

REB, The Book

Example 11.5.6 Solution Using a Linearized 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.



$$r = kC_A \quad (2)$$

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

Experiment	Adjusted Inputs			Response
	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 linearized model will be presented here, there are separate solutions that use a fitting function 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



Rate Expression

$$r = kC_A \quad (2)$$

Reactor: Isothermal BSTR

Given Constant: $V = 1 \text{ L}$

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.

Linearized BSTR Model

The reason for linearizing the BSTR model function is to allow parameter estimation using linear least squares. The design equations, which are IVODEs, must first be solved analytically, which results in an algebraic model equation. The 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 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 BSTR Model Equation:

$$\frac{dn_A}{dt} = -rV = -kC_A V = -k \left(\frac{n_A}{V} \right) V = -kn_A$$

$$\int_{C_{A,0}V}^{C_{A,meas}V} \frac{dn_A}{n_A} = -k \int_0^{t_{meas}} dt$$

$$\ln \frac{C_{A,meas}V}{C_{A,0}V} = \ln \frac{C_{A,meas}}{C_{A,0}} = -kt_{meas} \Rightarrow y = mx$$

$$y = \ln \frac{C_{A,meas}}{C_{A,0}} \quad (3)$$

$$x = -t_{meas} \quad (4)$$

$$m = k \quad (5)$$

Deliverables Function

The purpose of the deliverables function is to use the linearized BSTR model above 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)
 - 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)

$$k_{CI} = m_{CI} \quad (6)$$

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

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

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

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

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

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

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

$$R^2 = 1 - \frac{ss_{resid}}{ss_{total}} \quad (12)$$

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_lm.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 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. For all four temperatures, the upper and lower limits of the 95% confidence intervals for the rate coefficient are close to the estimated value, and the coefficients of determination are close to 1.0. The deviations of the data points from the model lines are relatively small, and there does not appear to be any trends in those deviations.

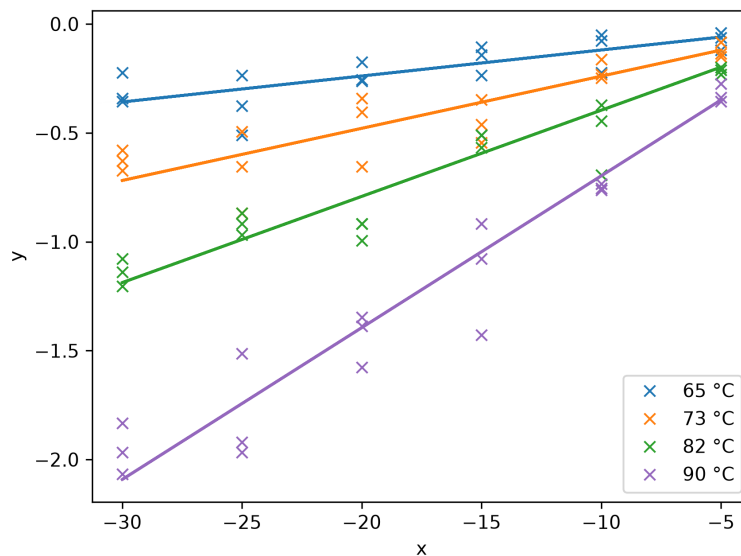


Figure 1. Model plots for the same-temperature data blocks.

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

T (°C)	k (min ⁻¹)	95% CI	R ²
65	0.0119	[0.00989, 0.0140]	0.899
73	0.0240	[0.0210, 0.0269]	0.946
82	0.0396	[0.0367, 0.0424]	0.980
90	0.0697	[0.0657, 0.0738]	0.987

The Arrhenius expression was fit to the $T - k$ data in Table 2. The Arrhenius plot is shown in Figure 2, and the fitting results are listed in Table 3. The 95% confidence intervals for both the pre-exponential factor and the activation energy are large compared to the estimated values, but the coefficient of determination from the Arrhenius plot is close to 1.0, and the plot itself evidences an accurate fit.

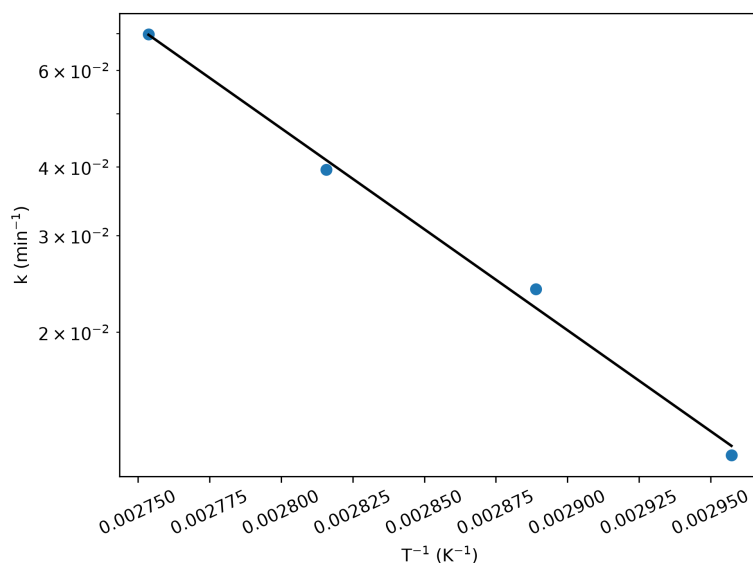


Figure 2. Arrhenius plot for the rate coefficients from the same-temperature data blocks.

Table 3. Arrhenius Parameters Obtained Using a Linearized Model

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

Overall within the range of the inputs that was studied, the rate expression provides an adequate representation of the experimental results when the pre-exponential factor and activation energy reported in Table 3 are used. Table 3 additionally reports the coefficient of determination for the complete data set. It, too, is quite close to 1.0

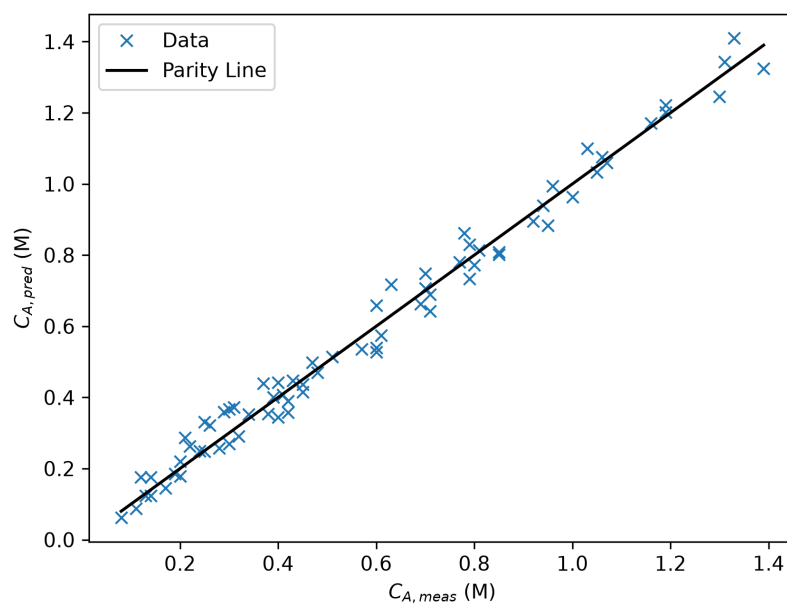


Figure 3. Parity plot for the full data set.

The parity plot based upon the complete data set, shown in Figure 3, again shows modest deviations of the data from the parity line. In addition, 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.

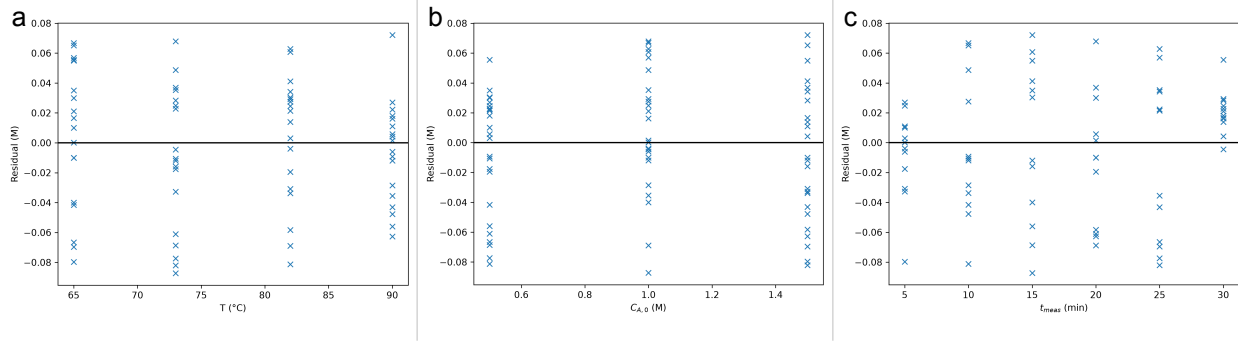


Figure 4. Residuals plots for a) temperature, b) initial concentration of A, and c) measurement time.

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.