REB, The Course
Class 25 Practice Assignment Solution

Gas phase reaction (1) was studied in a 2 L batch reactor. Three experiments were performed, each at a different temperature. The initial reactor pressure in all experiments was 1 atm, and the starting mixture consisted of only A and B. The initial ratio of A to B was different for each experiment, and the mole fraction of Z was measured as a function of reaction time (in min) in each experiment. Determine the best values of the activation energy and pre-exponential factor for k in the proposed rate expression, equation (2), and determine whether that rate expression is accurate.

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

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

The experimental data are provided in the file, practice_25_data.csv. The first few data points from that file are shown in Table 1.

Table 1. First 6 of the 27 experimental data points.

	Adjusted Inputs			Response
Experiment	T (°C)	Initial A to B	t_{meas} (min)	y_Z
1	25	1.0	119.0	0.35
1	25	1.0	239.0	0.516
1	25	1.0	358.0	0.615
1	25	1.0	478.0	0.66
1	25	1.0	597.0	0.715
1	25	1.0	717.0	0.763

Assignment Summary

A succinct summary of the information contained in the assignment narrative is presented below. The initial A to B ratio is denoted as γ. Note that deliverables list includes the confidence intervals for the estimated parameters and the coefficient of determination which were not specifically requested in the assignment narrative. It also includes a parity plot and residuals plots because while they were not requested, they are needed for assessing the accuracy of the reactor model.

Reaction

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

Rate Expression

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

Reactor: Isothermal, gas-phase BSTR

Given Constants: V = 2.0 L, P_0 = 1.0 atm, and $n_{Z,0}$ = 0 mol.

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

Given Experimental Responses: $\underline{y}_{Z,meas}$

Parameters to Estimate: k_0 and E

Deliverables: Parameter estimates and their 95% confidence intervals, 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 design equations for the BSTR that was used in the experiments. This is done numerically by calling an IVODE solver. The additional uncomputable unknowns listed below must be passed to the BSTR model function as arguments. If necessary, it will then make them available to the

BSTR derivatives function as as global variables. The BSTR derivatives function described here also must be written.

<u>BSTR Model Equations</u>:

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

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

$$\frac{dn_Z}{dt} = rV \tag{5}$$

<u>BSTR Model Variables</u>: $\underline{t}$, $\underline{n}_A$, $\underline{n}_B$, and $\underline{n}_Z$

<u>Additional Computable Unknowns</u>: r, k, C_A, and C_B

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \tag{6}$$

$$C_i = \frac{n_i}{V} \qquad i = A \text{ and } B \tag{7}$$

<u>Additional Uncomputable Unknowns</u>: T, γ, t_{meas}, k_0, and E

<u>IVODE Solver Inputs</u>:

1. Initial values of the reactor model variables

$$t_0 = 0 \tag{8}$$

$$n_{B,0} = \frac{P_0 V}{\left(1 + \gamma\right) RT} \tag{9}$$

$$n_{A,0} = \gamma n_{B,0} \tag{10}$$

$$n_{Z,0} = 0 \tag{11}$$

2. Stopping criterion

$$t_f = t_{meas} \tag{12}$$

3. Derivatives function that
   a. receives the BSTR model variables at the start of an integration step
   b. has access to the uncomputable unknowns: T, γ, t_{meas}, k_0, and E
   c. calculates the additional unknowns using equations (2), (6), and (7)
   d. evaluates and returns the BSTR derivatives using equations (3) - (5).

Deliverables Function

The purpose of the deliverables function is to use the BSTR model function above to estimatek_0 and E and their confidence intervals, calculate the coefficient of determination, and calculate the predicted responses and experiment residuals for use in parity and residuals functions. 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.

<u>Deliverables Function</u>

1. Define guesses for the parameters

$$\beta = 0.0 \tag{13}$$

$$E = 40.0 \text{ kJ mol}^{-1} \tag{14}$$

2. Call a numerical fitting function.
   a. Arguments
      i. The experimental data: $\underline{T}$, $\underline{\gamma}$,$\underline{t}_{meas}$, and $\underline{y}_{Z,meas}$
      ii. The Initial guesses for the parameters from step 1
      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, R^2

iii. the predicted responses: $\underline{y}_{Z,pred}$

3. Calculate k_0 and its confidence interval

$$k_0 = 10^{\beta} \tag{15}$$

$$k_{0,CI} = 10^{\beta_{CI}} \tag{16}$$

4. Calculate the experiment residuals

$$\underline{\epsilon}_{expt} = \underline{y}_{Z,meas} - \underline{y}_{Z,pred} \tag{17}$$

5. Generate
   a. a parity plot showing $\underline{y}_{Z,pred}$ *vs.* $\underline{y}_{Z,meas}$
   b. residuals plots showing $\underline{\epsilon}_{expt}$ vs. $\underline{T}$, $\underline{\gamma}$, and $\underline{t}_{meas}$

<u>Predicted Responses Function</u>

1. receives the adjusted experimental inputs and guesses for the parameters
2. calculates the pre-exponential factor using equation (15)
3. loops through all of the experiments
   a. calls the BSTR model function
   b. calculates the model-predicted response

$$y_{Z,pred} = \left.\frac{\underline{n}_Z}{\underline{n}_A + \underline{n}_B + \underline{n}_Z}\right|_{t=t_{meas}} \tag{18}$$

4. returns the predicted responses for all of the experiments

Implementation of the Calculations

The Python script, practice_25.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.

Results and Discussion

The parameter estimation results are presented in Table 2, the parity plot in Figure 2, and the residuals plots in Figure 3. The coefficient of determination is close to 1, the data all lie close to the parity line, and there do not appear to be any obvious trends in the deviations in the residuals plots. These are all indicators of an accurate model. The confidence interval for k_0 is broad, but that isn't uncommon. The uncertainty in E is less than 5% of the estimated value which also suggests that the fitted model is accurate.

Table 2. Arrhenius Parameter Estimates.

Parameter	Value	95% CI
k_0 (L mol^{-1} min^{-1})	1.82×10^9	[6.71×10^8, 4.94×10^9]
E (kJ mol^{-1})	55.0	[52.4, 57.5]
R^2	0.997	

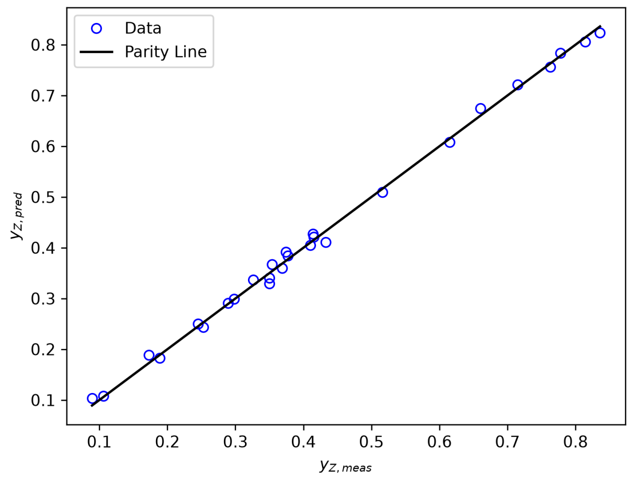

Figure 1. Parity plot.

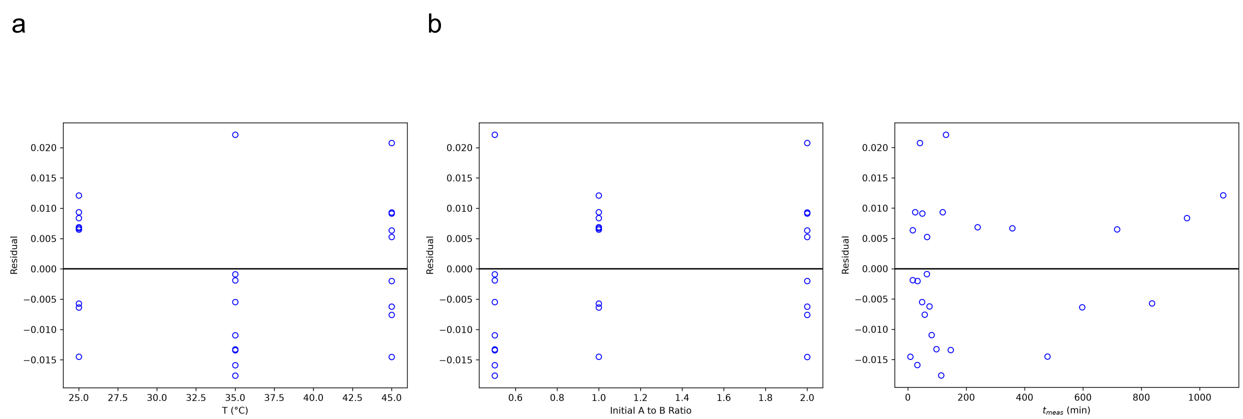

Figure 2. Residuals plots for a) T, b) $n_{A/B,0}$, and c) t_{meas}

Accuracy Assessment

When used with k_0 = 1.82 x 10^9 L mol^{-1} min^{-1} and E = 55 kJ mol^{-1} in the rate expression, the BSTR model accurately predicts the results of the experiments. As such, when used with those parameter values, the rate expression is accurate and acceptable.