REB, The Book
Example 11.5.2 Solution

The liquid-phase reaction between reactants A and B, reaction (1), was studied in a 100 cm^3 laboratory CSTR. The reactor operated at steady state, the volumetric flow rate and the inlet concentrations of each of the reagents were adjusted from one experiment to the next, and the steady-state outlet concentration of reagent Y was measured. Use the experimental data to assess the accuracy with which the rate expression shown in equation (2) describes the rate of reaction (1). The rate coefficient in equation (2) can be assumed to exhibit Arrhenius temperature dependence.

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

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

The first few data points are shown in Table 1. The full data set is available in the file, example_11_5_2_data.csv.

Table 1. First 6 of the 2048 experiments

T (K)	$\dot{V}$ (cm^3 min^{-1})	$C_{A,in}$ (M)	$C_{B,in}$ (M)	$C_{Y,in}$ (M)	$C_{Z,in}$ (M)	$C_{Y,out}$ (M)
300	50	0.5	0.5	0.5	0.5	0.86
300	50	0.5	0.5	0.5	1	0.82
300	50	0.5	0.5	0.5	2.5	0.69
300	50	0.5	0.5	0.5	5	0.61
300	50	0.5	0.5	1	0.5	1.38
300	50	0.5	0.5	1	1	1.33

Assignment Summary

Reaction

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

Rate Expression

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

Reactor: Steady-state, isothermal CSTR

Adjusted Experimental Inputs: T, $\dot{V}$, $C_{A,in}$, $C_{B,in}$, $C_{Y,in}$, and $C_{Z,in}$

Experimental Response: $C_{Y,out}$

Given Constant: V = 100 cm^3

Given Experimental Data: $\underline{T}$, $\underline{\dot{V}}$, $\underline{C}_{A,in}$, $\underline{C}_{B,in}$, $\underline{C}_{Y,in}$, $\underline{C}_{Z,in}$, and $\underline{C}_{Y,out}$

Parameters to Estimate: k_0, and E

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

Formulation of the Equations

CSTR Model Equations:

$$0 = \dot{n}_{A,in} - \dot{n}_{A,out} - rV = \epsilon_1 \tag{3}$$

$$0 = \dot{n}_{B,in} - \dot{n}_{B,out} - rV = \epsilon_2 \tag{4}$$

$$0 = \dot{n}_{Y,in} - \dot{n}_{Y,out} + rV = \epsilon_3 \tag{5}$$

$$0 = \dot{n}_{Z,in} - \dot{n}_{Z,out} + rV = \epsilon_4 \tag{6}$$

CSTR Model Variables: $\dot{n}_{A,out}$, $\dot{n}_{B,out}$, $\dot{n}_{Y,out}$, and $\dot{n}_{Z,out}$

Additional Computable Unknowns: $\dot{n}_{A,in}$, $\dot{n}_{B,in}$, $\dot{n}_{Y,in}$, $\dot{n}_{Z,in}$, r, k, C_A, and C_B

$$\dot{n}_{i,in} = C_{i,in}\dot{V} \qquad i = A, B, Y, \text{ and } Z \tag{7}$$

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

$$C_i = \frac{\dot{n}_{i,out}}{\dot{V}} \qquad i = A \text{ and } B \tag{9}$$

Additional Uncomputable Unknowns: k_0 and E

ATE Solver Inputs:

1. Initial guesses for the CSTR model variables

$$\dot{n}_{i,out,guess} = \dot{n}_{i,in} = C_{i,in}\dot{V} \qquad i = A, B, Y, \text{ and } Z \tag{10}$$

2. Residuals function that
   a. receives a guess for the CSTR model variables
   b. has access to k_0 and E
   c. calculates the additional unknowns using equations (2), (7) - (9)
   d. evaluates and returns the CSTR model residuals using equations (3) through (6)

Fitting Function Inputs:

1. Experimental data: $\underline{T}$, $\underline{\dot{V}}$, $\underline{C}_{A,in}$, $\underline{C}_{B,in}$, $\underline{C}_{Y,in}$, $\underline{C}_{Z,in}$, and $\underline{C}_{Y,out}$
2. Initial guess for the parameters being estimated

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

$$E_{guess} = 10 \text{ kcal mol}^{-1} \tag{12}$$

3. Predicted Responses Function that
   a. receives the adjusted experimental inputs and guesses for the parameters

b. calculates the pre-exponential factor and makes it and the activation energy available to the residuals function

$$k_0 = 10^{\beta} \tag{13}$$

c. loops through all of the experiments
   i. defines an initial guess for the CSTR model variables, equation (10)
   ii. solves the CSTR design equations
   iii. calculates the model-predicted response

$$C_{Y,out,pred} = \frac{\dot{n}_{A,out}}{\dot{V}} \tag{14}$$

d. returns the predicted responses for all of the experiments

Parameter Estimate Equation:

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

Implementation of the Calculations

The Python script, example_11_5_2.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 residuals function as arguments.
4. Define the CSTR model, CSTR residuals, and predicted responses functions as described above.
5. Define an initial parameter guess and fit the BSTR model to the experimental data using a fitting function.
6. Tabulate, graph, and save the results, as appropriate.

Results and Discussion

The calculations were performed as described above. The ATE solver and the fitting function converged with the initial guesses defined above. Table 2 presents the parameter estimation results. The upper and lower limits of the 95% confidence interval for k_0 and E are reasonably close to their estimated values and the coefficient of determination is close to 1. These all indicate an accurate fit.

Table 2. Parameter Estimation Results

Quantity	Value	Units
k_0	8.72 x 10^6	L mol^{-1} min^{-1}
$k_{0,low}$	4.61 x 10^6	L mol^{-1} min^{-1}
$k_{0,high}$	1.65 x 10^7	L mol^{-1} min^{-1}
E	9.92	kcal mol^{-1}
E_{low}	9.52	kcal mol^{-1}
E_{high}	10.3	kcal mol^{-1}
R^2	0.993	

Figure 1 shows the parity plot. While there is some scatter, the data points are close to the red parity line, again indicating an accurate fit.

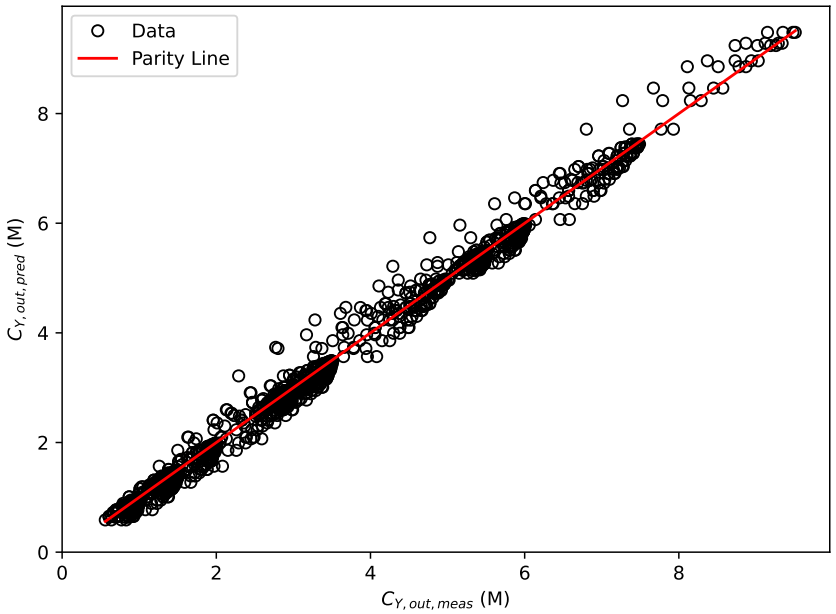
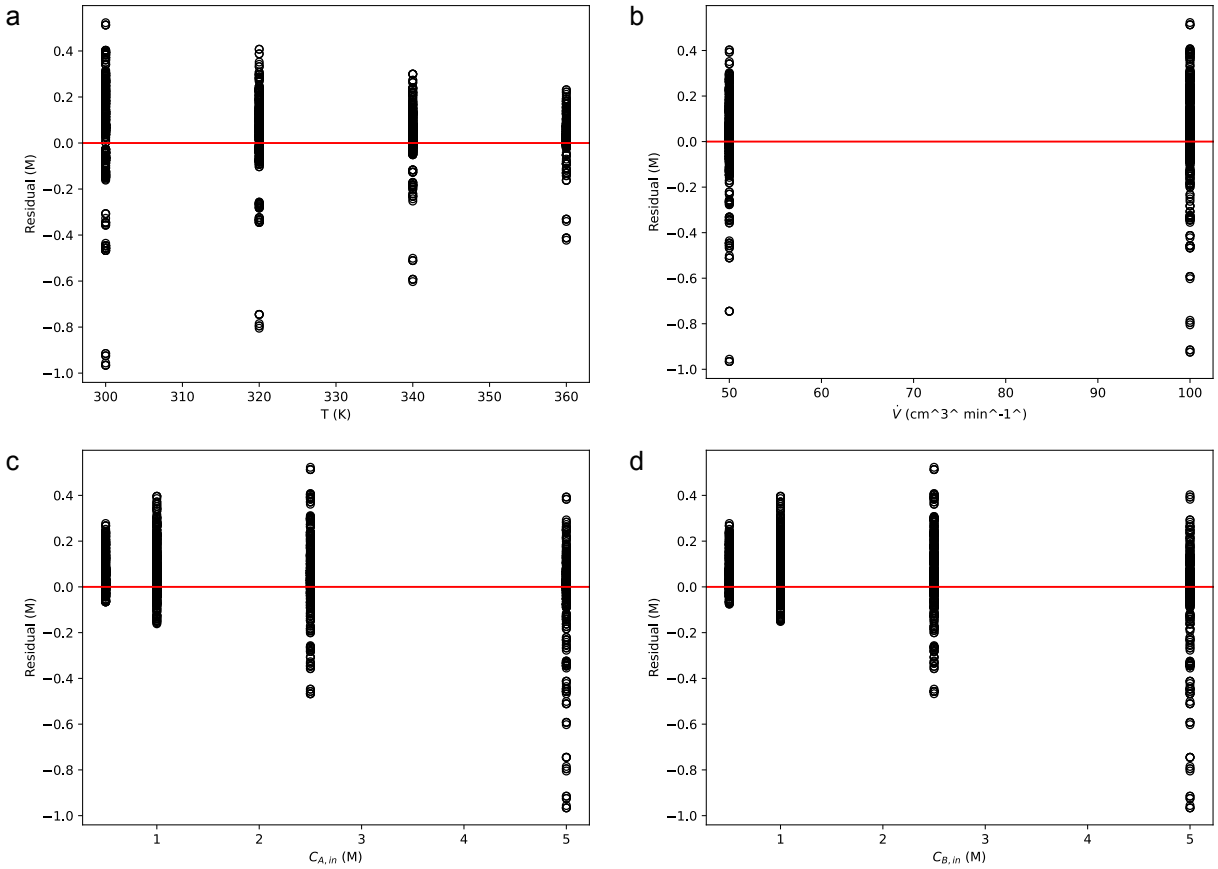


Figure 1. Parity plot.



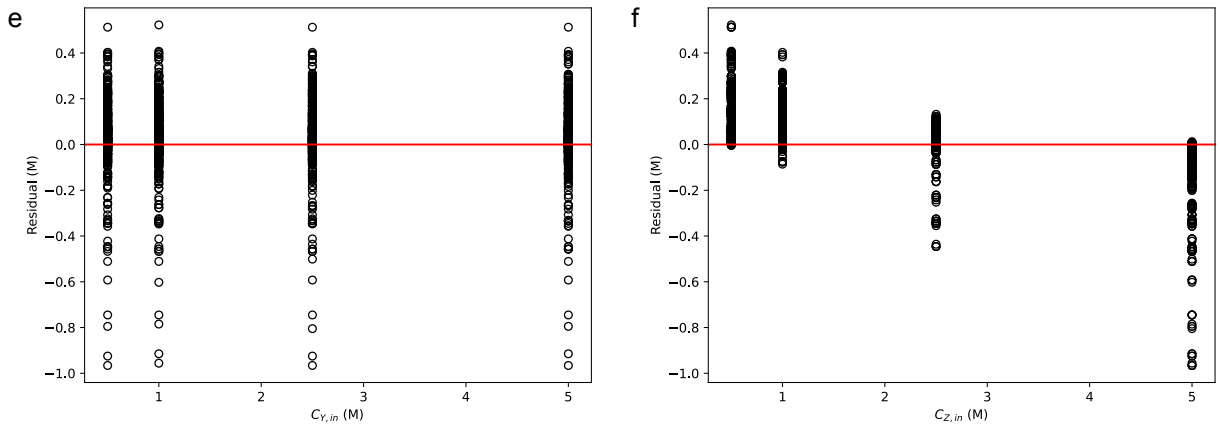


Figure 2. Residuals Plots for a) Temperature, b) Volumetric Flow Rate, and Feed Concentrations of c) Reagent A, d) Reagent B, e) Reagent Y, and f) Reagent Z.

Residuals plots are presented in Figure 2. The residuals plots for T, $\dot{V}$ and C_Y show random deviations of the residuals about zero, too. However, in the residuals plots for the concentrations of A and B the residuals at low concentration do not scatter equally about zero. The residuals for the concentration of Z show a definite trend, decreasing steadily as C_Z increases. This suggests that the reaction rate may have some functional dependence on the concentration of Z that is not captured in the rate expression.

Deliverables

With the estimated pre-exponential factor of 8.72 x 10^6 L mol^{-1} min^{-1} and the estimated activation energy, 9.92 kcal mol^{-1}, the rate expression is reasonably accurate, but there are indications that the it may not fully capture the dependence of the rate on the concentration of reagent Z. Rate expressions that include a functional dependence on the concentration of Z should be postulated and assessed to determine whether they can represent the experimental results more accurately.