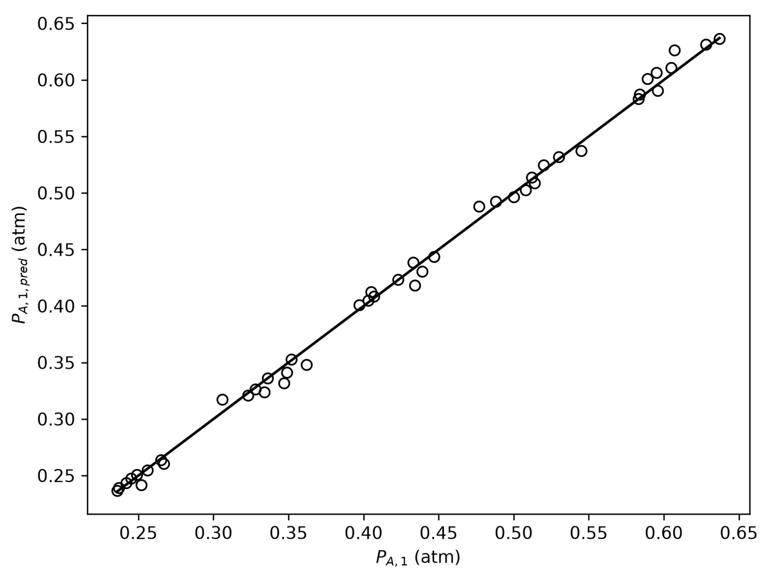

Figure 1. Parity plot for simplified rate expression, equation (22).

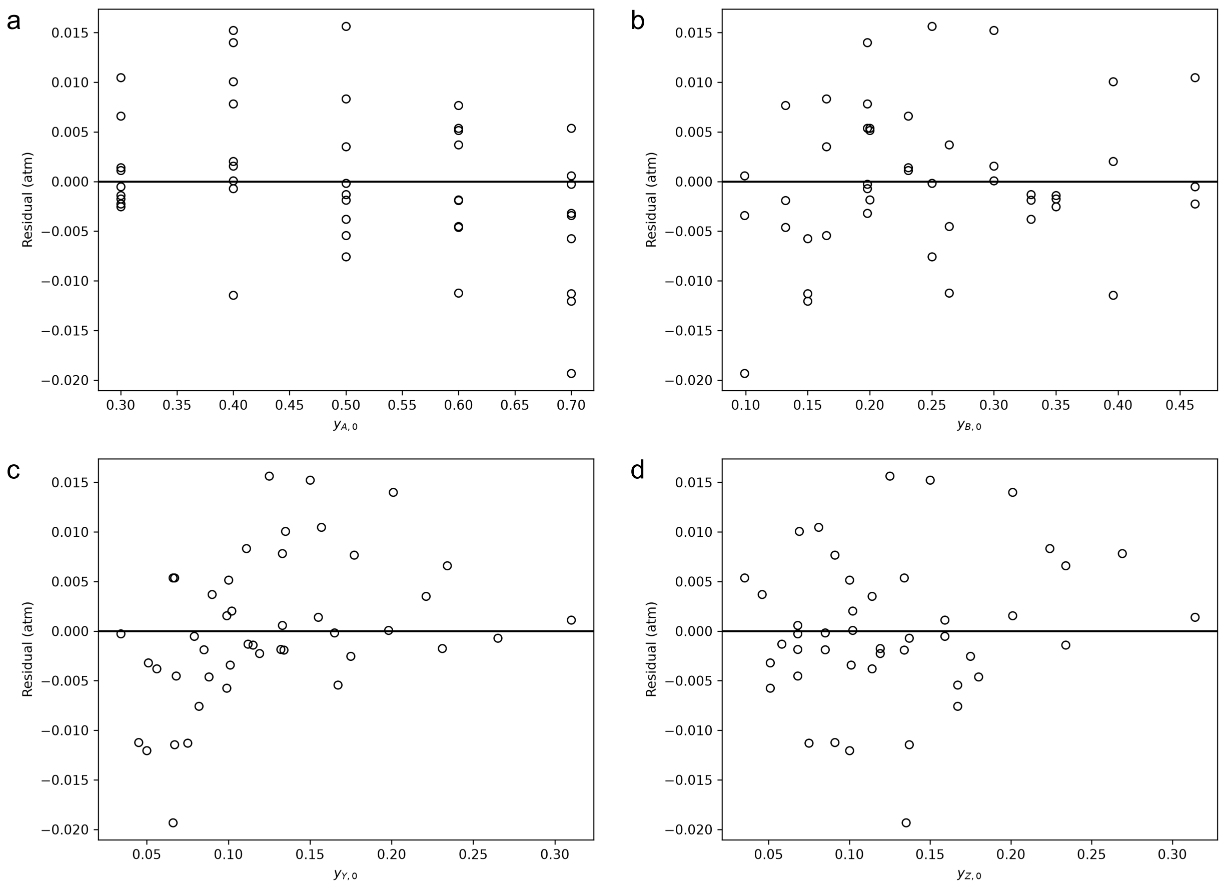

Figure 2. Residuals plots for simplified rate expression, equation (22), for the inlet mole fractions of a) A, b) B, c) Y, and d) Z.

Given the comparable accuracy, the rate expression in equation (22) is preferred. However, the data set is relatively small and only one temperature was studied. Generating data at several temperatures might reveal situations where the other parameters are significant and needed.

Accuracy Assessment

The available data can be accurately described using the rate expression shown in equation (22). It is recommended that additional data at multiple temperatures be generated and used to re-evaluate the rate expression.