REB, The Book
Example 11.5.6 Solution Using a Fitting Function

Kinetics data for liquid-phase reaction (1) were generated using an ideal, isothermal, 1 L BSTR. The reaction is irreversible, and preliminary analysis indicated that the rate is not affected by the concentration of the product, Z. The experimental design used the initial concentration of A and the temperature as factors. Twelve experiments were performed wherein the temperature and initial concentration of reagent A were set after which the concentration of reagent A was measured at six reaction times, giving a set of 72 experimental data points. The rate expression shown in equation (2) has been proposed for this reaction. The rate coefficient in equation (2) is expected to display Arrhenius temperature dependence. Compare the best values for the Arrhenius pre-exponential factor and activation energy determined using (a) a fitting function, (b) a linearized model, and (c) an approximate model. Then assess the accuracy of the proposed first order rate expression.

$$A \rightarrow Z \tag{1}$$

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

Note that these data were generated using the experimental design from Example 11.5.1. The experimental data are provided in the file, example_11_5_6_data.csv. The first few data points from that file are shown in Table 1.

Table 1. First 6 of 72 Isothermal BSTR Data

	Adjusted Inputs			Response
Experiment	T (°C)	$C_{A,0}$ (M)	t_{meas} (min)	$C_{A,f}$ (M)
1	65.0	0.5	5.0	0.48
1	65.0	0.5	10.0	0.4
1	65.0	0.5	15.0	0.45
1	65.0	0.5	20.0	0.42
1	65.0	0.5	25.0	0.3
1	65.0	0.5	30.0	0.4

Assignment Summary

The analysis using a fitting function will be presented here, there are separate solutions that use a linearized model and an approximate model. As in most parameter estimation assignments, the deliverables listed here include items that are needed for assessing the accuracy of the final model, but are not specifically requested in the assignment narrative.

Reaction

$$A \rightarrow Z \tag{1}$$

Rate Expression

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

Reactor: Isothermal BSTR

Given Constant: V = 1 L

Given Adjusted Experimental Inputs: $\underline{T}$, $\underline{C}_{A,0}$, and $\underline{t}_{meas}$

Given Experimental Responses: $\underline{C}_{A,meas}$

Parameters to Estimate: k_0 and E

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

BSTR Model Function

The purpose of the BSTR model function is to solve the BSTR reactor design equations for the reactor used in the experiments. This is done numerically by calling an IVODE solver. The additional uncomputable unknowns listed here will need to be passed to the BSTR model function as arguments, and it will need to make them available to the BSTR derivatives function as global variables. The BSTR derivatives function described here also must be written.

BSTR Model Equations:

$$\frac{dn_A}{dt} = -rV \tag{3}$$

$$\frac{dn_Z}{dt} = rV \tag{4}$$

BSTR Model Variables: t, n_A, and n_Z

Additional Computable Unknowns: r, k, and C_A

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \tag{5}$$

$$C_A = \frac{n_A}{V} \tag{6}$$

Additional Uncomputable Unknowns: T, k_0, and E

IVODE Solver Inputs:

1. Initial values of the reactor model variables.

$$t = 0 \tag{7}$$

$$n_{A,0} = C_{A,0}V \tag{8}$$

$$n_{Z,0} = 0 \tag{9}$$

2. Stopping criterion

$$t = t_{meas} \tag{10}$$

3. Derivatives function that
   a. receives the BSTR model variables at the start of an integration step as arguments
   b. has access to the current values of T, k_0, and E
   c. calculates the additional computable unknowns using equations (2) , (5), and (6)

d. evaluates and returns the BSTR design equation derivatives using equations (3) and (4).

Deliverables Function

The purpose of the deliverables function is to use the BSTR model function above to estimate the pre-exponential factor and activation energy for k, along with quantities that are needed for assessing the model's accuracy. 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 β and E.

$$\beta_{guess} = 0.0 \tag{11}$$

$$E_{guess} = 40.0 \text{ kJ mol}^{-1} \tag{12}$$

2. Call a numerical fitting function.
   a. Arguments
      i. The experimental data: $\underline{T}$, $\underline{C}_{A,0}$, $\underline{t}_{meas}$, and $\underline{C}_{A,meas}$
      ii. The Initial guesses for the parameters, equations (18) and (19)
      iii. A predicted responses function as described below
   b. Returned values
      i. estimates and confidence intervals for β and E
      ii. the coefficient of determination
      iii. the predicted responses: $\underline{C}_{A,pred}$
3. Calculate k_0 and its confidence interval

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

$$k_{0,CI} = 10^{\beta_{CI}} \tag{14}$$

4. Calculate the experiment residuals

$$\underline{\epsilon}_{expt} = \underline{C}_{A,meas} - \underline{C}_{A,pred} \tag{15}$$

5. Generate
   a. a parity plot showing $\underline{C}_{A,pred}$ *vs.* $\underline{C}_{A,meas}$
   b. 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 (13)
3. loops through all of the experiments
   a. calls the BSTR model function
   b. calculates the model-predicted response

$$C_{A,pred} = \frac{\underline{n}_A\Big|_{t=t_{meas}}}{V} \tag{16}$$

4. returns the predicted responses for all of the experiments, $\underline{C}_{A,pred}$

Implementation of the Calculations

The Python script, example_11_5_6_ff.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 BSTR model, BSTR derivatives, predicted responses, and deliverables functions as described above.
5. Call the deliverables function.

When the parameter guesses in equations (18) and (19) were used, the fitting function ran for a very long time. The guess for β was changed to β_{guess} = 4.0, after which the parameter estimation process converged very quickly.

Results and Discussion

The parameter estimation results are shown in Table 2. The parity plot is presented in Figure 1, and Figure 2 shows the residuals plots. The range of the uncertainty in the pre-exponential factor is more than 4 times its value, but all other criteria suggest that the model is accurate. The range of the uncertainty in the activation energy is 12% of its value, the coefficient of determination is close to 1.0, the deviation of the data from the parity line in Figure 1 is relatively small, and there are no apparent trends in the deviations with respect to any of the experimentally adjusted inputs.

Table 2. Arrhenius Parameters Obtained Using a Fitting Function

Parameter	Value	95% CI
k_0 (min^{-1})	1.40×10^9	[3.22×10^8, 6.11×10^9]
E ($kJ\ mol^{-1}$)	71.6	[67.3, 75.9]
R^2	0.985	

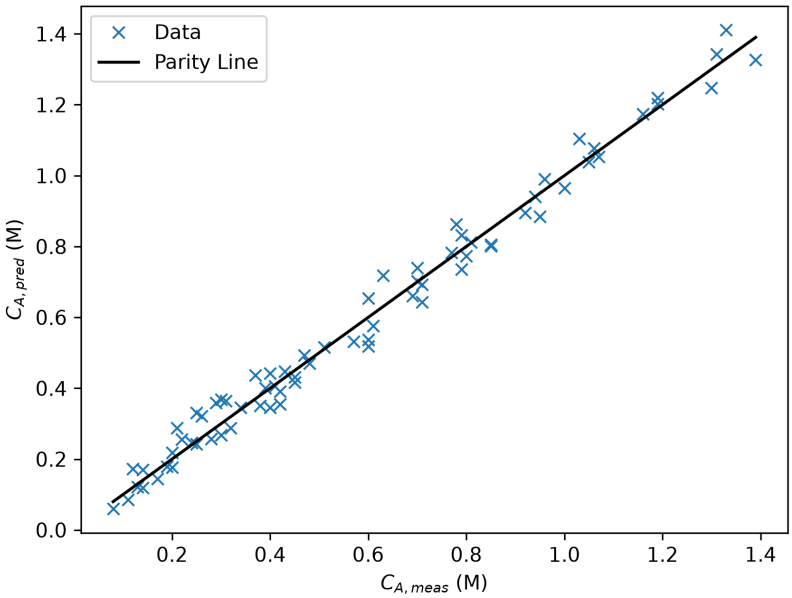

Figure 1. Parity Plot

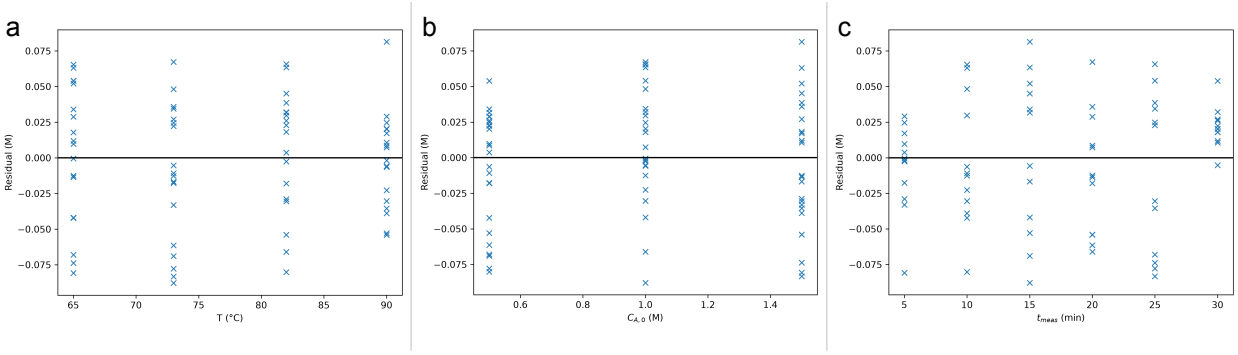

Figure 2. Residuals plots for a) temperature, b) initial concentration of A, and c) measurement time.

Accuracy of the Model

When used with the pre-exponential factor and activation energy shown in Table 2, the reactor model, and by extension, the proposed rate expression, is reasonably accurate.