

A First Course on Kinetics and Reaction Engineering

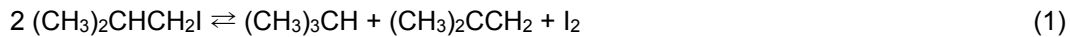
Example 13.1

Problem Purpose

This problem illustrates the generation of a rate expression using kinetics data obtained from a CSTR.

Problem Statement

A 1.7 L CSTR was used to study the kinetics of reaction (1) which takes place in the liquid phase using an inert solvent. The reaction is suspected of being auto-catalytic with I_2 serving as a catalyst. For this reason the experiments were run isothermally at a constant space time of 8.5 min, but with varying inlet concentrations of $(CH_3)_2CHCH_2I$ and I_2 . The fractional conversion of $(CH_3)_2CHCH_2I$ was measured at steady-state in each experiment. The data in the table below were accumulated in a series of experiments that all used the same reactor temperature.



$[(CH_3)_2CHCH_2I]^0$ (mol/L)	Inlet $[I_2]^0$ (mol/L)	<i>fractional conversion</i>
0.10	0.75	9.93E-03
0.25	0.37	6.93E-03
0.30	0.19	4.95E-03
0.48	0.61	8.92E-03
0.65	2.48	1.81E-02
0.79	3.07	1.98E-02
0.93	0.09	3.61E-03
1.00	3.39	2.09E-02
1.33	1.27	1.28E-02
1.50	1.70	1.53E-02
1.68	1.94	1.59E-02
2.00	0.47	8.08E-03

a. Test a first order rate expression, $r_{(CH_3)CHCH_2I} = -kC_{(CH_3)CHCH_2I}$, for consistency with these data.

b. Test a rate expression that is first order in the reactant and one-half order in the catalyst,

$$r_{(CH_3)CHCH_2I} = -kC_{(CH_3)CHCH_2I}\sqrt{C_{I_2}}, \text{ for consistency with these data.}$$

- c. Test a rate expression that is first order in the reactant and first order in the catalyst,

$$r_{(CH_3)CHCH_2I} = -kC_{(CH_3)CHCH_2I}C_{I_2}, \text{ for consistency with these data.}$$

Problem Analysis

This problem clearly involves a chemical reaction taking place within a CSTR. It doesn't provide thermodynamic data or ask questions related to equilibrium, so it is most likely either a kinetics problem or a reaction engineering problem. Upon reading the question, we see that the rate expression is unknown and we are asked to test three rate expressions to see if they are suitable using CSTR kinetics data. Therefore, this problem is a kinetics type of problem, and to answer it we will write the design equation for the reactor, substituting the rate expression being tested into it, fit the resulting equation to the experimental kinetics data, and decide whether or not the fit is satisfactory.

Problem Solution

First, for simplicity sake, let A represent $(CH_3)_2CHCH_2I$, X represent $(CH_3)_3CH$, Y represent $(CH_3)_2CCH_2$, and Z represent I_2 . Equation (1) can be re-written using this notation.



Recall that the procedure for generating a rate expression involves choosing a reactor to use in the laboratory, generating a design equation for the reactor and validating that design equation, gathering experimental data, picking a mathematical function to test as a rate expression, substituting the chosen rate expression into the design equation, fitting the resulting design equation to the experimental data, deciding whether the fit is adequate and, if the fit is adequate, estimating the uncertainty in the rate expression parameters. If the fit is not adequate, the process is repeated using a different mathematical function for the rate expression. Here we assume that experiments have been performed to ensure that the reactor does indeed behave as an ideal CSTR. This is a single phase system, so we do not need to be concerned about interfacial concentration or temperature gradients.

For an isothermal CSTR operating at steady state and with only one reaction taking place, a mole balance design equation for species i is given in equation (2). When only one reaction is occurring, the reactor can be modeled by writing this equation one time with i representing any reactant or product taking part in the reaction. Choosing i to be the reactant, A, results in equation (3) as the mole balance design equation.

$$\dot{n}_i - \dot{n}_i^0 = Vr_{i,j} \quad (2)$$

$$\dot{n}_A - \dot{n}_A^0 = Vr_{A,1} \quad (3)$$

The rate expression to be tested in part (a) of the question is given in equation (4). Substituting equation (4) into equation (3) gives equation (5).

$$r_{A,1} = -kC_A \quad (4)$$

$$\dot{n}_A - \dot{n}_A^0 = -VkC_A \quad (5)$$

The next step in the process is to fit equation (5) to the experimental data. If we define x_a , y and m as given in equations (6) through (8), and substitute them into equation (5), equation (9) results. It is easy to see that equation (9) is the equation for a straight line through the origin with slope, m .

$$x_a = -VC_A \quad (6)$$

$$y = \dot{n}_A - \dot{n}_A^0 \quad (7)$$

$$m = k \quad (8)$$

$$y = mx_a \quad (9)$$

Since equation (9) is linear, linear least squares can be used to fit it to the experimental data (see Supplemental Unit S3). Linear least squares fitting can be performed manually, using a calculator, using a spreadsheet or using mathematics software. No matter which tool one chooses to use, it will be necessary to provide the following information and input data:

- the number of independent (x) variables
- whether or not the model includes an intercept (b)
- a set of experimental data points, each of which consists of a value for the dependent variable (y) and corresponding values for each of the independent variables (x_i)

Thus, we need to find values of x_a and y corresponding to each of the experimental data points in the table in the problem statement. To calculate x_a , we first apply the definition of concentration for a flow system to equation (6), giving equation (10). We then note that in a liquid phase system, the density can be assumed to be constant, so that the inlet volumetric flow rate equals the outlet volumetric flow rate. At the same time, the outlet molar flow rate can be expressed in terms of the inlet molar flow rate and the fractional conversion, leading to equation (11). The inlet molar flow rate of A divided by the inlet volumetric flow rate is, by definition, the inlet concentration of A, leading to equation (12). The reaction volume, V , that appears in equation (12) is given in the problem statement as being equal to 1.7 L. The table in the problem statement provides the values of C_A^0 and f_A for each data point, so x_a can be calculated for each data point using equation (12).

$$x_a = -V \frac{\dot{n}_A}{\dot{V}} \quad (10)$$

$$x_a = -V \frac{\dot{n}_A^0 (1 - f_A)}{\dot{V}^0} \quad (11)$$

$$x_a = -VC_A^0 (1 - f_A) \quad (12)$$

To calculate y we first express outlet molar flow rate in equation (7) in terms of the inlet molar flow rate and the fractional conversion, leading to equation (13). The inlet molar flow rate of A is equal to the inlet volumetric flow rate times the inlet concentration of A, giving equation (14). Finally, the inlet volumetric flow rate is related to the space time and the volume, leading to equation (15). The volume, V , and the space time, τ , are specified in the problem statement to have the same values (1.7 L and 8.5 min, respectively) for all experiments. The table in the problem statement provides the values of C_A^0 and f_A for each data point, so y can be calculated for each data point using equation (15).

$$y = \dot{n}_A - \dot{n}_A^0 = \dot{n}_A^0(1 - f_A) - \dot{n}_A^0 = -\dot{n}_A^0 f_A \quad (13)$$

$$y = -C_A^0 \dot{V}^0 f_A \quad (14)$$

$$y = -\frac{C_A^0 V f_A}{\tau} \quad (15)$$

Thus, we can generate a set of (x_a, y) data using equations (12) and (15). The model has only one independent variable, x_a , and it does not include an intercept. With this information and input data we have everything needed to fit the model to the data. Upon doing so, using whichever linear least squares fitting tool one chooses to employ, the resulting output shows that the correlation coefficient, r^2 , is equal to 0.6488 and the best value of the slope, m , is equal to 0.0015 ± 0.0004 (95% confidence limits based upon the data given in the problem statement). The fitting tool may also produce a model plot like that shown in Figure 1, but if such a plot is not created, one can be generated easily.

Before the best value for m can be accepted, one must decide whether the final model is sufficiently accurate. In this case, the accuracy of the model can be assessed using the correlation coefficient and the model plot. The closer the correlation coefficient is to a value of 1.0, the better the fit of the model to the data. In this case, the correlation coefficient of 0.6488 indicates a poor fit. Additionally, if the fit is accurate, then the scatter of the experimental data about the model should be small and random; there should not be any systematic deviations of the data from the model. Examining the model plot, Figure 1, it is apparent that deviations of the data points from the line are large. Thus, the model does not appear to be sufficiently accurate, meaning that the rate expression given in equation (4) is not acceptable.

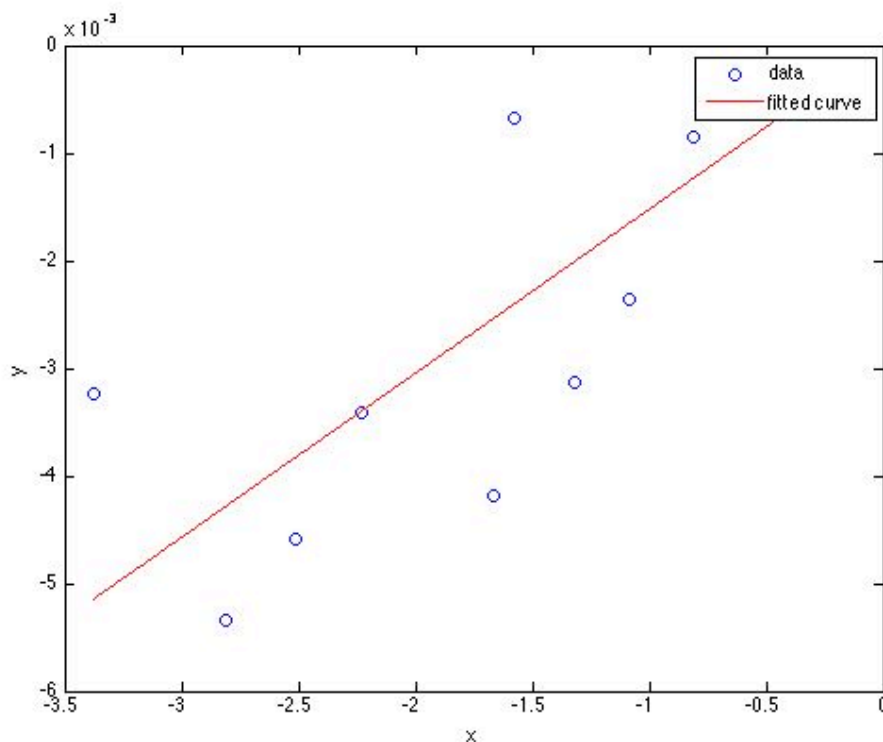


Figure 1. Model plot for part (a) showing the experimental data as points and the model's predictions as a line.

The analysis for part (b) is very similar to that for part (a), so only the differences will be highlighted here. The rate expression to be tested in part (b) of the question is given in equation (16). Substituting equation (16) into the reactor design equation, equation (3), gives equation (17).

$$r_{A,1} = -kC_A\sqrt{C_Z} \quad (16)$$

$$\dot{n}_A - \dot{n}_A^0 = -VkC_A\sqrt{C_Z} \quad (17)$$

If x_b is defined according to equation (18), y is again defined as in equation (7) and m is defined as in equation (8), this model equation also takes the form of a straight line through the origin with slope, m , equation (19).

$$x_b = -VC_A\sqrt{C_Z} = -x_a\sqrt{C_Z} \quad (18)$$

$$y = mx_b \quad (19)$$

Thus, before we can fit the model to the experimental data, we need to calculate values of x_b and y corresponding to each of the experimental data points in the table in the problem statement. The values of y are the same as in part (a). To calculate the values of x_b we need values for C_Z for each experimental

data point. C_Z can be expressed in terms of the molar flow rate of Z and the volumetric flow rate as shown in equation (20). This is a liquid phase system so the inlet and outlet volumetric flow rates are equal.

$$C_Z = \frac{\dot{n}_Z}{\dot{V}} = \frac{\dot{n}_Z}{\dot{V}^0} \quad (20)$$

The outlet molar flow rate of Z can be calculated knowing the inlet composition and the fractional conversion of A. To do so, first use a mole table or the definition of the extent of reaction to derive the relationship between the molar flow rates of A and Z, equation (21). Then express the outlet molar flow rate of Z in terms of the fractional conversion of A, equation (22). Substitution of this expression into equation (20) and simplification leads to equation (23) for C_Z , and substitution of that result into equation (18) gives the equation we need to calculate x_b , equation (24).

$$\dot{n}_Z = \dot{n}_Z^0 + \frac{\dot{n}_A^0 - \dot{n}_A}{2} \quad (21)$$

$$\dot{n}_Z = \dot{n}_Z^0 + \frac{\dot{n}_A^0 - \dot{n}_A^0(1 - f_A)}{2} \quad (22)$$

$$C_Z = \frac{2\dot{n}_Z^0 + \dot{n}_A^0 f_A}{2\dot{V}^0} = \frac{2C_Z^0 \dot{V}^0 + C_A^0 \dot{V}^0 f_A}{2\dot{V}^0} = \frac{2C_Z^0 + C_A^0 f_A}{2} \quad (23)$$

$$x_b = -x_a \sqrt{\frac{2C_Z^0 + C_A^0 f_A}{2}} \quad (24)$$

Thus, we can generate a set of (x_b, y) data using equations (24) and (15), and again the model has one independent variable and no intercept. That is all the information we need in order to fit equation (19) to the experimental data. Upon doing so, using whichever linear least squares fitting tool one chooses to employ, the resulting output shows that the correlation coefficient, r^2 , is equal to 0.9996 and the best value of the slope, m , is equal to 0.0014 ± 0.00001 (95% confidence limits based upon the data given in the problem statement). Figure 2 shows the corresponding model plot.

In this case, the correlation coefficient is very close to 1.0 and the data fall almost exactly on the line in the model plot, so this model does offer a sufficiently accurate description of the experimental data. We see from equation (8) that the slope, m , is equal to the rate coefficient, k , thus, the best value for k in equation (16) is $0.0014 \pm 0.00001 \text{ L}^{0.5} \text{ mol}^{-0.5} \text{ min}^{-1}$.

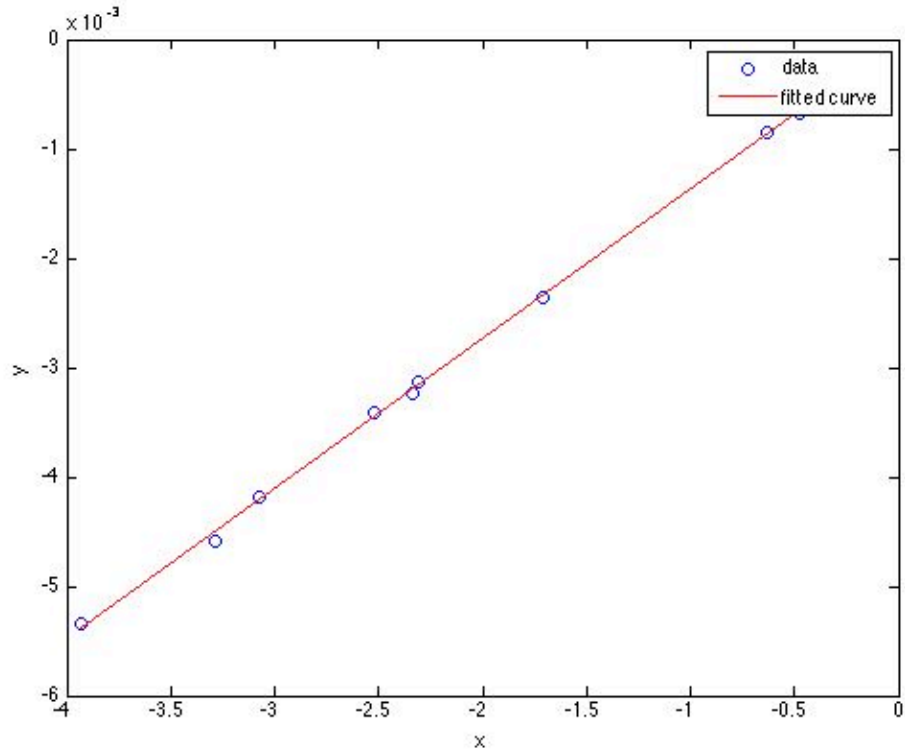


Figure 2. Model plot for part (b) showing the experimental data as points and the model's predictions as a line.

For part (c) the process is again the same, the difference being that the rate expression is given by equation (25) and x is defined by equation (26). The resulting plot, Figure 3, shows that the second order rate expression is not acceptable. There is significant scatter of the data about the line and the correlation coefficient is only 0.8378. Not surprisingly (since equation (16) offered a good fit to the data), the rate expression given in equation (25) is not satisfactory.

$$r_{A,1} = -kC_A C_Z \quad (25)$$

$$x = -V_{fluid} C_A C_Z \quad (26)$$

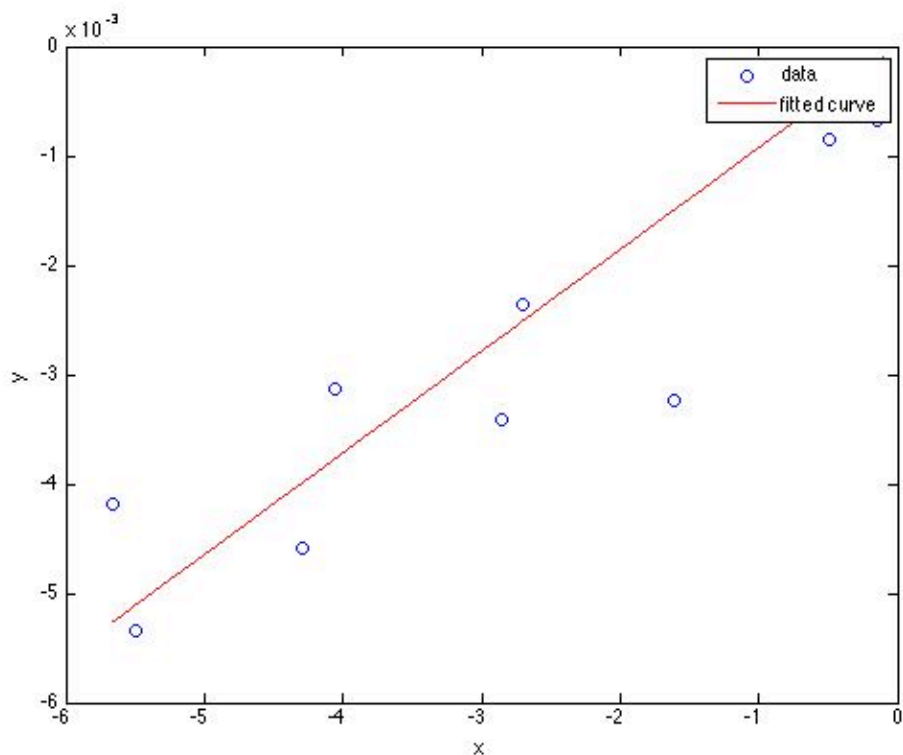


Figure 3. Model plot for part (c) showing the experimental data as points and the model's predictions as a line.

Calculation Details Using MATLAB

Three MATLAB script files are provided with Supplemental Unit S3. The file names indicate the number of independent variables and whether or not the model has an intercept. The script named FitLinmSR is used when the model has one independent variable (x) and does not include the intercept (b). FitLinmbSR is used when the model has one independent variable and does include the intercept, and FitLinSR is used when the model has two or more independent variables. (With MATLAB, when the model has two or more independent variables, it must have an intercept; Supplemental Unit S3 describes how to convert a model without an intercept into a model that has an intercept.) In this problem the model has one independent variable, but no intercept, so the script file named FitLinmSR will be used. To do so, the script file must be located in the current MATLAB working directory or in the MATLAB search path.

Before executing FitLinmSR, the experimental values of x must be stored in a vector named x , and the experimental values of y must be stored in a vector named y_hat . Upon execution of the script, it will return the correlation coefficient, r^2 , as $r_squared$, the slope, m , as m , and the 95% confidence limits on the slope, λ_m , as m_u . It will also generate a model plot. The commands for performing these tasks can be entered at the MATLAB command prompt, but here they have been recorded in the MATLAB files named

Example_13_1a.m, Example_13_1b.m and Example_13_1c.m which accompany this solution. Since the three files are very, very similar, only the solution for part (a) will be described here.

Example_13_1a.m begins with the entry of the data from the problem statement. The values of x and y are then calculated and stored in the arrays x and y_hat . FitLinmSR is then called to perform the fitting. This is shown in Listing 1. This generates the model plot shown previously as Figure 1 and the additional output shown in Listing 2.

```
% MATLAB file used in the solution of part (a) of Example 13.1 of
% "A First Course on Kinetics and Reaction Engineering."

% Data provided in the problem statement, in consistent units
V=1.7; % L
tau=8.5; % min
CA0=[0.10 0.25 0.30 0.48 0.65 0.79 0.93 1.00 1.33 1.50 1.68 2.00]'; % mol/L
CZ0=[0.75 0.37 0.19 0.61 2.48 3.07 0.09 3.39 1.27 1.70 1.94 0.47]'; % mol/L
fA=[9.93E-03 6.93E-03 4.95E-03 8.92E-03 1.81E-02 1.98E-02 3.61E-03 2.09E-02
    1.28E-02 1.53E-02 1.59E-02 8.08E-03]';

% Calculate x and y of the linearized model equation
x = -V*CA0.*(1-fA);
y_hat = (-V/tau)*CA0.*fA;

% Use the MATLAB script file "FitLinmSR.m" from "A First Course on
% Kinetics and Reaction Engineering" to fit a straight line through the
% origin to the data.
FitLinmSR
```

Listing 1. Code showing entry of the data from the problem statement, calculation of the vectors containing the dependent and independent variables and fitting of the model to the data.

```
>> Example_13_1a

r_squared =

    0.6488

m =

    0.0015

m_u =

    3.8261e-04
```

Listing 2. Output generated upon execution of Example_13_1a.m.