REB, The Book
Example 11.5.6 Solution Comparison

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

The analyses using each of the three parameter estimation models are presented separately. Here the results from the three methods are compared. The parameter estimation results for all three methods are shown in Table 2. The linear model and approximate model methods do not yield 95% confidence intervals that are based upon the full data set, so no values are listed. The coefficients of determination listed for those methods are based upon the full data set. Figure 1 shows the parity plots for all three methods and Figure 2 presents the residuals plots.

Table 2. Parameter Estimation Summary

Method	k_0 (min^{-1})	95% CI	E (kJ mol^{-1})	95% CI	R^2
fitting function	1.40×10^9	[3.22×10^8, 6.11×10^9]	71.6	[67.3, 75.9]	0.985
linearized model	9.30×10^8		70.4		0.985
approximate model	3.52×10^{10}		80.9		0.978

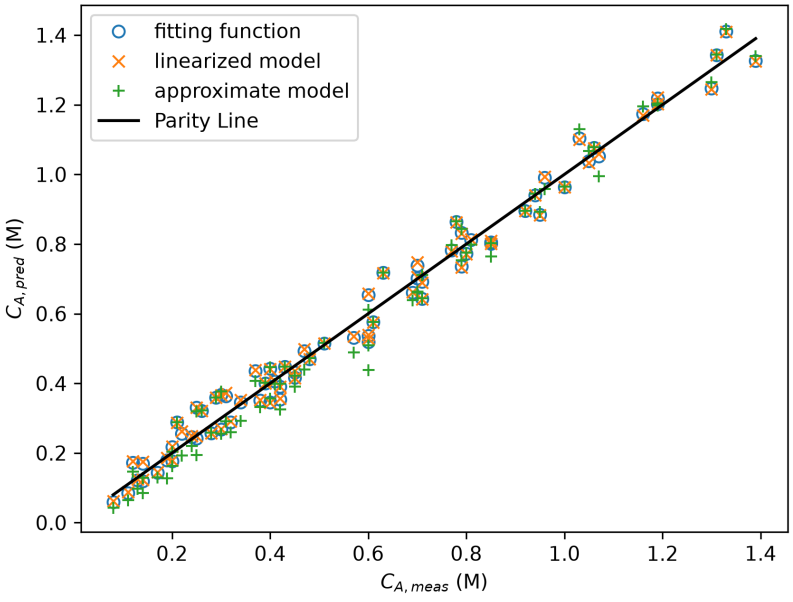

Figure 1. Parity plot comparison.

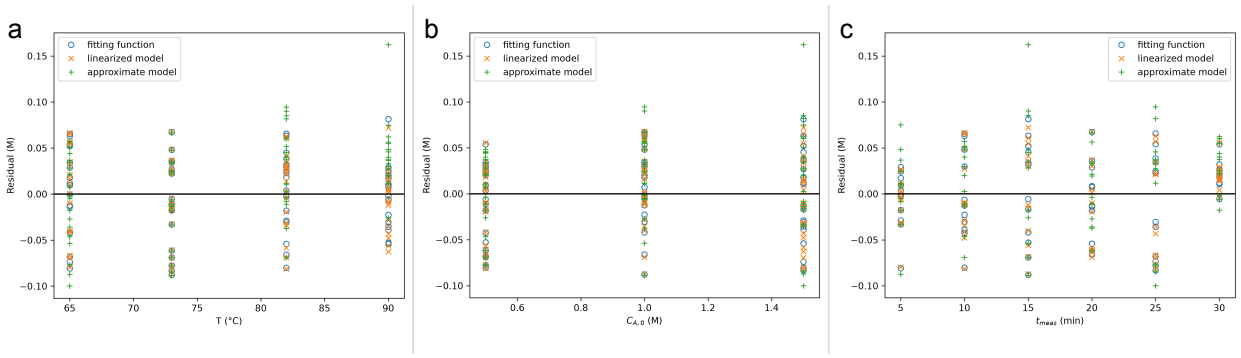

Figure 2. Residuals plots comparison for a) temperature, b) initial concentration of A, and c) measurement time.

It is apparent from the parity plots and coefficients of determination that all three methods yielded accurate models. The residuals plots similarly show comparable deviations. There are no obvious trends in the residuals plots deviations which indicates that the models capture the effects of the three adjusted inputs well.

So, the final rate expressions appear to be comparably accurate. This is surprising for the approximate model method when the results are examined more closely. In the linear and approximate model approaches, the data are split into same-temperature blocks and each block is analyzed separately. Figure 3 presents the model plots for each temperature block for the two approaches. Very clearly, the approximate model yields much noisier $x - y$ data. The slopes of the model plots yield the rate coefficient estimates for each temperature shown in Table 3. The coefficients of determination support the visual observation that the data are much noisier in the model plots for the approximate model approach.

What is surprising in light of the noisy approximate model plots is that two of the four approximate model rate coefficients fall within the 95% confidence interval for the linear model rate coefficients, and the other two fall just outside of the linear model rate coefficient confidence intervals. Apparently much of the noise in the approximate model plots averages out leading to rate coefficients that are quite similar.

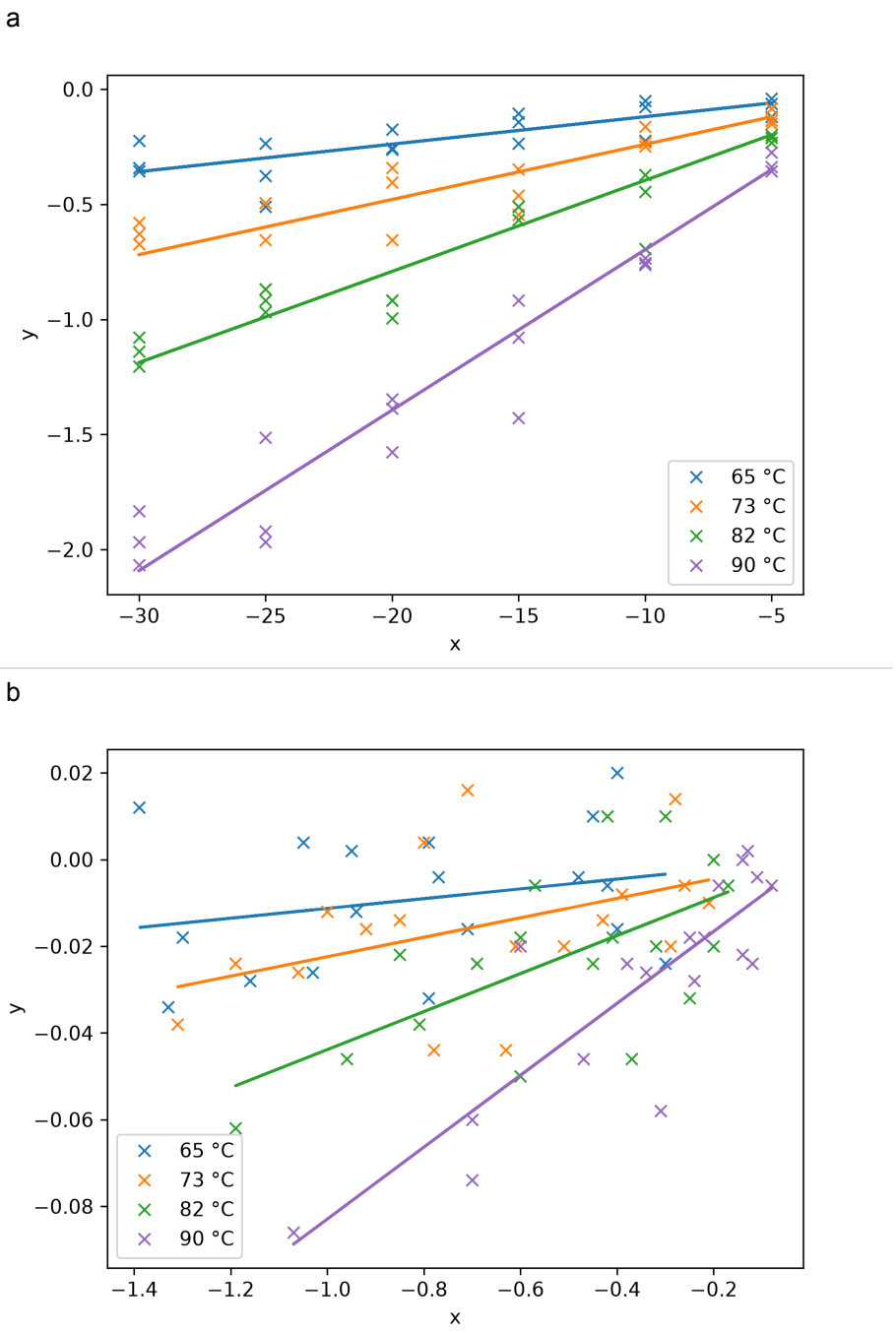

Figure 3. Model plots for a) the linear model and b) the approximate model.

Table 3. Model Plot Parameter Comparision

	Linear Model			Approximate Model		
T (°C)	k (min^{-1})	95% CI	R^2	k (min^{-1})	95% CI	R^2
65	0.0119	[0.00989, 0.0140]	0.899	0.0113	[0.00248, 0.0201]	0.301
73	0.0240	[0.0210, 0.0269]	0.946	0.0224	[0.0122, 0.0327]	0.557
82	0.0396	[0.0367, 0.0424]	0.980	0.0439	[0.0304, 0.0573]	0.737
90	0.0697	[0.0657, 0.0738]	0.987	0.0829	[0.0674, 0.0985]	0.882

The Arrhenius expression is then fit to the $T - k$ data in Table 3 to estimate the pre-exponential factors and activation energies. The results are included in Table 2. Since the uncertainties are based on the $T - k$ which, in turn, are estimated using the data from only one of the same-temperature blocks. For that reason, the uncertainties are not included in Table 2.

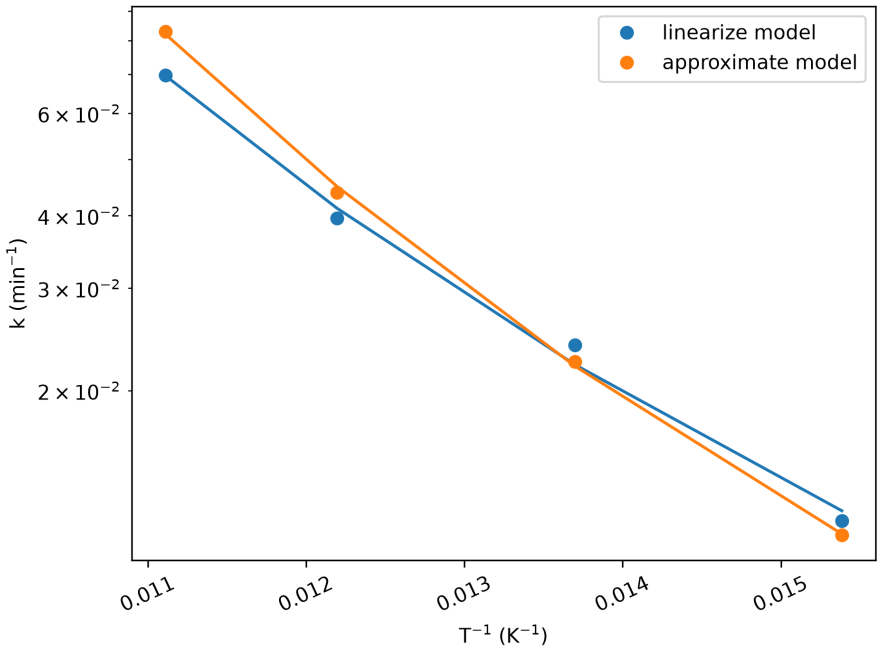

Figure 4. Arrhenius plot comparison.

The Arrhenius plots for the two approaches are shown in Figure 4. Despite the greater scatter in the model plots for the approximate model, the scatter in the Arrhenius plots is comparable and quite minimal. As shown in Table 4, the coefficients of determination are essentially equal to 1. While the models provide comparable accuracy, the pre-exponential factors and activation energies are quite different.

Table 4. Comparison of Arrhenius Parameters from Model Plots

	Linear Model		Approximate Model	
Parameter	Value	95% CI	Value	95% CI
k_0 (min^{-1})	9.30×10^8	[3.99×10^6, 2.17×10^{11}]	3.52×10^{10}	[5.87×10^9, 2.11×10^{11}]
E (kJ mol^{-1})	70.4	[54.5, 86.3]	80.9	[75.7, 86.1]
R^2 (Arrhenius Plot)	0.995		1.000	
R^2 (Full Data Set)	0.985		0.978	

As noted already, in the range of composition and temperature that was studied, all three rate expressions are acceptably accurate. Nonetheless, the Arrhenius parameters found using a fitting function are preferred because all of the data are used to estimate each of them. The linearized model gave similar Arrhenius parameters and could be used. The Arrhenius parameters from the approximate model differ, and are the least preferred because of the large amount of scatter in the model plots.