

A First Course on Kinetics and Reaction Engineering

Example 14.1

Problem Purpose

This problem illustrates the testing of a rate expression using differential analysis of batch reactor initial rate data.

Problem Statement

The initial rate of reaction between formaldehyde and ammonia in aqueous solution was measured in a series of experiments varying the weight fraction of ammonia in solution while holding the formaldehyde concentration constant. The experiments were performed at 0°C in a perfectly mixed batch reactor with a volume of 1 L. Use the initial rate data, given below, to ascertain the order of the reaction with respect to ammonia.

<i>Initial NH₃ Content (wt. %)</i>	<i>Initial Rate (mol HCHO min⁻¹ L⁻¹)</i>
0.8	0.025
0.6	0.02
0.41	0.01
0.2	0.002
0.016	0.00002

Problem Analysis

This problem provides initial rates as a function of ammonia concentration. Initial rates are equivalent to estimated values of the derivative that appears in the batch reactor mole balance design equation. Therefore, the data presented here can be used in a differential data analysis.

Problem Solution

One thing to notice about this problem is that it only asks us to determine the order of the reaction with respect to ammonia. It does not ask us to test any particular rate expression, nor does it ask for the reaction order with respect to any reagent other than ammonia. Differential data analysis using initial rates is ideal for answering this type of question. By using initial rates, the changes in the concentrations of species other than ammonia don't matter *as long as the initial concentrations of those species are each constant throughout all of the experiments*. To illustrate, consider the experiments performed here. Five different experiments were performed, and each experiment used a starting solution that contained the same amount of formaldehyde but different amounts of ammonia. The rates, or equivalently, the derivatives of the moles of a reagent with respect to time, that are estimated at time zero of those five experiments each correspond to the same concentration of formaldehyde, but a different concentration of ammonia. Contrast this to a single batch kinetics experiment that started with the same concentration of

formaldehyde, but where the derivative was estimated at several different elapsed times. At each elapsed time, both the formaldehyde concentration and the ammonia concentration would be different from their initial concentrations, and so the estimated values of the derivative would each correspond to a different concentration of ammonia and a different concentration of formaldehyde.

Looking at the units in the data table, we can see that the initial rates provided in the problem statement are equal to the derivative of the moles of formaldehyde per L. That is, if we write the batch reactor mole balance design equation for formaldehyde as in equation (1), the quantity in the data table is the value of the left hand side of equation (1).

$$\frac{1}{V} \frac{dn_{HCHO}}{dt} = r_{HCHO} \quad (1)$$

We are asked to find the reaction order with respect to ammonia. That is, we are asked to find the value of α when the rate expression takes the form shown in equation (2). In equation (2) the function f gives the dependence of the rate on all other variables including temperature and the concentrations of formaldehyde and any additional species other than ammonia. Since each of the other variables has the same value in every experiment, the function f will be a constant for the data set being considered here.

$$r_{HCHO} = f(T, C_i) C_{NH_3}^\alpha \quad (i \neq NH_3) \quad (2)$$

To find the best value of α , we will substitute the rate expression given in equation (2) into the mole balance design equation given in equation (1) and fit the resulting equation to the experimental data. Before doing so, notice that the problem does not list the concentration of ammonia for each experiment, but instead it lists the weight percent. If we assume the density of the liquid phase to be constant, the concentration of ammonia can be found using equation (3), where ρ represents the liquid density, M_{NH_3} represents the molecular weight of ammonia and w_{NH_3} represents the given weight fraction of ammonia. Substitution of equation (3) into equation (2) followed by substitution of the result into equation (1) leads to equation (4). Note that the quantity in the square brackets in equation (4) is a constant, so it can be replaced with a constant that we will arbitrarily call J . Substitution of this value and recognition that the left hand side of equation (4) is just the initial rate, r_{init} , given in the problem statement leads to equation (5).

$$C_{NH_3} = \frac{n_{NH_3}}{V} = \frac{\left(\frac{V \rho w_{NH_3}}{M_{NH_3}} \right)}{V} = \frac{\rho}{M_{NH_3}} w_{NH_3} \quad (3)$$

$$\frac{1}{V} \frac{dn_{HCHO}}{dt} = \left[f(T, C_i) \left(\frac{\rho}{M_{NH_3}} \right)^\alpha \right] w_{NH_3}^\alpha \quad (4)$$

$$r_{init} = J w_{NH_3}^\alpha \quad (5)$$

We next need to fit equation (5) to the experimental data, but that will be easier if equation (5) is first linearized. Taking the logarithm of each side of equation (5) leads to equation (6), which is a linear equation. That is, if x , y , m and b are defined as in equations (7) through (10), then equation (6) becomes equation (11), which is clearly linear.

$$\ln(r_{init}) = \alpha \ln(w_{NH_3}) + \ln(J) \quad (6)$$

$$x = \ln(w_{NH_3}) \quad (7)$$

$$y = \ln(r_{init}) \quad (8)$$

$$m = \alpha \quad (9)$$

$$b = \ln(J) \quad (10)$$

$$y = mx + b \quad (11)$$

At this point, linear least squares can be used to fit equation (11) 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 this case it is trivially easy to calculate values of x and y for each of the experimental data points by application of equations (7) and (8), and so we can generate the necessary set of (x,y) data. 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 0.9975, the best value of the slope, m , is equal to 1.87 ± 0.17 and the best value of the y -intercept, b , is equal to -3.09 ± 0.35 (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.

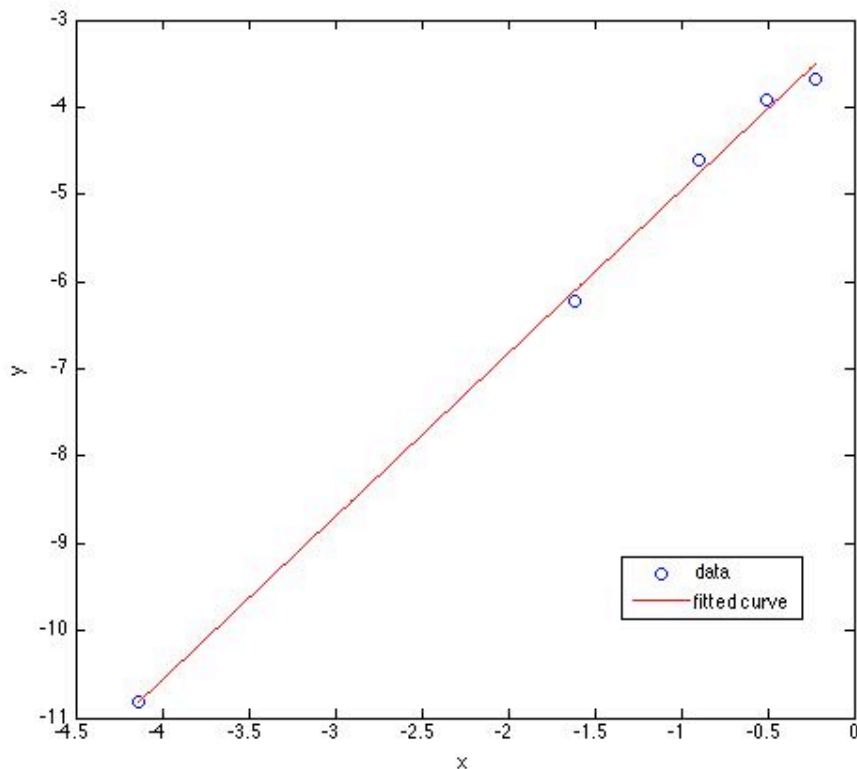


Figure 1. Model plot showing the experimental data as points and the model's predictions as a line.

Before the best values for m and b 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 0.9975 indicates an excellent 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 model does appear to be sufficiently accurate and the values of the slope and intercept can be accepted.

Normally it is necessary to calculate the values of the kinetics parameters and their uncertainties from the slope and intercept. However, in this problem we are only interested in one parameter, α , and according to equation (9) α is exactly equal to the slope (1.87 ± 0.17), so we are finished.

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 and an intercept, so the script file named FitLinmbSR 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 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 the model plot, Figure 1. Once these values are available, the best values for the kinetics parameters can be calculated, but in this problem that isn't necessary. 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 Example_14_1.m which accompanies this solution. Listing 1 shows the code from Example_14_1.m and Listing 2 shows the output that it produces, except for the model plot.

```
% MATLAB file used in the solution of Example 14.1 of
% "A First Course on Kinetics and Reaction Engineering."

% Data provided in the problem statement, in consistent units
wtPctNH3 = [0.8; 0.6; 0.41; 0.2; 0.016];
r_init = [0.025; 0.02; 0.01; 0.002; 0.00002]; % mol/min/L

% Calculate x and y using equations 7 and 8 from the solution

x = log(wtPctNH3);
y_hat = log(r_init);

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

% In this case, the desired parameter, alpha, is equal to the slope so
alpha = m
alpha_u = m_u
```

Listing 1. Contents of the file Example_14_1.m used to solve this problem using MATLAB.

```
>> Example_14_1
```

```
r_squared =
```

```
0.9975
```

```
m =
```

```
1.8697
```

```
m_u =
```

```
0.1720
```

```
b =
```

```
-3.0920
```

```
b_u =
```

```
0.3509
```

```
alpha =
```

```
1.8697
```

```
alpha_u =
```

```
0.1720
```

Listing 2. Output generated upon execution of Example_14_1.m.