REB, The Course
Class 28 Practice Assignment Solution

Preliminary experiments have indicated that gas-phase reaction (1) is irreversible and that the rate is not affected by the concentration of the product Z. To generate kinetics data, experiments were performed at three temperatures. An ideal CSTR operating at 3 atm was used for all experiments. The feed in every experiment contained only reagents A and B. The temperature, space time, and mole fraction of A in the feed were varied from experiment to experiment, and the outlet concentration of Z was measured. Use the resulting data to assess the accuracy of the rate expression shown in equation (2) where the power-law reaction orders, α_A and α_B, must be estimated along with the pre-exponential factor and activation energy for the rate coefficient, k.

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

$$r = k P_A^{\alpha_A} P_B^{\alpha_B} \tag{2}$$

The experimental data are provided in the file, practice_28_data.csv. The first few data points from that file are shown in Table 1.

Table 1. First 6 of the 108 experimental results.

T	τ	$y_{A,in}$	$C_{Z,out}$
440	30	0.1	0.46
440	30	0.2	0.71
440	30	0.3	1.27
440	30	0.4	1.56
440	30	0.5	2.03
440	30	0.6	2.33

Temperatures in °C, space times in s, and concentrations in mmol L

Assignment Summary

The information provided in the assignment narrative is summarized below. None of the given data are extensive, so a basis could be chosen. The deliverables list includes items that were not specifically requested in the assignment narrative, but that are needed for assessing the accuracy of the reactor model.

Reaction

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

Rate Expression

$$r = k P_A^{\alpha_A} P_B^{\alpha_B} \tag{2}$$

Reactor: Steady-state, isothermal, gas-phase CSTR

Given Constants: P = 3 atm, $\dot{n}_{Z,in}$ = 0

Given Adjusted Experimental Inputs: $\underline{T}$, $\underline{\tau}$, and $\underline{y}_{A,in}$

Given Experimental Responses: $\underline{C}_{Z,out}$

Parameters to Estimate: k_0, E, α_A, and α_B

Basis: V = 1.0 L

Deliverables: Parameter estimates and confidence intervals, coefficients of determination, parity and residuals plots, and an assessment of the accuracy of the fitted model.

CSTR Model Function

The purpose of the CSTR model function is to solve the CSTR design equations for the reactor that was used in the experiments. This is done numerically by calling an ATE solver. Any quantities that are not given and are required for solving the design equations will be passed to it as arguments. If necessary, the CSTR function will then make them available to the CSTR residuals function as as global variables. The CSTR residuals function described here also must be written.

CSTR Model Equations:

$$0 = \dot{n}_{A,in} - \dot{n}_{A,out} - rV = \epsilon_1 \tag{3}$$

$$0 = \dot{n}_{B,in} - \dot{n}_{B,out} - rV = \epsilon_2 \tag{4}$$

$$0 = -\dot{n}_{Z,out} + rV = \epsilon_3 \tag{5}$$

CSTR Model Variables: $\dot{n}_{A,out}$, $\dot{n}_{B,out}$, and $\dot{n}_{Z,out}$

Additional Computable Unknowns: $\dot{n}_{A,in}$, $\dot{n}_{B,in}$, $\dot{V}_0$, r, k, P_A, and P_B

$$\dot{n}_{i,in} = y_{i,in}\frac{P\dot{V}_{in}}{RT} \quad i = A \text{ and } B \tag{6}$$

$$\dot{V}_{in} = \frac{V}{\tau} \tag{7}$$

$$y_{B,in} = 1 - y_{A,in} \tag{8}$$

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \tag{9}$$

$$P_i = \frac{\dot{n}_{i,out}P}{\dot{n}_{A,out} + \dot{n}_{B,out} + \dot{n}_{Z,out}} \quad i = A \text{ and } B \tag{10}$$

Additional Uncomputable Unknowns: $y_{A,in}$, T, τ, k_0, E, α_A, and α_B

ATE Solver Inputs:

1. Initial guesses for the reactor model variables

$$\dot{n}_{i,out,guess} = \dot{n}_{i,in} \quad i = A, B, \text{ and } Z \tag{11}$$

2. Residuals function that
   a. receives guesses for the CSTR model variables
   b. has access to $y_{A,in}$, T, τ, k_0, E, α_A, and α_B as global variables
   c. calculates the additional unknowns using equations (6) through (10)
   d. evaluates and returns the ATE model equation residuals using equations (3) through (5)

Deliverables Function

The purpose of the deliverables function is to use the CSTR model function above to estimate the parameters 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.

Deliverables Function

1. Define guesses for the parameters

$$\beta_{guess} = 0.0 \tag{12}$$

$$E_{guess} = 40 \text{ kJ mol}^{-1} \tag{13}$$

$$\alpha_i = 1.0 \quad i = A \text{ and } B \tag{14}$$

2. Call a numerical fitting function.
   a. Arguments
      i. The experimental data: $\underline{T}$, $\underline{\tau}$, and $\underline{y}_{A,in}$, and $\underline{C}_{Z,out}$

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 the parameters, k_0, E, α_A, and α_B

ii. the coefficient of determination, R^2

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

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 residual

$$\underline{\epsilon}_{expt} = \underline{C}_{Z,out} - \underline{C}_{Z,out,pred} \tag{17}$$

5. Generate

a. a parity plot showing $\underline{C}_{Z,out,pred}$ *vs.* $\underline{C}_{Z,out}$

b. residuals plots showing $\underline{\epsilon}_{expt}$ vs. $\underline{T}$, $\underline{\tau}$, and $\underline{y}_{A,in}$

Predicted Responses Function

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 CSTR model function

b. calculates the model-predicted response

$$C_{Z,out,pred} = \frac{\dot{n}_{Z,out}}{\dot{V}_{out}} \tag{18}$$

$$\dot{V}_{out} = \frac{\left(\dot{n}_{A,out} + \dot{n}_{B,out} + \dot{n}_{Z,out}\right) RT}{P} \tag{19}$$

4. returns the predicted responses for all of the experiments

Implementation of the Calculations

The Python script, practice_28.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 CSTR model, CSTR residuals, predicted responses, and deliverables functions as described above.
5. Call the deliverables function.

The fitting function did not converge using the guesses in (12) - (14). After modifying the guesses for the pre-exponential factor and activation energy, the fitting function did converge.

Results and Discussion

The estimated rate expression parameters are presented in Table 2. The corresponding parity and residuals plots are shown in Figures 1 and 2. The data fall close to the parity line in Figure 1, and the coefficient of determination is 0.995. The uncertainty in all four parameters are small, and in the residuals plots there are no apparent trends in the deviations. All of these factors indicate that the reactor model, and, by extension, the proposed rate expression are accurate.

The model assumes the power-law exponents to be constants that do not change with temperature. If this was not true, it would have been necessary to guess the functional form of their dependence on the temperature.

Table 2. Estimated Rate Expression Parameters.

Parameter	Value	95% Confidence Interval
k_0 ($L\ mol^{-1}\ min^{-1}\ atm^{-2}$)	1.16×10^4	$[5.84 \times 10^3, 2.32 \times 10^4]$
E ($kJ\ mol^{-1}$)	117.0	[112.0, 121.0]
α_A	1.4	[1.35, 1.44]
α_B	0.587	[0.562, 0.611]
R^2	0.995	

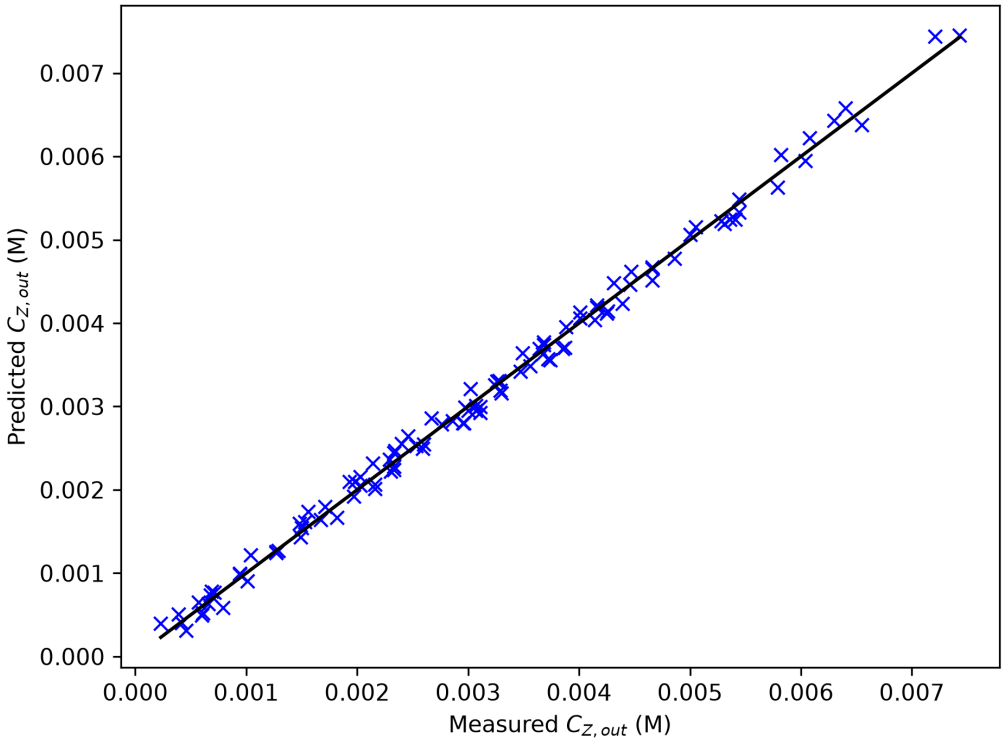

Figure 1. Parity Plot Generated Using the Rate Expression Parameters in Table 2.

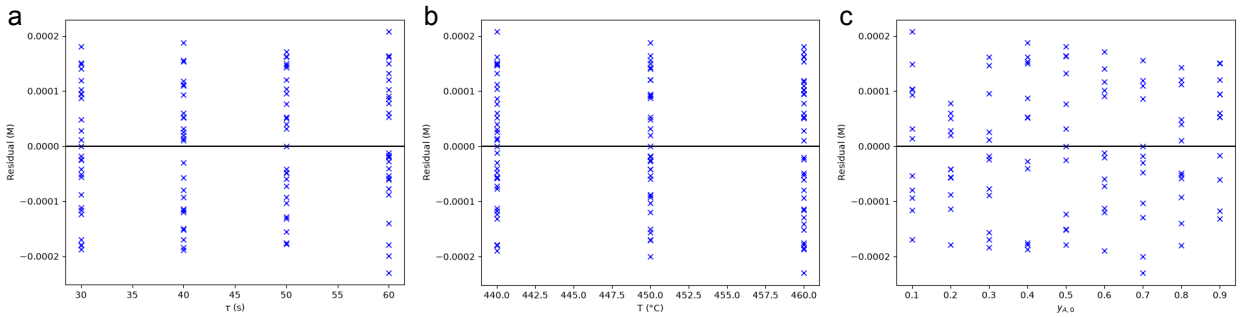

Figure 2. Residuals plots for a) the space time, b) the temperature, and c) the initial mole fraction of A generated using the rate expression parameters in Table 3.

Accuracy Assessment

With the parameters shown in Table 2, the proposed rate expression is accurate and acceptable for use.