Activity 4.2 Solution

In class, you will work in a group of three to set up the solution to one of the following questions:

1. The rate coefficient for a reaction is 0.304 min⁻¹ at 30 °C. The activation energy for that rate coefficient is 61.1 kJ mol⁻¹. Assuming Arrhenius behavior, what is the rate coefficient at 65 °C?
2. If a rate coefficient doubles when the temperature is raised from 22 °C to 45 °C, what is the value of the corresponding activation energy? If the rate coefficient at 40 °C is 3.07 x 10⁻⁴ s⁻¹, what is its value at 32 °C?
3. The rate coefficients for a particular reaction vary with temperature as follows:

T (°C)	10³ x k (min⁻¹)
25	0.8
35	3.8
45	15.1
55	46.7
65	151

Determine the pre-exponential factor and the activation energy.

Solution

The Arrhenius expression, equation (1), is most commonly used to describe the temperature dependence of rate coefficients. Absolute temperatures must be used in the Arrhenius equation.

$$k = k_0 \exp\left(\frac{-E}{RT}\right)$$
(1)

1. In the first question, we are given the value of the activation energy, E = 61.1 kJ mol⁻¹. We are also given the value of k = 0.304 min⁻¹ at a temperature of 30 °C (303 K). Substitution of these known quantities into equation (1) allows the pre-exponential factor, k_0, to be computed.

$$0.304 \text{ min}^{-1} = k_0 \exp\left(\frac{-61.1 \text{ kJ mol}^{-1} \times 1000 \text{ J kJ}^{-1}}{8.3144 \text{ J mol}^{-1} \text{ K}^{-1} \times 303 \text{ K}}\right)$$

k_0 = 1.04 x 10¹⁰ min⁻¹

Now, knowing k_0 and E, equation (1) can be used to compute the value of k at 65 °C (338 K).

$$k = \left(1.04 \times 10^{10} \text{ min}^{-1}\right) \exp\left(\frac{-61.1 \text{ kJ mol}^{-1} \times 1000 \text{ J kJ}^{-1}}{8.3144 \text{ J mol}^{-1} \text{ K}^{-1} \times 338 \text{ K}}\right)$$

k = 3.78 min^{-1}

2. The second question tells us that a rate coefficient doubles when the temperature increases from 22 °C (295 K) to 45 °C (318 K). This is enough information to answer the first question. To do so, we set the ratio of the two rate coefficients equal to 2, and write each in terms of the Arrhenius expression. The pre-exponential factor, being a constant, cancels out and we can calculate the activation energy.

$$2 = \frac{k(318 \text{ K})}{k(295 \text{ K})} = \frac{k_0 \exp\left(\dfrac{-E}{R(318 \text{ K})}\right)}{k_0 \exp\left(\dfrac{-E}{R(295 \text{ K})}\right)} = \exp\left(\frac{E}{R(295 \text{ K})} - \frac{E}{R(318 \text{ K})}\right)$$

$$\ln(2) = \frac{E}{R}\left(\frac{1}{(295 \text{ K})} - \frac{1}{(318 \text{ K})}\right)$$

E = 23.5 kJ mol^{-1}

Knowing the activation energy (E = 23.5 kJ mol^{-1}), and being given a value of the rate coefficient (k = 3.07 x 10^{-4} s^{-1}) at one temperature (T = 40 °C =313 K), the pre-exponential factor can be calculated in the same was that it was calculated in the first problem. Doing so gives k_0 = 2.56 s^{-1}.

Then, knowing both the pre-exponential factor (k_0 = 2.56 s^{-1}) and the activation energy (E = 23.5 kJ mol^{-1}), the rate coefficient can be calculated at any other temperature. Doing so at 32 °C (305 K) gives the desired value for the second question.

$$k = k_0 \exp\left(\frac{-E}{RT}\right) = 2.56 \text{ s}^{-1} \times \exp\left(\frac{-23.5 \text{ kJ mol}^{-1} \times 1000 \text{ J kJ}^{-1}}{8.3144 \text{ J mol}^{-1} \text{ K}^{-1} \times 305 \text{ K}}\right)$$

k = 2.42 x 10^{-4} s^{-1}

3. In the third problem we are given experimental data and asked to find the best values for the pre-exponential factor and the activation energy. This is most easily accomplished by first linearizing the Arrhenius equation by taking the log of both sides, giving equation (2). Since E, R and k_0 are constants, equation (2) can be seen to have the form of a straight line, equation (3), if y is equal to the log of the rate coefficient, equation (4) and x is equal to the reciprocal of the temperature, equation (5).

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

$$y = mx + b \tag{3}$$

$$y = \ln\left(k\right) \tag{4}$$

$$x = \frac{1}{T} \tag{5}$$

In this problem, we must test whether a mathematical model offers an accurate representation of 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 equal to 0.9988, the best value of the slope, m, is equal to m = -1.31 ± 0.08 x 10⁴ K and the best value of the y-intercept, b, is equal to 36.9 ± 2.6. (Here the uncertainties are the 95% confidence limits based on 5 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.

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 0.9988 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 model does appear to be sufficiently accurate and the values of the slope and intercept can accepted.
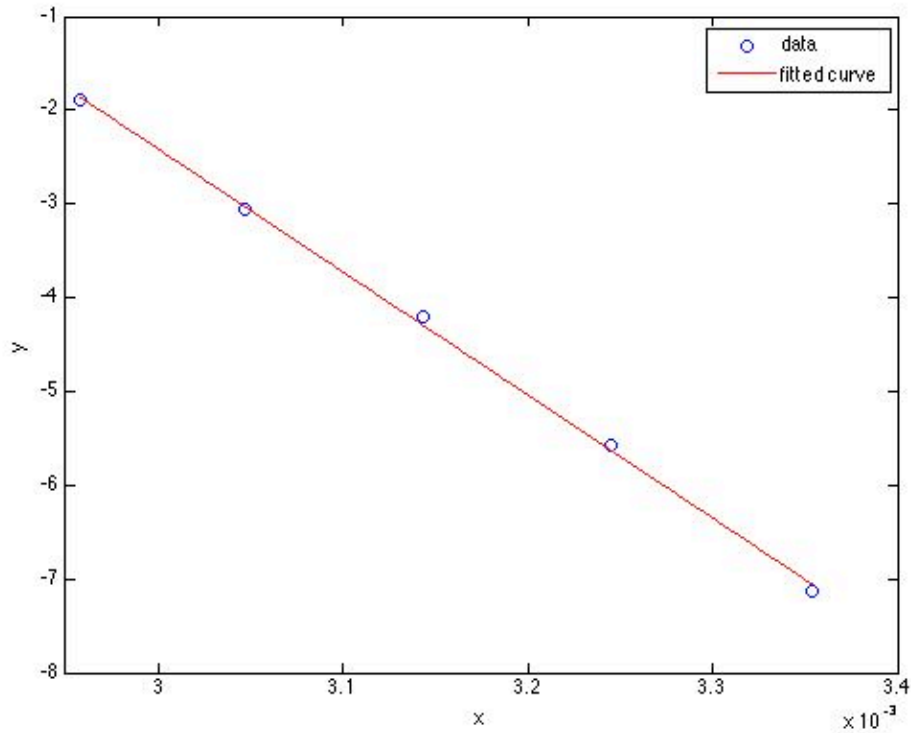
Figure 1. Model plot showing the experimental data as points and the model's predictions as a line.

The slope is related to the activation energy according to equation (6) and the intercept is related to the pre-exponential factor according to 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 from 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).

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

$$b = \ln\left(k_0\right) \quad \Rightarrow \quad k_0 = e^b \tag{7}$$

$$p = f\left(m, b\right) \tag{8}$$

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

$$\lambda_E = R\lambda_m \tag{10}$$

$$\lambda_{k_o} = e^b \lambda_b \tag{11}$$

Using these equations one finds E = 109 ± 7 kJ mol^{-1} and k_0 = (1.11 ± 2.93) x 10^{16} 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 Activity_4_2.m; its contents are presented in Listing 1. (It also performs the calculations for questions 1 and 2.) 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. The output generated upon execution of Activity_4_2.m is shown in Listings 2 through 4; the model plot is shown in Figure 1.

```
% MATLAB file used in the solution of the problem from Activity 4.2 of
% "A First Course on Kinetics and Reaction Engineering."

% Question 1

k = 0.304
T = 30+273 % T must be in K in Arrhenius equation
k0 = k/exp(-61.1*1000/8.3144/T)
k_65 = k0*exp(-61.1*1000/8.3144/(273.15+65))

% Question 2

E = log(2)*8.3144/(1/295-1/318)
k0 = 3.07e-4/exp(-E/8.3144/313)
k = k0*exp(-E/8.3144/305)

% Question 3

% Enter the data from the table and the gas constant
R = 8.3144e-3; % kJ/mol/K
t = [25; 35; 45; 55; 65]
k = [0.8e-3; 3.8e-3; 15.1e-3; 46.7e-3; 151e-3]

% 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. MATLAB template file used in the solution of this problem.

```
>> Activity_4_2

k =
    0.3040

T =
   303

k0 =
   1.0372e+10

k_65 =
    3.7823
```

Listing 2. Output for from Activity_4_2 for question 1.

```
E =
    2.3506e+04

k0 =
    2.5695

k =
    2.4224e-04
```

Listing 3. Output for from Activity_4_2 for question 2.

```
t =
    25
    35
    45
    55
    65

k =
    0.0008
    0.0038
    0.0151
    0.0467
    0.1510

r_squared =
    0.9988

m =
  -1.3118e+04

m_u =
  839.4424

b =
    36.9444

b_u =
    2.6464

E =
  109.0703

lambda_E =
    6.9795

k0 =
    1.1085e+16

lambda_k0 =
    2.9335e+16
```

Listing 4. Output for from Activity_4_2 for question 3.