

A First Course on Kinetics and Reaction Engineering

Example 4.6

Problem Purpose

This example illustrates the use of an Arrhenius plot to determine the best values of a pre-exponential factor and an activation energy.

Problem Statement

Kinetic studies were performed at a number of different temperatures to find the value of a second order rate coefficient at each of the temperatures. The results are given in the table below. Determine whether the temperature dependence of this rate coefficient is consistent with the Arrhenius equation, and find the best values for the pre-exponential factor and the activation energy.

<i>Temperature</i> (°C)	<i>Rate Coefficient</i> (L mol ⁻¹ min ⁻¹)
10	2.63 x 10 ⁻⁴
22	4.78 x 10 ⁻⁴
40	1.52 x 10 ⁻³
54	4.18 x 10 ⁻³
65	9.07 x 10 ⁻³
78	2.14 x 10 ⁻²
89	4.2 x 10 ⁻²
103	9.42 x 10 ⁻²

Problem Analysis

This problem clearly involves the use of the Arrhenius expression for the temperature dependence of a rate coefficient. The Arrhenius expression contains two unknown constants, the pre-exponential factor and the activation energy. Here we are given the value of the rate coefficient at eight different temperatures. If we substituted each of those eight data points into the Arrhenius expression, we would have eight equations in two unknowns. Unless the data were “made up” using the Arrhenius expression, there won’t be a single value of the pre-exponential factor and a single value of the activation energy that together satisfy the eight equations. Instead, we need to find the “best” values for those two parameters, i. e. the values that result in the smallest overall error when predicting the values of the eight rate coefficients. To do this, we must fit the Arrhenius expression to the experimental data. (If you aren’t familiar with least-squares fitting of a model to data, see Supplemental Unit S3.)

Problem Solution

The Arrhenius expression for the temperature dependence of a rate coefficient is given in equation (1), where the temperature must be in absolute units. For this problem, the subscript j can be dropped since there is only one reaction under consideration. Taking the natural logarithm of each side of equation (1) leads to equation (2). When written as in equation (2), it can be seen to take the form of a straight line, equation (3), if y and x are defined as shown in equations (4) and (5).

$$k_j = k_{0,j} \exp\left\{\frac{-E_j}{RT}\right\} \quad (1)$$

$$\ln(k) = \frac{-E}{R}\left(\frac{1}{T}\right) + \ln(k_0) \quad (2)$$

$$y = mx + b \quad (3)$$

$$y = \ln(k) \quad (4)$$

$$x = \frac{1}{T} \quad (5)$$

In this problem, we are asked to test whether this mathematical model offers an accurate representation of the experimental data. Problems of this type can be solved by fitting the model equation to the data and then assessing the quality of the fit statistically and visually. In this particular problem, the model equation 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)

Clearly, there is only one independent variable in equation (3), and it does include an intercept. For each row in the data table, corresponding values of x and y can be computed using equations (4) and (5). These will constitute the experimental data set used in the fitting. When this information and input data are provided to whichever linear least squares fitting tool one chooses to employ, the resulting output shows that the correlation coefficient, r^2 , is greater than 0.99, the best value of the slope, m , is equal to $(-6.88 \pm 0.63) \times 10^3$ K and the best value of the y-intercept, b , is equal to 15.8 ± 1.9 . (Here the uncertainties are the 95% confidence limits based on 8 data, other least squares fitting tools might provide different measures of the uncertainties in the fitted parameter values.) In most cases, a model plot like that shown in Figure 1 is also provided, but if such a plot is not provided, one can be generated easily.

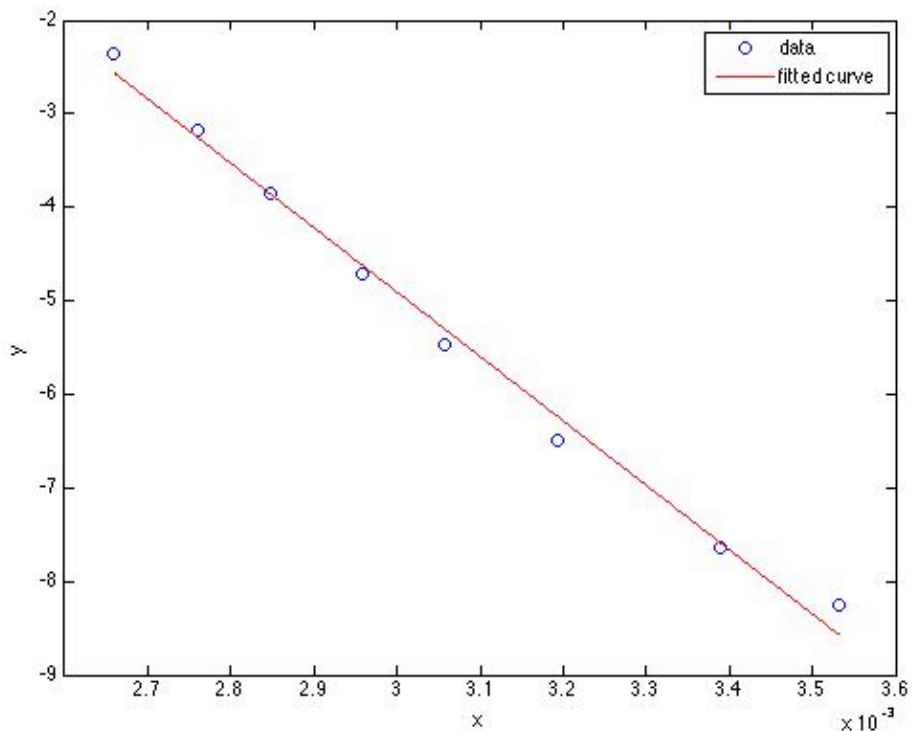


Figure 1. Model plot showing the experimental data as points and the model's predictions as a line.

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 0.99 indicates a 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 model does appear to be sufficiently accurate and the values of the slope and intercept can be accepted.

The problem asks for the best values for the pre-exponential factor and activation energy, not the best values of the slope and intercept of the Arrhenius plot. Comparing equation (3) to equation (2), and noting the definitions of x and y , equations (4) and (5), it can be seen that the slope is related to the activation energy as given in equation (6) and the intercept is related to the pre-exponential factor as given in 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 (8), 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 (9). Applying that relationship to the present problem shows that the uncertainties in E and k_0 should be calculated using equations (10) and (11).

$$m = \frac{-E}{R} \Rightarrow E = -mR \quad (6)$$

$$b = \ln(k_0) \Rightarrow k_0 = e^b \quad (7)$$

$$p = f(m, b) \quad (8)$$

$$\lambda_p = \sqrt{\left(\frac{\partial f}{\partial m}\right)^2 \lambda_m^2 + \left(\frac{\partial f}{\partial b}\right)^2 \lambda_b^2} \quad (9)$$

$$\lambda_E = R\lambda_m \quad (10)$$

$$\lambda_{k_0} = e^b \lambda_b \quad (11)$$

Thus, using the values of m , λ_m , b and λ_b given above from fitting the linear form of the Arrhenius expression to the data, the best values of the activation energy and the pre-exponential factor can be calculated to be $E = 57.3 \pm 5.2 \text{ kJ mol}^{-1}$ and $k_0 = (7.0 \pm 13.4) \times 10^6 \text{ L mol}^{-1} \text{ min}^{-1}$.

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 . This could be done at the MATLAB command prompt, but here I have created a MATLAB script that accomplishes these tasks and then executes FitLinmbSR. That script file is provided as Example_4_6.m; its contents are presented in Listing 1. In that file the data from the table in the problem statement are entered as vectors named t and k . The vector t contains the temperatures in degrees Celsius; a vector named T that contains the corresponding temperatures in Kelvins is generated, and from that, the vector x is generated using equation (5). The vector k contains the rate coefficients; it is used to generate the vector y_hat using equation (4). The script FitLinmbSR is then called to perform the fitting. It returns 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 also generates a model

plot (Figure 1). Finally, best values of the activation energy and the pre-exponential factor, along with their 95% confidence limits, are calculated using equations (6), (7), (10) and (11).

```
% MATLAB file used in the solution of Example 4.6 of "A First Course on
% Kinetics and Reaction Engineering."

% Enter the data from the table and the gas constant
R = 8.3144e-3; % kJ/mol/K
t = [10; 22; 40; 54; 65; 78; 89; 103];
k = [2.63E-04; 4.78E-04; 1.52E-03; 4.18E-03; 9.07E-03; 2.14E-02;...
     4.20E-02; 9.42E-02];

% Convert the temperatures to K and calculate the x values
T = t + 273.15;
x = 1./T;

% Calculate the y_hat values
y_hat = log(k);

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

% Calculate the activation energy and its 95% confidence limits
E = -m*R
lambda_E = R*m_u

% Calculate the pre-exponential factor and its 95% confidence limits
k0 = exp(b)
lambda_k0 = b_u*exp(b)
```

Listing 1. Contents of MATLAB script file Example_4_6.m used in the solution of this problem.

Listing 2 shows the results of running Example_4_6.m from the MATLAB command window.

```
>> Example_4_6  
  
r_squared =  
    0.9917  
  
m =  
-6.8862e+03  
  
m_u =  
    629.4527  
  
b =  
    15.7565  
  
b_u =  
    1.9278  
  
E =  
    57.2548  
  
lambda_E =  
    5.2335  
  
k0 =  
    6.9657e+06  
  
lambda_k0 =  
    1.3429e+07
```

Listing 2. MATLAB command window output upon running Example_4_6.m