REB, The Book
Example 11.5.5 Solution

Reversible, gas-phase reaction (1) was studied in a PFR at 1 atm. In all experiments 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 total inlet molar flow rate was also the same in all experiments and equal to 2.5 mol h^{-1}. The inlet mole fractions of A, B, Y, and Z and the temperature were varied in the experiments and the partial pressure of A, in atm, at the reactor outlet was recorded.

Preliminary experiments showed that the rate does not depend upon the partial pressure of reagent Z, and the reaction is inhibited by reagent Y. The power-law rate expression shown in equation (2) has been proposed to model the rate. The equilibrium constant, K, in equation (2) can be calculated using equation (3) where K_0 equals 0.0132 and ΔH equals –9096 cal mol^{-1}.

Use the resulting data to assess the accuracy of the proposed rate expression.

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

$$r = k\, P_A^{\alpha_A} P_B^{\alpha_B} P_Y^{\alpha_Y} \left(1 - \frac{P_Y P_Z}{K P_A P_B}\right) \tag{2}$$

$$K = K_0 \exp\left(\frac{-\Delta H}{RT}\right) \tag{3}$$

The experimental data are provided in the file, example_11_5_5_data.csv. The first few data points from that file are shown in Table 1.

Table 1. First 6 of the 45 experimental data points

$y_{A,in}$	$y_{B,in}$	$y_{Y,in}$	$y_{Z,in}$	T (°C)	$P_{A,out}$ (atm)
0.3	0.231	0.155	0.314	350	0.256
0.3	0.231	0.234	0.234	350	0.267
0.3	0.231	0.31	0.159	350	0.265
0.3	0.35	0.115	0.234	350	0.242
0.3	0.35	0.175	0.175	350	0.245
0.3	0.35	0.231	0.119	350	0.249

Assignment Summary

Reaction

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

Rate Expression

$$r = k\, P_A^{\alpha_A}\, P_B^{\alpha_B}\, P_Y^{\alpha_Y} \left(1 - \frac{P_Y P_Z}{K P_A P_B}\right) \tag{2}$$

Reactor: Steady-state, isothermal, isobaric PFR

Given Constants: P = 1 atm, m_{cat} = 3 g, $\dot{n}_{total,in}$ = 2.5 mol h^{-1}, K_0 = 12 0.0132, and ΔH = –9096 cal mol^{-1}.

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

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

Parameters to Estimate: k_0, E, α_A, α_B, and α_Y

Deliverable: Assessment of the accuracy of the rate expression, equation (2).

Formulation of the Equations

PFR Model Equations:

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

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

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

$$\frac{d\dot{n}_Z}{dm} = r \tag{7}$$

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

Additional Computable Unknowns: r, k, k_0, P_A, P_B, P_Y, P_Z, and K

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

$$k_0 = 10^{\beta} \tag{9}$$

$$P_i = \frac{\dot{n}_i}{\dot{n}_A + \dot{n}_B + \dot{n}_Y + \dot{n}_Z} P \quad i = A, B, Y, \text{ and } Z \tag{10}$$

Additional Uncomputable Unknowns: β, E, α_A, α_B, and α_Y

IVODE Solver Inputs:

1. Initial values of the reactor model variables shown in Table 2.
2. Stopping criterion that m equals the final value shown in Table 2.
3. Derivatives function that

a. receives the PFR model variables, $\dot{n}_A$, $\dot{n}_B$, $\dot{n}_Y$, $\dot{n}_Z$, and m at the start of an integration step
b. has access to the parameters, k_0, E, α_A, α_B, and α_Y
c. calculates the additional unknowns using equations (2), (3), and (8) - (10)
d. evaluates and returns the PFR model derivatives using equations (4) - (7)

Table 2. Initial and final values of the design equation variables.

Variable	Initial Value	Final Value
m	0	m_{cat}
$\dot{n}_A$	$\dot{n}_{A,in} = y_{A,in}\dot{n}_{total,in}$	
$\dot{n}_B$	$\dot{n}_{B,in} = y_{B,in}\dot{n}_{total,in}$	
$\dot{n}_Y$	$\dot{n}_{Y,in} = y_{Y,in}\dot{n}_{total,in}$	
$\dot{n}_Z$	$\dot{n}_{Z,in} = y_{Z,in}\dot{n}_{total,in}$	

<u>Fitting Function Inputs</u>:

1. Experimental data: $\underline{y}_{A,in}$, $\underline{y}_{B,in}$, $\underline{y}_{Y,in}$, $\underline{y}_{Z,in}$, and $\underline{P}_{A,out}$
2. Initial guesses for the parameters being estimated

$$\beta_{guess} = 0 \tag{11}$$

$$E_{guess} = 10{,}000 \text{ cal mol}^{-1} \tag{12}$$

$$\alpha_{i,guess} = 1.0 \qquad i = A \text{ and } B \tag{13}$$

$$\alpha_{Y,guess} = -1.0 \tag{14}$$

3. Predicted Responses Function that
   a. receives the adjusted experimental inputs and guesses for the parameters
   b. calculates the pre-exponential factor, equation (9), and makes all of the rate expression parameters available to the derivatives function

c. loops through all of the experiments

   i. solves the PFR model equations

   ii. calculates the model-predicted response

$$P_{A,out,pred} = \left(\frac{\underline{\dot{n}}_A}{\underline{\dot{n}}_A + \underline{\dot{n}}_B + \underline{\dot{n}}_Y + \underline{\dot{n}}_Z}\right)\Bigg|_{m=m_{cat}} P \tag{15}$$

d. returns the predicted responses for all of the experiments

Parameter Estimate Equation:

$$k_{0,CI} = 10^{\beta_{CI}} \tag{16}$$

Implementation of the Calculations

The Python script, example_11_5_5.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 and predicted responses function sas described above.
5. Define an initial parameter guess and fit the PFR model to the data using a fitting function.
6. Calculate the experiment residuals.
7. Tabulate, graph, and save the results, as appropriate.

The fitting function converged using the initial parameter guesses given above, so it was not necessary to modify them.

Results and Discussion

Table 2 presents the parameter estimation results. The range of the 95% confidence interval for each of the estimates is closely centered on the estimated values and the coefficient of determination is nearly equal to 1.0. These facts indicate that the fitted model is quite accurate.

Table 2. Parameter Estimation Results

Parameter	**Value**	**95% CI**	**Units**
k_0	3.06 x 10^5	[1.07 x 10^5, 8.79 x 10^5]	mol g^{-1} min^{-1} $atm^{-0.56}$
E	27237	[25895, 28580]	cal mol^{-1}
α_A	0.91	[0.72, 1.1]	
α_B	0.21	[0.12, 0.31]	
α_Y	-0.56	[-0.68, -0.44]	
R^2	0.998		

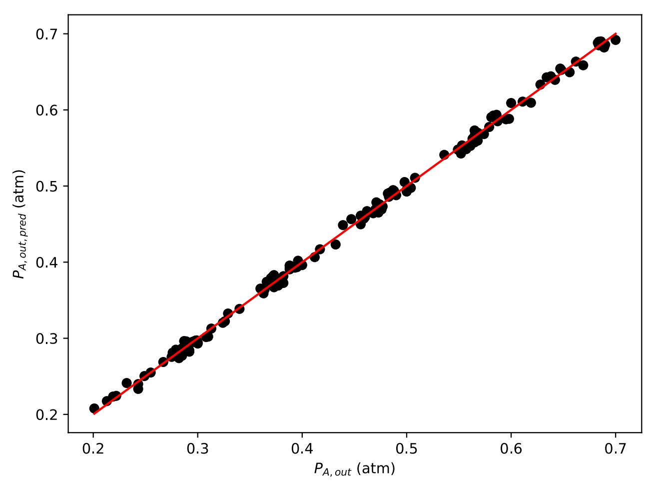

Figure 1. The experimental data lie very close to the parity line indicating an accurate model.

The accuracy of the fitted model is additionally verified by the parity plot shown in Figure 1. The data all lie close to the parity line. Additionally, the deviations in the residuals plots shown in Figure 2 do not show any trends. This indicates that within the range of each adjusted input, the model captured the effects of varying it.

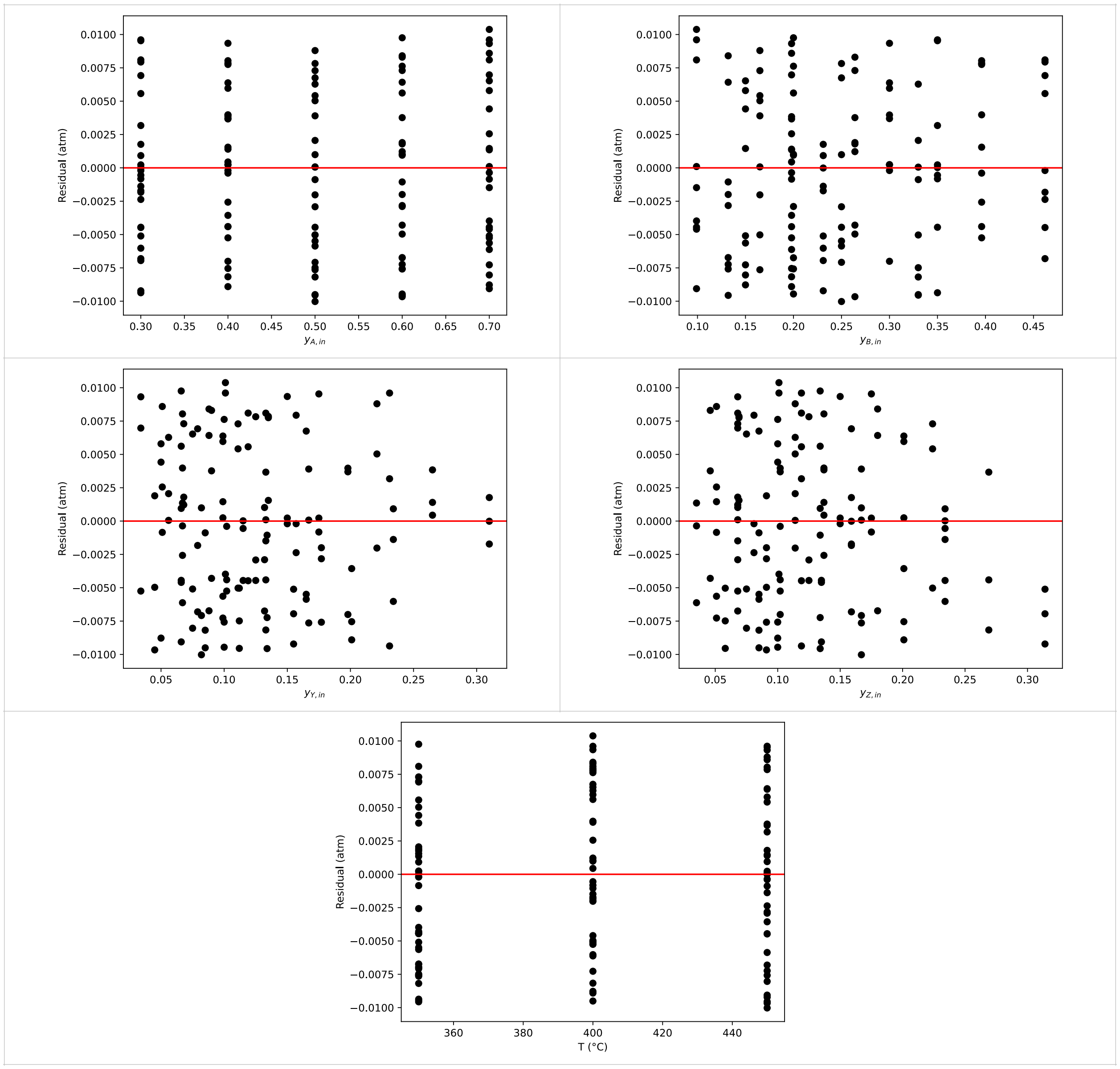

Figure 2. The residuals plots do not suggest any trends as the adjusted inputs were varied.

Deliverables

The proposed rate expression is acceptably accurate when the parameters have the values shown in Table 2.