REB, The Book
Example 11.5.4 Solution

The gas-phase reaction between reagents A and B was studied in an ideal, isothermal, 500 cm^3 BSTR. In all experiments the reactor was charged with reagents A and B only, but with varying partial pressures. The fractional conversion of reagent A was measured at seven different elapsed times in each experiment. Experiments were performed at three different temperatures. Assess the accuracy of the rate expression shown in equation (2) using both a fitting function approach and a linear model approach.

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

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

The experimental data are provided in the file, example_11_5_4_data.csv. The first few data points from that file are shown in Table 1.

Table 1. First 6 of the 189 experimental data points

T (°C)	$P_{A,0}$ (atm)	$P_{B,0}$ (atm)	t_{meas} (min)	f_A
475	0.5	0.5	0.5	0.022
475	0.5	0.5	1	0.031
475	0.5	0.5	1.5	0.049
475	0.5	0.5	2	0.06
475	0.5	0.5	2.5	0.078
475	0.5	0.5	5	0.135

Assignment Summary

Reaction

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

Rate Expression

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

Reactor: Isothermal BSTR

Given Constant: V = 500 cm^3

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

Given Experimental Responses: $\underline{f}_A$

Parameters to Estimate: k_0 and E

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

Formulation of the Equations Using a Fitting Function

BSTR Model Equations:

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

$$\frac{dn_B}{dt} = -Vr \tag{4}$$

$$\frac{dn_Y}{dt} = Vr \tag{5}$$

$$\frac{dn_Z}{dt} = Vr \tag{6}$$

BSTR Model Variables: $\underline{n}_A$, $\underline{n}_B$, $\underline{n}_Y$, $\underline{n}_Z$, and $\underline{t}$

Additional Computable Unknowns: r, k, P_A, and P_B

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \tag{7}$$

$$P_i = \frac{n_i RT}{V} \qquad i = A \text{ and } B \tag{8}$$

Additional Uncomputable Unknowns: k_0 and E

IVODE Solver Inputs:

1. Initial values of the reactor model variables shown in Table 2.
2. Stopping criterion that t equals the final value shown in Table 2.
3. Derivatives function that
   a. receives the BSTR model variables
   b. has access to k_0 and E
   c. calculates the additional unknowns using equations (2), (7), and (8)
   d. evaluates and returns the BSTR derivatives using equations (3) - (6)

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

Variable	Initial Value	Final Value
t	0	t_{meas}
n_A	$n_{A,0} = \frac{P_{A,0}V}{RT}$	
n_B	$n_{B,0} = \frac{P_{B,0}V}{RT}$	
n_Y	0	
n_Z	0	

Fitting Function Inputs:

1. Experimental data: $\underline{T}$, $\underline{P}_{A,0}$, $\underline{P}_{B,0}$, $\underline{t}$, and $\underline{f}_A$
2. Initial guesses for the parameters being estimated

$$\beta = 0 \tag{9}$$

$$E = 10 \text{ kcal mol}^{-1} \tag{10}$$

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 derivatives function

$$k_0 = 10^{\beta} \tag{11}$$

   c. loops through all of the experiments
      i. solves the BSTR model equations
      ii. calculates the model-predicted response

$$f_{A,pred} = \frac{n_{A,0} - \underline{n}_A \Big|_{t=t_{meas}}}{n_{A,0}} \tag{12}$$

   d. returns the predicted responses for all of the experiments

Parameter Estimate Equation:

$$k_{0,CI} = 10^{\beta_{CI}} \tag{13}$$

Formulation of the Equations Using a Linearized Model

BSTR Model Equations:

$$\frac{dn_A}{dt} = -Vr = -kVP_AP_B$$

$$\frac{dn_A}{dt} = -kV\left(\frac{n_ART}{V}\right)\left(\frac{n_BRT}{V}\right) = \frac{-k\,(RT)^2}{V}n_An_B$$

$$n_B = n_{B,0} - \xi$$

$$n_A = n_{A,0} - \xi \qquad \Rightarrow \qquad \xi = n_{A,0} - n_A$$

$$n_B = n_{B,0} - n_{A,0} + n_A$$

$$\frac{dn_A}{dt} = \frac{-k\,(RT)^2}{V} n_A \left(n_{B,0} - n_{A,0} + n_A\right)$$

$$\frac{dn_A}{n_A \left(n_{B,0} - n_{A,0} + n_A\right)} = \frac{-k\,(RT)^2}{V} dt$$

$$\int_{n_{A,0}}^{n_A} \frac{dn_A}{n_A \left(n_{B,0} - n_{A,0} + n_A\right)} = \frac{-k\,(RT)^2}{V} \int_{t_0}^{t} dt$$

if $n_{A,0} = n_{B,0}$

$$\frac{1}{n_{A,0}} - \frac{1}{n_A} = \frac{-k\,(RT)^2}{V} t \quad \Rightarrow \quad y = mx \tag{14}$$

if $n_{A,0} \neq n_{B,0}$

$$\begin{aligned}\frac{1}{n_{A,0} - n_{B,0}} \ln \frac{n_{A,0}\left(n_{B,0} - n_{A,0} + n_A\right)}{n_{B,0} n_A} \\ = \frac{-k\,(RT)^2}{V} t\end{aligned} \quad \Rightarrow \quad y = mx \tag{15}$$

<u>Linear Model Least Squares Inputs</u>: (for each same-temperature data block)

$$n_A = n_{A,0}\left(1 - f_A\right) \tag{16}$$

$$y = \frac{1}{n_{A,0}} - \frac{1}{n_A} \tag{17}$$

$$y = \frac{1}{n_{A,0} - n_{B,0}} \ln \frac{n_{A,0}\left(n_{B,0} - n_{A,0} + n_A\right)}{n_{B,0} n_A} \tag{18}$$

$$x = \frac{-t_{meas}(RT)^2}{V} \tag{19}$$

<u>Linear Model Rate Coefficient Equation</u>: (for each same-temperature data block)

$$k = m \tag{20}$$

<u>Arrhenius Expression Least Squares Inputs</u>:

$$\underline{y} = \ln \underline{k} \tag{21}$$

$$\underline{x} = \frac{1}{\underline{T}} \tag{22}$$

<u>Arrhenius Parameter Equations</u>: (for k_f and k_r)

$$k_0 = \exp\left(b\right) \tag{23}$$

$$E = -mR \tag{24}$$

<u>Coefficient of Determination Equations</u>:

$$f_{A,mean} = \frac{\sum_i f_{A,i}}{n_{expts}} \tag{25}$$

$$ss_{resid} = \sum_i \left(f_{A,i} - f_{A,pred,i}\right)^2 \tag{26}$$

$$ss_{total} = \sum_i \left(f_{A,i} - f_{A,mean}\right)^2 \tag{27}$$

$$R^2 = 1 - \frac{ss_{resid}}{ss_{total}} \tag{28}$$

Implementation of the Calculations

The Python script, example_11_5_4.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 and predicted responses function sas described above.
5. Perform the analysis using a fitting function.
    a. Define an initial parameter guess and fit the BSTR model to the data using a fitting function.
    b. Calculate the experiment residuals.
6. Perform the analysis using a linear model
    a. Separate the data into same-temperature blocks and for each block
        i. calculate x and y
        ii. fit the straight line, $y = mx$, to the $\left(x - y\right)$ data using least squares
        iii. calculate k from the estimated slope
    b. Fit the Arrhenius expression to the $\left(T - k\right)$ data from step 6a using least squares.
    c. Calculate the predicted responses and coefficient of determination for all of the experiments using the Arrhenius expression parameters from the the linearized model analysis.
    d. Calculate the experiment residuals.
7. Tabulate, graph, and save the results, as appropriate.

The fitting function converged using the parameter guess given in equations (9) and (10), so it was not necessary to revise that guess.

Results and Discussion

The estimated pre-exponential factor and activation energy found using a fitting function are shown in Table 2. The accuracy is excellent as evidenced by all indicators. The upper and lower limits of the 95% confidence intervals are close in value to the estimates, the coefficient of determination is nearly equal to 1, the data in the parity plot, Figure 1, all lie very close to the parity line, and in all four residuals plots, Figure 2, the deviations are random with no trends.

Table 2. Results of parameter estimation using a fitting function

Parameter	**Value**	**95% CI**	**Units**
k_0	2.59	[2.08, 3.1]	mol cm^{-3} min^{-1} atm^{-2}
E	21.8	[21.5, 22.1]	kcal mol^{-1}
R^2	0.999		

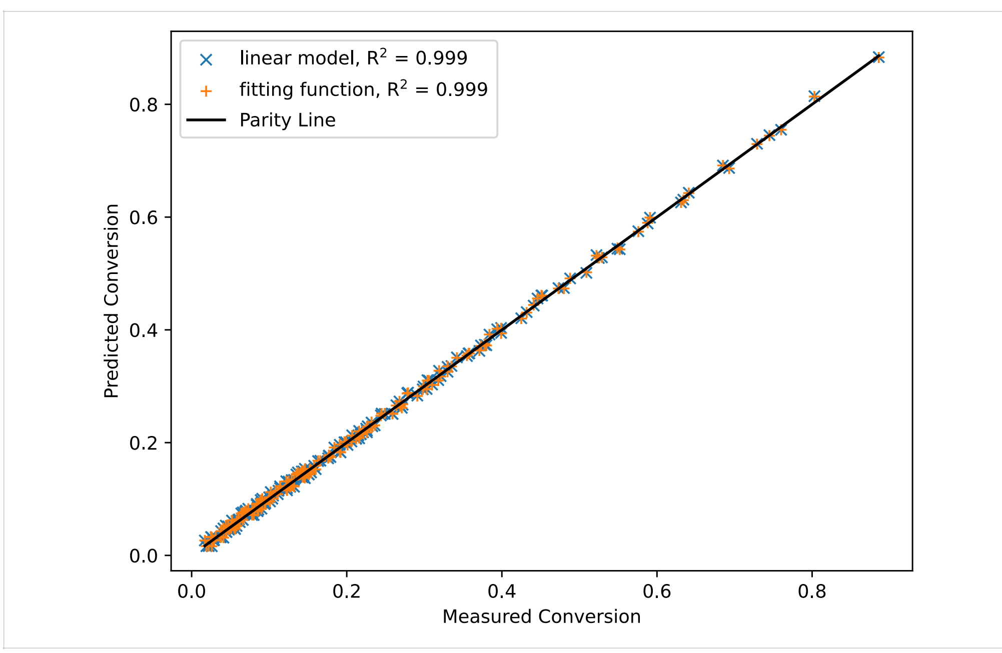

Figure 1. Parity plots for estimation using a fitting function and a linearized model.

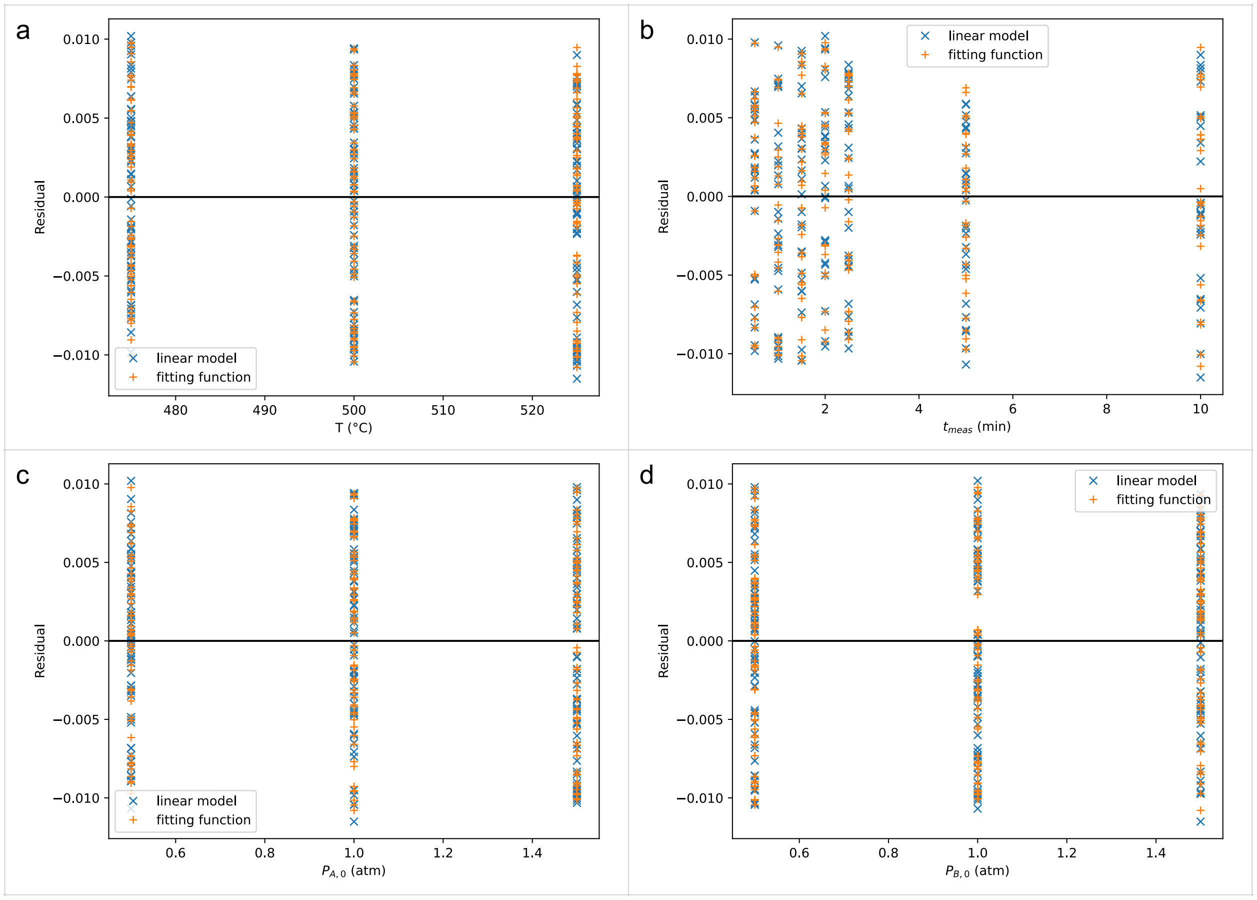

Figure 2. Residuals plots for a) temperature, b) measurement time, and the initial partial pressures of c) reagent A and d) reagent B for estimation using a fitting function and a linearized model.

When using the linearized model approach, the data are separated into same-temperature blocks. Model plots from fitting the linearized model to each of the data blocks are shown in Figure 3. There is minimal scatter of the data about the line at all three temperatures, indicating an accurate fit. The Arrhenius expression was fit to the resulting $(T-k)$ data. The results are presented in Table 3 and the Arrhenius plots are shown in Figure 4. As was the case for the estimates using a fitting function, A highly accurate fit is evidenced by all indicators (confidence intervals, coefficient of determination, model plots and Arrhenius plot).

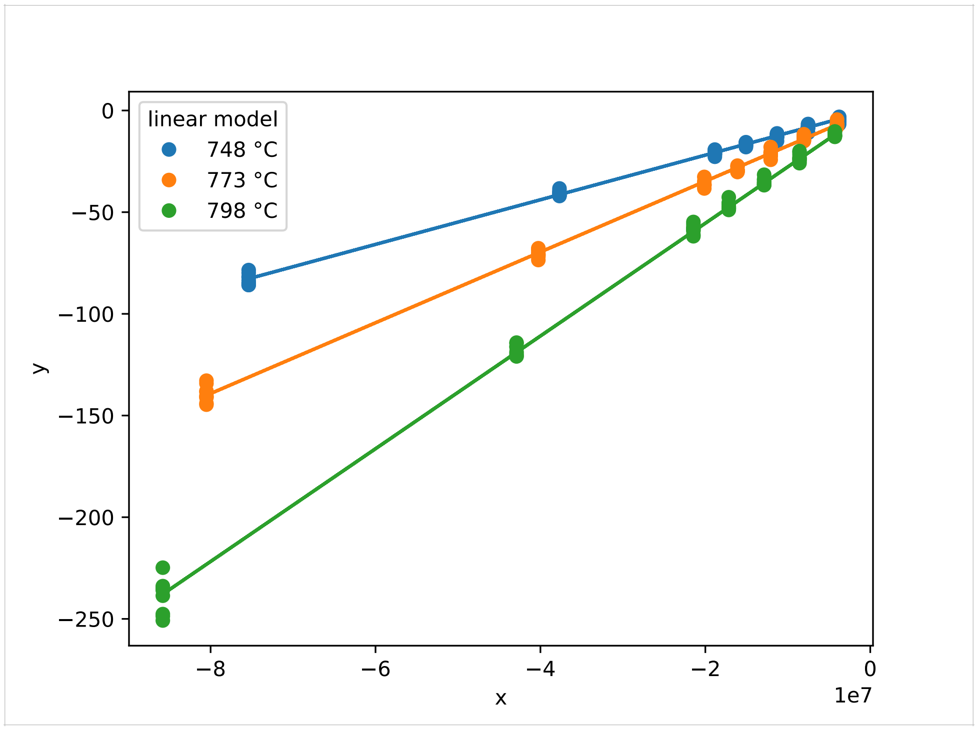

Figure 3. Model plots for the same-temperature data blocks.

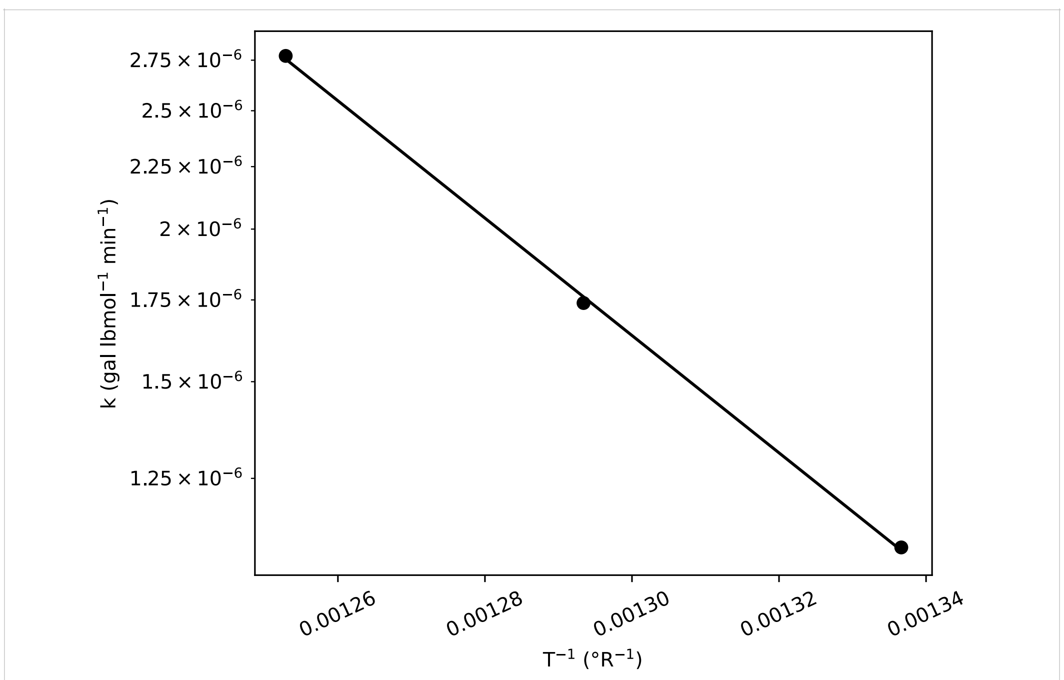

Figure 4. Arrhenius plot for the same-temperature data blocks.

Table 3. Comparison of the parameter estimation results for the fitting function and linearized model approaches.

Approach	Parameter	Value	95% CI
fitting function	k_0	2.59 mol cm^{-3} min^{-1} atm^{-2}	[2.08, 3.1]
	E	21.8 kcal mol^{-1}	[21.5, 22.1]
	R^2	0.999	
linear model	k_0	2.88 mol cm^{-3} min^{-1} atm^{-2}	[0.0541, 154]
	E	22.0 kcal mol^{-1}	[15.9, 28.1]
	R^2	0.999	

For this data set, the two approaches to parameter estimation gave the same results to within the experimental uncertainty. The parity and residuals plots and the coefficients of determination for the complete data sets are essentially the same. This is true because each of the same-temperature data blocks gave excellent estimates for the rate coefficient.

Deliverables

The proposed rate expression is acceptably accurate when either of the sets of Arrhenius parameters shown in Table 3 are used.