

A First Course on Kinetics and Reaction Engineering

Example 15.1

Problem Purpose

This example illustrates the integral method of kinetics data analysis. The problem is the same as in Example 14.2, where the differential method of data analysis was used, thus allowing interested readers to make a direct comparison of the two methods.

Problem Statement

The kinetics of reaction (1) were studied using a 2.3 L batch reactor. The reaction takes place in the gas phase at a constant temperature of 848K. An experiment began with pure reactant at a pressure of 1036 Torr. The partial pressure of I_2 was measured as a function of time. The data are given in the table below.



- Using the integral method, test a first order rate expression, $r_{C_3H_5I} = -kC_{C_3H_5I}$, using these data.
- Using the integral method, test a second order rate expression, $r_{C_3H_5I} = -kC_{C_3H_5I}^2$, using these data.

Table 1. Experimental data.

Time (ms)	P_{I_2} (Torr)
0	0
0.1	121
0.2	202
0.3	275
0.4	336
0.5	375
0.6	417
0.7	416
0.8	433
0.9	457
1.0	476

Problem Analysis

This problem gives batch reactor kinetics data and asks us to test two rate expressions using integral data analysis. To do this, we will write the mole balance design equation, substitute the rate expression, integrate to obtain an algebraic equation and fit the result to the experimental data. We will then assess the accuracy of the resulting fitted models and decide whether either is sufficiently accurate.

Problem Solution

First, to simplify the notation, we will let A denote C_3H_5I , Y denote C_6H_{10} and Z denote I_2 . Equation (1) can be re-written using this notation.



(a) We assume that experiments have been performed to ensure that the reactor does indeed behave as an ideal, perfectly mixed batch reactor and to ensure that physical processes are not limiting the rate of chemical reaction. For an isothermal batch reactor with a single reaction taking place a mole balance design equation on any reactant or product is all that is needed to model the reactor. If the mole balance is written for A, equation (2) results. The problem statement specifies that in part (a) we are to test the rate expression given in equation (3). Substitution of that rate expression into the design equation leads to equation (4).

$$\frac{dn_A}{dt} = Vr_{A,1} \quad (2)$$

$$r_{A,1} = -kC_A \quad (3)$$

$$\frac{dn_A}{dt} = -kVC_A \quad (4)$$

It is also specified that an integral data analysis should be used, so equation (4) must be integrated to obtain an algebraic model equation. Before it can be integrated, all variables must be re-expressed in terms of the dependent variable, here n_A , and the independent variable, here t . The rate coefficient, k , is constant (because the reactor was isothermal) as is the reaction volume, V . However, the concentration of A will change as the reaction proceeds. The definition of a concentration, equation (5) can be used to re-express the concentration of A in terms of the moles of A, after which the design equation is given by equation (6).

$$C_A = \frac{n_A}{V} \quad (5)$$

$$\frac{dn_A}{dt} = -kn_A \quad (6)$$

At this point, equation (6) contains no variables other than the moles of A and time, and so, it can be integrated by separation of the variables. An initial condition is needed in order to integrate, and here

we know that at $t = 0$ there are n_A^0 moles of A present. A common mistake in problems like this is to fail to evaluate the integrand at the lower limit. Correctly remembering to do so leads to the integrated form of the design equation given in equation (7), where n_A represents the moles of A present at any later time, t .

$$\frac{dn_A}{n_A} = -kdt$$

$$\int_{n_A^0}^{n_A} \frac{dn_A}{n_A} = -k \int_0^t dt$$

$$\ln\left(\frac{n_A}{n_A^0}\right) = -k(t - 0)$$

$$\ln\left(\frac{n_A}{n_A^0}\right) = -kt \tag{7}$$

The next step in the process is to fit equation (7) to the experimental data. Equation (7) has the form of a straight line through the origin, equation (8). This can be seen if x , y and m are defined as given in equations (9) through (11). Notice that the dependent (y) and independent (x) variables each include quantities that varied from experiment to experiment while the slope (m) includes only quantities that had a the same value in every experiment, and the slope also includes an unknown constant parameter from the rate expression (k).

$$y = mx \tag{8}$$

$$x = -t \tag{9}$$

$$y = \ln\left(\frac{n_A}{n_A^0}\right) \tag{10}$$

$$m = k \tag{11}$$

Here, the model, equation (8), is linear, so 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 calculate values of y and x for each data point. The calculation of x by equation (9) is trivial since the value of t is given for each data point. In order to calculate y using equation (10), we

will need to first calculate the moles of A at the start of the experiment, n_A^0 , and the moles of A, n_A , for each of the data points. Since the reactor was initially charged with pure A, the initial moles of A can be found using the ideal gas law, equation (12).

$$n_A^0 = \frac{P^0 V}{RT} \quad (12)$$

The problem statement does not provide the moles of A for each data point; instead it gives the partial pressure of Z. The partial pressure of Z can be related to the moles of A, however. To do so, the partial pressure of Z is first used to calculate the moles of Z via the ideal gas law as shown in equation (13).

$$n_Z = \frac{P_Z V}{RT} \quad (13)$$

The moles of Z are related to the moles of A through the reaction stoichiometry. The specific equation relating the two can be derived using the definition of extent of reaction, or through the use of a mole table, Table 2. The mole table shows that the moles of Z, n_Z , is equal to the extent of reaction, ξ_1 , which is also related to the moles of A, n_A , as shown in equation (14). Combining those relationships with equations (10), (12) and (13) leads to equation (15) which can be used to calculate y for each experimental data point from information given in the problem statement.

Table 2. Mole table.

Species	Initial number of moles	number of moles after reaction
A	n_A^0	$n_A^0 - 2\xi_1$
Y	0	ξ_1
Z	0	ξ_1
Total Moles	n_A^0	n_A^0

$$n_A = n_A^0 - 2\xi_1 \quad (14)$$

$$y = \ln\left(\frac{n_A}{n_A^0}\right) = \ln\left(\frac{n_A^0 - 2\xi_1}{n_A^0}\right) = \ln\left(\frac{\frac{P^0 V}{RT} - 2\frac{P_Z V}{RT}}{\frac{P^0 V}{RT}}\right) = \ln\left(\frac{P^0 - 2P_Z}{P^0}\right) \quad (15)$$

Thus, we can generate a set of (x,y) data using equations (9) and (15). The model has only one independent variable, x , 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 0.988 and the best value of the slope, m , is equal to $2.45 \pm 0.10 \text{ ms}^{-1}$ (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.

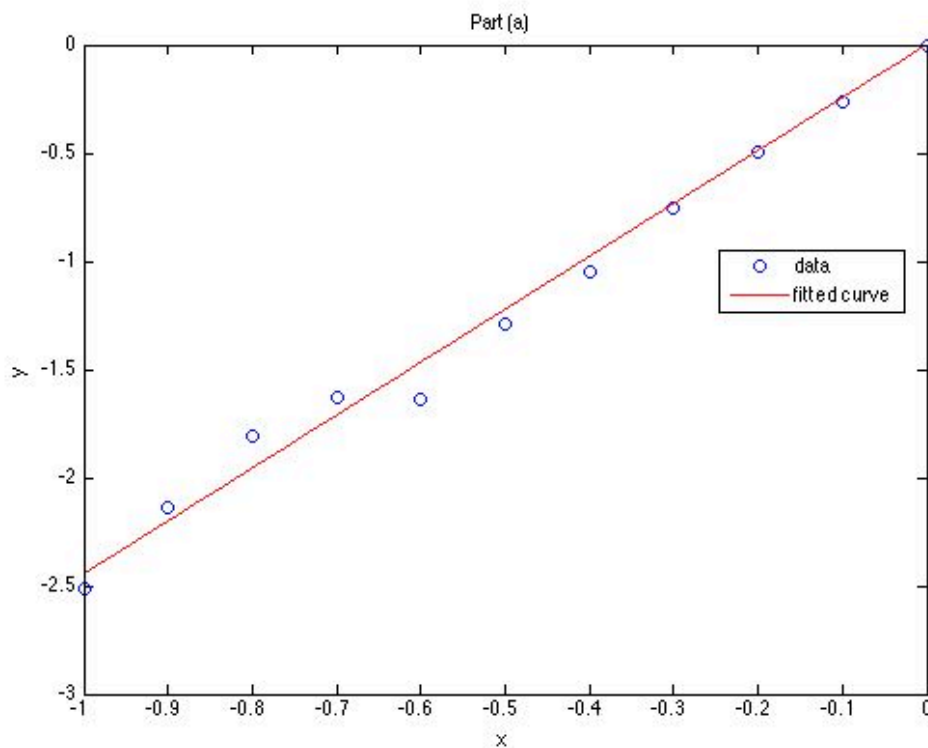


Figure 1. Model plot for part (a) showing the experimental data as points and the model's predictions as a line.

One next 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 0.998 indicates a very good 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 these criteria also are satisfied. Thus, the first order rate expression does appear to offer a sufficiently accurate representation of the kinetics, and the values of the slope and intercept can be accepted. Normally it

would be necessary to calculate k and its uncertainty from m and its uncertainty, but in this problem, they are equal, so the best value of k is taken to be $2.45 \pm 0.10 \text{ ms}^{-1}$.

(b) In part (b) of the problem, the rate expression to be tested is given by equation (16). Substitution of the rate expression into the design equation, equation (2), leads to equation (17).

$$r_{A,1} = -kC_A^2 \quad (16)$$

$$\frac{dn_A}{dt} = -kVC_A^2 \quad (17)$$

Once again, this equation must be integrated, but before doing so, any variables appearing in the equation must be re-expressed in terms of the dependent and independent variables. The concentration of A again is re-expressed in terms of the moles of A as before using equation (5); substitution into equation (17) gives equation (18).

$$\frac{dn_A}{dt} = -\frac{k}{V}n_A^2 \quad (18)$$

Since k and V are constants, equation (18) can now be solved by separating the variables and integrating, leading to equation (16). The initial conditions for integration are the same as in part (a).

$$\begin{aligned} -\frac{dn_A}{n_A^2} &= \frac{k}{V}dt \\ -\int_{n_A^0}^{n_A} \frac{dn_A}{n_A^2} &= \frac{k}{V} \int_0^t dt \\ \left(\frac{1}{n_A} - \frac{1}{n_A^0} \right) &= \frac{k}{V}(t-0) \\ \left(\frac{1}{n_A} - \frac{1}{n_A^0} \right) &= \frac{kt}{V} \end{aligned} \quad (19)$$

Equation (19) is again in the form of a straight line through the origin, equation (8), the differences being that y and x are defined as in equations (20) and (21). We therefore proceed in the same manner as part (a). This time we find that the correlation coefficient is equal to 0.817 and the best value for the slope, m , is $398 \pm 86 \text{ L mol}^{-1} \text{ ms}^{-1}$. The corresponding model plot is shown in Figure 2.

$$y = \left(\frac{1}{n_A} - \frac{1}{n_A^0} \right) \quad (20)$$

$$x = \frac{t}{V_{fluid}} \quad (21)$$

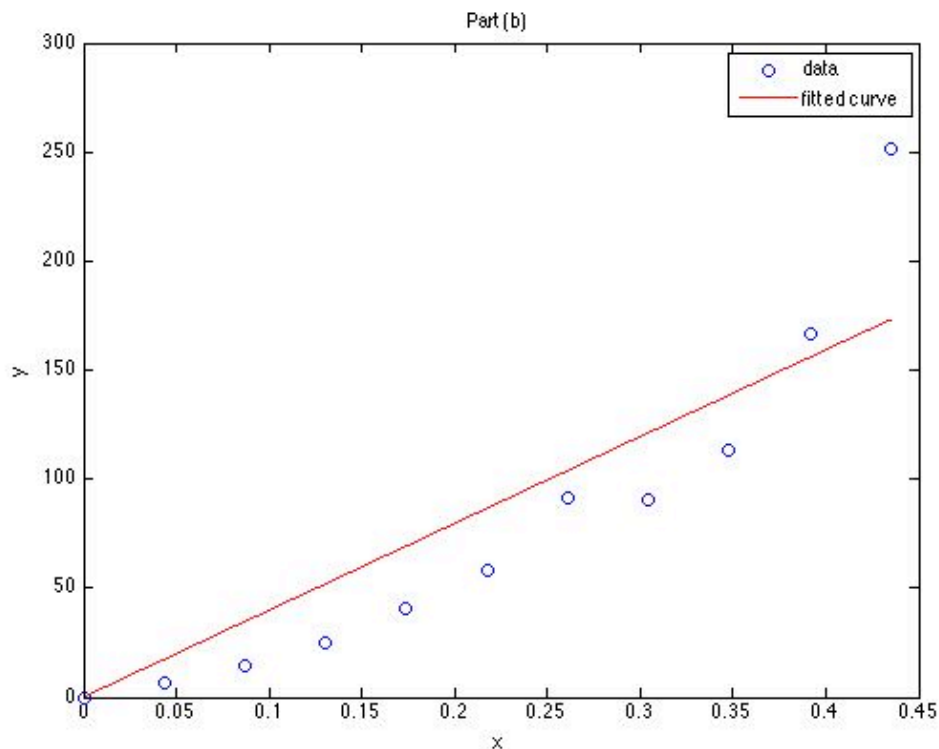


Figure 2. Model plot for part (b) showing the experimental data as points and the model's predictions as a line.

Clearly this fit is not as good as that in part (a). The correlation coefficient is not as close to 1.0 and a trend in the deviations of the data from the model is evident in Figure 2. That is, the deviations are not random. Thus, not unexpectedly, the second order rate expression is not acceptable as a rate expression.

Calculation Details Using MATLAB

Supplemental Unit S3 presents an overview of linear least squares fitting and three MATLAB script files that implement it. The file named FitLinmSR is used to fit a straight line through the origin, equation (8), to experimental (x,y) data. No editing of the file is required to do so, but 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. Since the slope is equal to the rate coefficient in this problem, no additional calculations are needed after the fitting is complete. The commands for performing these tasks can be entered at the MATLAB command prompt, but here they have been

recorded in the MATLAB file named Example_15_1.m which accompanies this solution. The contents of that file are presented in Listing 1.

```
% MATLAB file used in the solution of Example 15.1 of
% "A First Course on Kinetics and Reaction Engineering."

% Data provided in the problem statement, in consistent units
V=2.3; % L
T=848.0; % K
P0=1036.0; % Torr
Rgas=62.366; % L-Torr/mol/K
t = [0; 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; 0.8; 0.9; 1.0]; % ms
Pz = [0; 121; 202; 275; 336; 375; 417; 416; 433; 457; 476]; % Torr

% Calculate x and y for part (a)
disp('Part (a)');
nA0 = P0*V/Rgas/T;
extent = (V/Rgas/T)*Pz;
nA = nA0 - 2*extent;
x = -t;
y_hat = log(nA/nA0);

figure;
% 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;
title('Part (a)');

% Calculate x and y for part (b) and fit a straight line through the
origin
% to the resulting data
disp('Part (b)');
x = t/V;
y_hat = (1./nA - 1/nA0);
figure
FitLinmSR;
title('Part (b)');
```

Listing 1. MATLAB code that uses FitLinmSR to fit a straight line through the origin to the x-y data of this example.

As can be seen in the listing, the code begins with the entry of all the data provided in the problem statement, making sure the units are consistent. The values of x and y are next calculated for part (a) after which equation (8) is fit to the results by executing FitLinmSR. The process is then repeated for part (b). Upon execution, Figures 1 and 2 are produced along with the output shown in Listing 2.


```
>> Example_15_1
Part (a)
r_squared =
    0.9881
m =
    2.4458
m_u =
    0.0989
Part (b)
r_squared =
    0.8170
m =
    398.1907
m_u =
    86.0237
```

Listing 2. Output from the execution of Example_15_1.m.