

A First Course on Kinetics and Reaction Engineering

Example 15.3

Problem Purpose

This problem illustrates the use of the method of half lives to check whether a reaction obeys simple n^{th} order kinetics.

Problem Statement

Neopentane at low pressures decomposes at temperatures above ca. 450 °C, producing methane. Several reactions actually take place, but the rate of neopentane conversion can be modeled as if it is a single reaction as given in equation (1) with a rate expression of the type given in equation (2). The exponent, n , in equation (2) must be determined experimentally. To do so, the half-life of neopentane was measured at 500 °C in a set of experiments using different initial pressures of neopentane. A constant volume batch reactor was used in these experiments. Using the resulting data given below, determine the order of the reaction.



$$-r_{\text{C}_5\text{H}_{12}} = kC_{\text{C}_5\text{H}_{12}}^n \quad (2)$$

Initial Pressure (mm Hg)	Half Life (h)
25	4.51
73	2.61
136	1.92
186	1.61
215	1.50

Problem Solution

As mentioned in the information reading, if a reaction is first order, that is, if n in equation (2) is equal to one, then the half-life will be independent of the initial concentration. It is clear from the data table that as the initial pressure (and consequently the initial concentration) varies, the half life changes. If the reaction is not first order, then the half-life is related to the initial concentration according to equation (3).

$$\ln(t_{1/2}) = \ln\left(\frac{(2^{n-1} - 1)}{k(n-1)}\right) + (1-n)\ln(C_A^0) \quad (3)$$

If y and x are defined as in equations (4) and (5), equation (3) can be seen to have the form of a straight line, equation (6) with a slope, m , given by equation (7) and a y -intercept given by equation (8). Therefore, to find the reaction order we will calculate y and x for each data point, plot the results, and fit a straight line to the data. If the fit is good, the reaction order can be calculated from the slope.

$$y = \ln(t_{1/2}) \quad (4)$$

$$x = \ln(C_A^0) \quad (5)$$

$$y = mx + b \quad (6)$$

$$m = (1 - n) \quad (7)$$

$$b = \ln\left(\frac{(2^{n-1} - 1)}{k(n-1)}\right) \quad (8)$$

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)

Calculation of y is straightforward since the problem statement gives the values of the half-life. To calculate x , the initial concentration of A is needed. That can be found from the initial pressure using the ideal gas law, leading to equation (9).

$$x = \ln(C_A^0) = \ln\left(\frac{P_A^0}{RT}\right) \quad (9)$$

Thus, we can generate a set of (x,y) data using equations (4) and (9). The model has only one independent variable, x , and it *does* 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 1.0, the best value of the slope, m , is equal to -0.51 ± 0.01 and the best value of the y -intercept, b , is equal to -2.36 ± 0.08 (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.

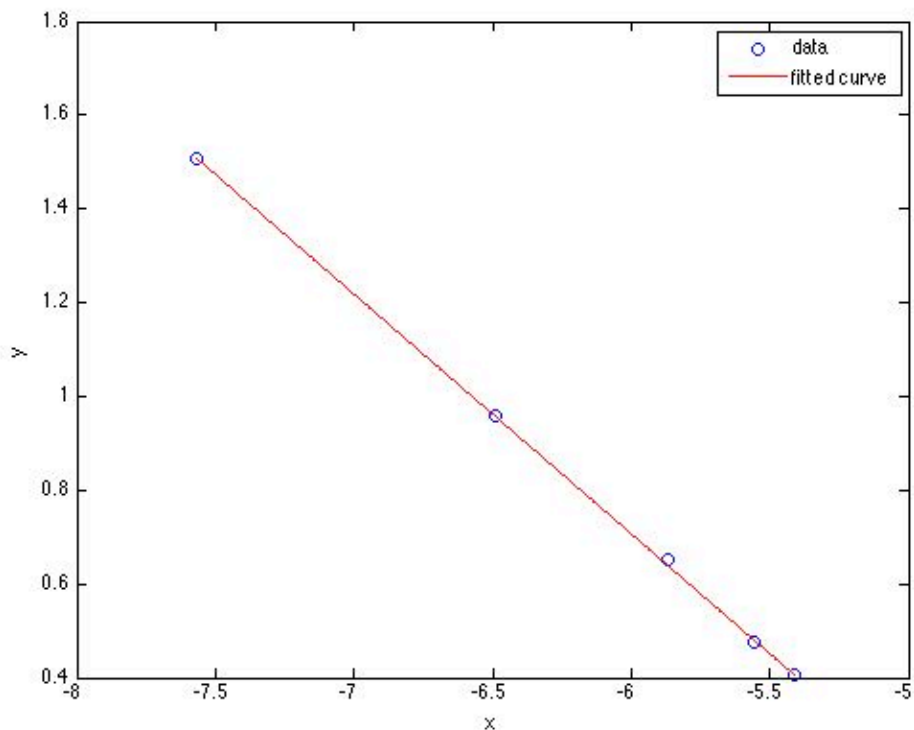


Figure 1. Model plot showing the experimental data as points and the model's predictions as a line.

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 ~ 1.0 indicates an excellent 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 experimental data are accurately described by equation (3).

It remains to calculate the reaction order and its uncertainty. It is trivial to calculate the reaction order using equation (7). A differential error analysis shows that if a model parameter, p , is related to the slope, m , and intercept, b , of a linearized form of the model, as in equation (10), then the uncertainty in that parameter, λ_p , is related to the slope, intercept and their uncertainties, λ_m and λ_b , according to equation (11). Applying that relationship to the present problem shows that the uncertainty in n should be calculated using equation (12). Applying these relationships one finds that the reaction order is 1.51 ± 0.01 .

$$p = f(m, b) \quad (10)$$

$$\lambda_p = \sqrt{\left(\frac{\partial f}{\partial m}\right)^2 \lambda_m^2 + \left(\frac{\partial f}{\partial b}\right)^2 \lambda_b^2} \quad (11)$$

$$\lambda_n = \lambda_m \quad (12)$$

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 FitLinmbSR is used to fit a straight line, equation (6), 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 FitLinmbSR, 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 , the 95% confidence limits on the slope, λ_m , as m_u , the intercept, b , as b and the 95% confidence limits on the intercept, λ_b , as b_u . It will also generate a model plot. Once these values are available, the best value for n and its uncertainty can be computed using equations (7) and (12). The commands for performing all these tasks can be entered at the MATLAB command prompt, but here they have been recorded in the MATLAB file named 15_Example_3.m which accompanies this solution. Listing 1 shows the code from 15_Example_3.m and Listing 2 shows the output that it produces, except for the model plot, which was presented previously as Figure 1.

```
% MATLAB file used in the solution of Example 15.3 of
% "A First Course on Kinetics and Reaction Engineering."

% Data provided in the problem statement, in consistent units
T=500.+273.15; % K
Rgas=62.366; % (L-mm Hg)/(mol-K0
P0=[25 73 136 186 215]'; % mm Hg
hl=[4.51 2.61 1.92 1.61 1.50]'; % h

% Calculate x and y as described in the solution
x = log(P0/Rgas/T);
y_hat = log(hl);

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

% Calculate the reaction order and its uncertainty
order = 1 - m
order_u = m_u
```

Listing 1. Contents of the file Example_15_3.m used to solve this problem using MATLAB.

The code begins with the entry of all of the data provided in the problem statement, making sure the units are consistent. The values of x and y are next calculated and stored in the vectors x and y_hat .

FitLinmbSR is then used to fit equation (6) to the data and obtain the best value for m and its uncertainty. Finally, the reaction order and its uncertainty are calculated via equations (7) and (12).

```
>> Example_15_3
r_squared =
    0.9998
m =
   -0.5111
m_u =
    0.0127
b =
   -2.3588
b_u =
    0.0793
order =
    1.5111
order_u =
    0.0127
```

Listing 2. Output generated upon execution of [filename].