REB, The Book
Example 11.5.6 Solution Using an Approximate Model

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 an approximate model will be presented here, there are separate solutions that use a fitting function and a linearized 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.

Approximate BSTR Model

The reason for approximating the derivative in the BSTR model function is to eliminate the need to solve the design equations analytically. The approximate BSTR model is an algebraic equations and allows parameter estimation using linear least squares. That approximate, algebraic model equation is rearranged and new variables are defined to convert it to a linear form. Generally, the data are then separated into same-temperature blocks, and the linear approximate model is fit to the data in each block. This yields rate coefficient estimates for each data block temperature. To complete the analysis, the Arrhenius expression is fit to those data.

Linearized Approximate BSTR:

$$\frac{dn_A}{dt} \approx \frac{\Delta n_A}{\Delta t} \approx \frac{n_A\Big|_{t=t_i} - n_A\Big|_{t=t_{i-1}}}{t_i - t_{i-1}} = -kC_{A,f}\Big|_{t=t_i} V$$

$$\frac{C_A\Big|_{t=t_i} - C_A\Big|_{t=t_{i-1}}}{t_i - t_{i-1}} = -kC_{A,f}\Big|_{t=t_i} \quad \Rightarrow \quad y = kx$$

$$y_i = \frac{C_A\Big|_{t=t_i} - C_A\Big|_{t=t_{i-1}}}{t_i - t_{i-1}} \tag{3}$$

$$x_i = -C_{A,f}\Big|_{t=t_i} \tag{4}$$

$$m = k \tag{5}$$

Deliverables Function

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

Deliverables Function

1. Group the experimental data to form same-temperature data blocks
2. For each data block
   a. calculate x and y, equations (3) and (4)
      i. for the first data point in each experiment, the initial concentration and $t = 0$ must be used as the previous data point.
   b. call a linear least squares fitting function to fit $y = mx$ to the $x - y$ data
      i. it will return the slope and its uncertainty, the coefficient of determination for that data block, and model-predicted y values
   c. calculate k and its confidence interval, equations (5) and (6)

$$k_{CI} = m_{CI} \tag{6}$$

3. Call a linear least squares fitting function to fit the Arrhenius expression to the $T - k$ data from step 2 (see Example 3.6.3 in *REB, The Book*)
    a. it will return estimates and confidence intervals for k_0 and E, the coefficient of determination for the Arrhenius expression, and model-predicted k values
4. Generate an Arrhenius plot
5. Calculate the experiment residuals and overall coefficient of determination using the full data set (using the exact analytical solution - see the linearized model solution)

$$\ln \frac{C_A}{C_{A,0}} = -kt \quad \Rightarrow \quad C_A = C_{A,0} \exp\left(-kt\right)$$

$$\underline{C}_{A,pred} = \underline{C}_{A,0} \exp\left(-k_0 \exp\left(\frac{-E}{R\underline{T}}\right)\underline{t}_{meas}\right) \tag{7}$$

$$\underline{\epsilon}_{expt} = \underline{C}_{A,meas} - \underline{C}_{A,pred} \tag{8}$$

$$C_{A,mean} = \frac{\sum_i C_{A,meas,i}}{n_{expts}} \tag{9}$$

$$ss_{resid} = \sum_i \left(C_{A,meas,i} - C_{A,pred,i}\right)^2 \tag{10}$$

$$ss_{total} = \sum_i \left(C_{A,meas,i} - C_{A,mean}\right)^2 \tag{11}$$

$$R^2 = 1 - \frac{ss_{resid}}{ss_{total}} \tag{12}$$

6. 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 $\underline{t}_{meas}$

Implementation of the Calculations

The Python script, example_11_5_6_am.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. Define the deliverables function as described above.
4. Call the deliverables function.

Results and Discussion

The linearized approximate model was fit to the $x - y$ data for each of the same-temperature blocks. Figure 1 presents the resulting model plots, and Table 2 shows the parameter estimates, their confidence intervals and the coefficients of determination. By all measures, the fit is not good. The data scatter widely about the model lines, the coefficients of determination are all less than 0.9. However, the 95% confidence intervals are relatively narrow.

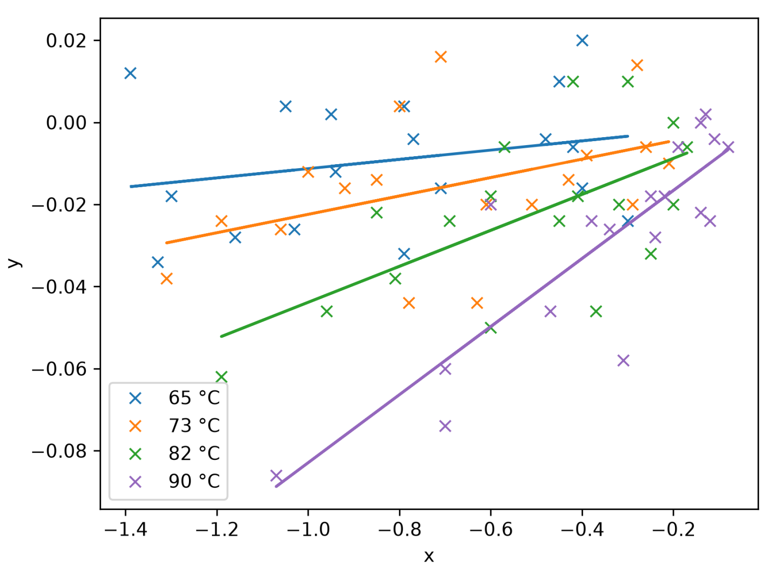

Figure 1. Model plots for the same-temperature data blocks.

Table 2. Results from fitting the approximate model to the same-temperature data blocks

T (°C)	k (min^{-1})	95% CI	R^2
65	0.0113	[0.00248, 0.0201]	0.301
73	0.0224	[0.0122, 0.0327]	0.557
82	0.0439	[0.0304, 0.0573]	0.737
90	0.0829	[0.0674, 0.0985]	0.882

Given the poor quality of the model plot fits, it is quite surprising that the Arrhenius plot of the model plot T vs. k data is very good. There is effectively no scatter and the coefficients of determination, shown in Table 3, is equal to 1.0.

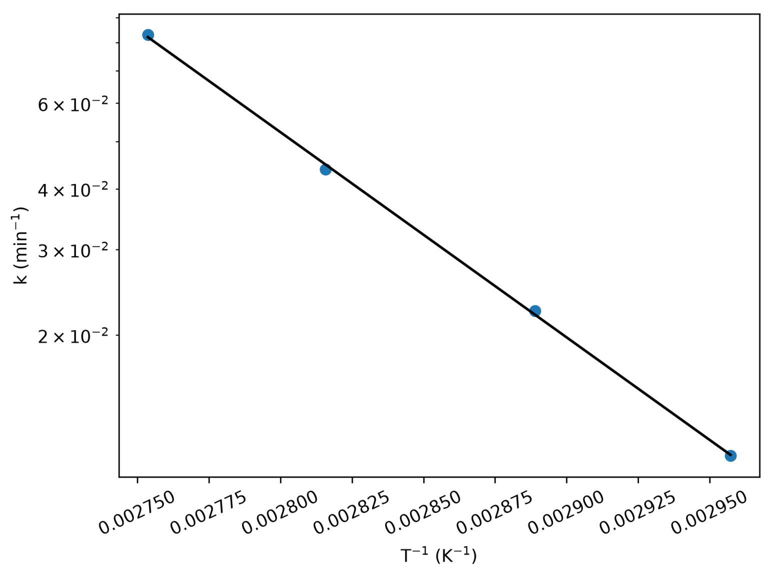

Figure 2. Arrhenius plot for the rate coefficients from the same-temperature data blocks.

Table 3. Arrhenius Parameters Obtained Using an Approximate Model

Parameter	Value	95% CI
k_0 (min^{-1})	3.52×10^{10}	[5.87×10^{9}, 2.11×10^{11}]
E ($kJ\ mol^{-1}$)	80.9	[75.7, 86.1]
R^2 (Arrhenius Plot)	1.000	
R^2 (Full Data Set)	0.978	

The Arrhenius parameters shown in Table 3 were used in the exact linear model to calculate model-predicted responses, from which experiment residuals were calculated. That allowed calculation of a coefficient of determination based on the full data set, also shown in Table 3. The value is nearly equal to 1.0, again suggesting the final rate expression is quite accurate despite the poor model plots.

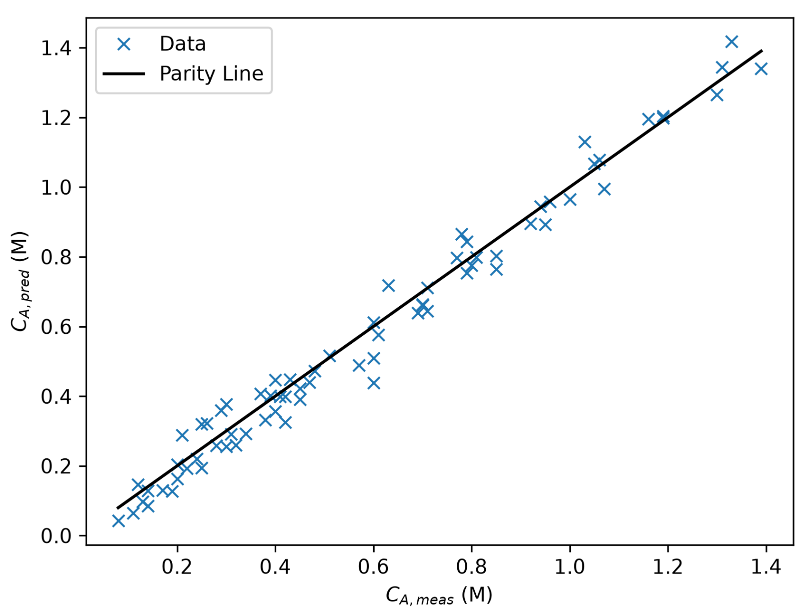

Figure 3. Parity plot for the full data set.

The parity plot based upon the complete data set, shown in Figure 3, also shows modest deviations of the data from the parity line, and there aren't any apparent trends in the scatter in the residuals plots in Figure 4. Overall the rate expression is accurate and captures the effects of the three input that were varied in the experiments.

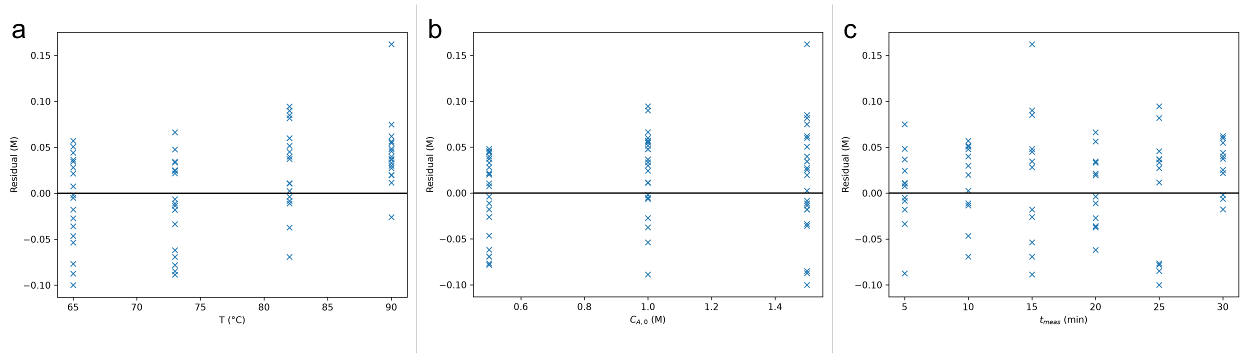

Figure 4. Residuals plots for a) temperature,
b) initial concentration of A, and c) measurement time.

Accuracy Assessment

When used with the pre-exponential factor and activation energy shown in Table 2, the rate expression in equation (2) is acceptably accurate.