

A First Course on Kinetics and Reaction Engineering

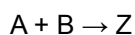
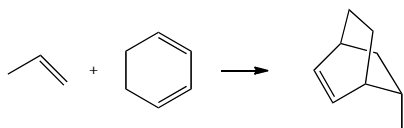
Example 15.2

Problem Purpose

This example illustrates the use of the integral method of data analysis with a rate expression that depends on the concentrations of more than one species.

Problem Statement

Reaction (1) was studied at 600 K in a constant volume batch reactor. The initial charge to the reactor consisted of 150 Torr of A and 450 Torr of B. A spectrophotometer was used to record a signal from which the fractional conversion of A could be recorded versus time. Use the data given in the table below to test the validity of the rate expression, $r = k \cdot C_A \cdot C_B$, and find the “best” value for k . Use the integral method of data analysis.



(1)

<i>time (h)</i>	<i>fractional conversion of A</i>
23.1	0.17
33.3	0.22
58.2	0.34
69.7	0.41
90.7	0.49
127.7	0.58
192.1	0.7
240.6	0.77
281.1	0.83

Problem Analysis

This problem gives batch reactor kinetics data for a gas phase reaction and asks us to test a specified rate expression 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 model and decide whether it is sufficiently accurate.

Problem Solution

For an isothermal batch reactor with a single reaction taking place a mole balance design equation written for any reactant or product is all that is needed to model the reactor. For this problem, if the

reactant, A, is chosen, equation (2) results. The problem specifies the rate expression in equation (3) as the one to be tested, so it is substituted into the mole balance design equation, leading to equation (4). (Note: the rate expression given in the problem statement is for the generalized rate of reaction (1), r_1 . Equation (2) requires the rate of reaction (1) with respect to A. That is found by multiplying the generalized rate by the stoichiometric coefficient of A, as discussed in Unit 4. That is why there is a negative sign in equation (3); the stoichiometric coefficient of A is negative one.)

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

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

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

Since we are instructed to use an integral analysis, this equation must be integrated to convert the differential equation into an algebraic 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 and the concentration of B will change as the reaction proceeds. The definition of concentration can be used to re-express these concentrations in terms of the moles of A and B, equations (5) and (6). This is all that is needed for the concentration of A, but the moles of B in equation (6) will need to be expressed in terms of the moles of A because the moles of B will change as the reaction proceeds.

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

$$C_B = \frac{n_B}{V} \quad (6)$$

The moles of B can be related to the moles of A through the extent of reaction (or a mole table), leading to equation (7).

$$\xi = \frac{n_i - n_i^0}{\nu_i} = \frac{n_A - n_A^0}{\nu_A} = \frac{n_B - n_B^0}{\nu_B}$$

$$\frac{n_A - n_A^0}{-1} = \frac{n_B - n_B^0}{-1}$$

$$n_B = n_A - n_A^0 + n_B^0 \quad (7)$$

After substitution of equations (5) through (7), the design equation contains no variables other than the moles of A and time, equation (8). Therefore, equation (8) now can be integrated by separation of the variables. This leads to the integrated form of the design equation given in equation (9). When integrating

the design equation, it is important to remember to evaluate the integrand at both the upper and lower limits.

$$\frac{dn_A}{dt} = -kV \left(\frac{n_A}{V} \right) \left(\frac{n_A - n_A^0 + n_B^0}{V} \right) \quad (8)$$

$$\int_{n_A^0}^{n_A} \frac{dn_A}{n_A (n_A - n_A^0 + n_B^0)} = \frac{-k}{V} \int_0^t dt$$

$$\frac{1}{n_A^0 - n_B^0} \ln \left(\frac{n_A^0 (n_A - n_A^0 + n_B^0)}{n_B^0 n_A} \right) = \frac{-kt}{V} \quad (9)$$

The next step in the process is to fit equation (9) to the experimental data. Equation (9) has the form of a straight line through the origin, equation (10), as can be seen if x , y and m are defined as given in equations (11) through (13).

$$y = mx \quad (10)$$

$$x = \frac{-t}{V} \quad (11)$$

$$y = \frac{1}{n_A^0 - n_B^0} \ln \left(\frac{n_A^0 (n_A - n_A^0 + n_B^0)}{n_B^0 n_A} \right) \quad (12)$$

$$m = k \quad (13)$$

Since the model equation 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)

In order to calculate values of y and x for each data point, we will first need to calculate the reaction volume, the initial moles of A, the initial moles of B and the moles of A at the sampled time for each data point; the reaction time is given. Looking at the problem statement, we can see that every variable that is provided is an intensive variable. This means that we are free to assume a basis for our calculations. In this case, a convenient basis is the reaction volume; we will choose $V = 1$ L as our basis. Since all of the data points are for the same experimental run, the initial moles of A and the initial moles of B are the

same for every data point. The problem specifies the initial pressures of A and B, and that information can be used, along with the ideal gas law, to calculate the initial moles of A and B according to equations (14) and (15). The problem does not provide the moles of A at each sampled time, but it does provide the fractional conversion of A which allows the moles of A to be calculated using equation (16) and the previously calculated initial moles of A.

$$n_A^0 = \frac{P_A^0 V}{RT} \quad (14)$$

$$n_B^0 = \frac{P_B^0 V}{RT} \quad (15)$$

$$n_A = n_A^0 (1 - f_A) \quad (16)$$

Thus, we can generate a set of (x,y) data. 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 0.997 and the best value of the slope, m , is equal to $0.629 \pm 0.017 \text{ L mol}^{-1} \text{ h}^{-1}$ (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.

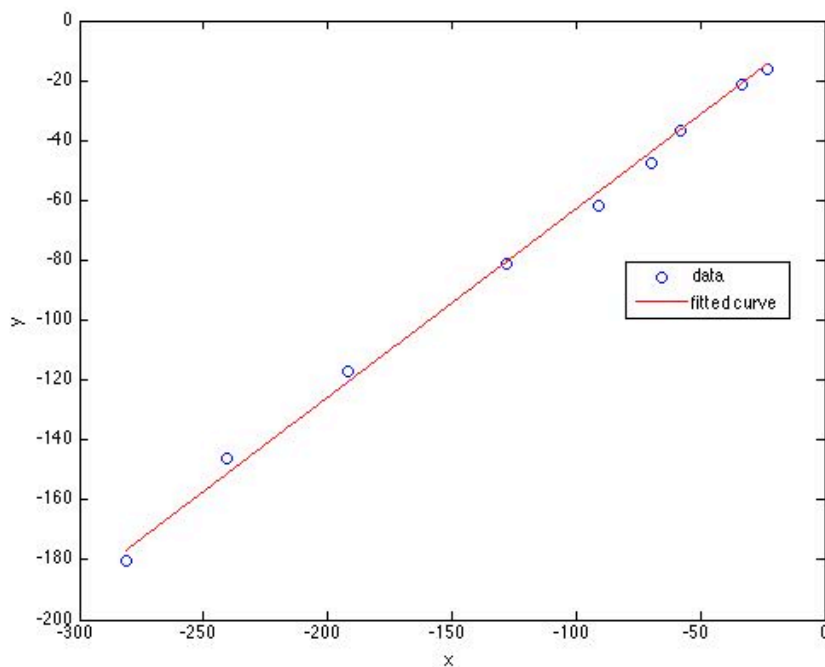


Figure 1. Model plot showing the experimental data as points and the model's predictions as a line.

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 0.997 indicates a very good fit. Additionally, if the fit is accurate, then the scatter of the experimental data about the line representing 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, shows this to be true. Thus, the model does appear to be sufficiently accurate and therefore the second order rate expression that was tested is a good rate expression for this reaction. Normally it would be necessary to calculate the value of the rate coefficient and its uncertainty from the slope and its uncertainty, but in this problem, the slope is equal to the rate coefficient. Hence k is equal to $0.629 \pm 0.017 \text{ L mol}^{-1} \text{ h}^{-1}$.

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 (10), 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_2.m which accompanies this solution. The contents of that file are presented in Listing 1.

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, after which equation (10) is fit to the results. Upon execution, Figure 1 is produced along with the output shown in Listing 2.

A First Course on Kinetics and Reaction Engineering

```
% MATLAB file used in the solution of Example 15.2 of
% "A First Course on Kinetics and Reaction Engineering."

% Data provided in the problem statement, in consistent units
T=600.; % K
P0A=150.; % Torr
P0B=450.; % Torr
Rgas=62.366; % Torr-L/(mol-K)
V=1; % L (basis)
t=[23.1 33.3 58.2 69.7 90.7 127.7 192.1 240.6 281.1]'; % h
f=[0.17 0.22 0.34 0.41 0.49 0.58 0.7 0.77 0.83]';

% Calculate x and y as described in the solution
nA0=P0A*V/Rgas/T;
nB0=P0B*V/Rgas/T;
nA = nA0*(1-f);
x = -t/V;
y_hat = (1.0/(nA0-nB0))*log(nA0/nB0./nA.*(nA-nA0+nB0));

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

```
>> Example_15_2
r_squared =
    0.9965

m =
    0.6291

m_u =
    0.0172
```

Listing 2. Output from the execution of Example_15_2.m.