REB, The Book
Example 3.6.3 Solution

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

Table 1. Rate coefficients measured experimentally at different temperatures.

i (Experiment Number)	T (°C)	k (L mol^{-1} min^{-1})
1	10	2.63 x 10^{-4}
2	22	4.78 x 10^{-4}
3	40	1.52 x 10^{-3}
4	54	4.18 x 10^{-3}
5	65	9.07 x 10^{-3}
6	78	2.14 x 10^{-2}
7	89	4.2 x 10^{-2}
8	103	9.42 x 10^{-2}

The data are available in the file, example_3_6_3_data.csv.

The linearized Arrhenius expression is given by equation (1). When y and x are defined as shown in equation (2), the equation has the form of a straight line, $y = mx + b$, with the slope, m, equal to $\frac{-E}{R}$ and the y-intercept, b, equal to $\ln k_0$.

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

$$
\begin{aligned} y &= \ln\left(k\right) \\ x &= \frac{1}{T} \end{aligned} \quad \Rightarrow \quad y = mx + b \quad \Rightarrow \quad \begin{aligned} m &= \frac{-E}{R} \\ b &= \ln\left(k_0\right) \end{aligned} \tag{2}
$$

After converting the temperature from °C to K, the data in Table 1 were used to calculate corresponding sets of values of $\underline{x}$ and $\underline{y}$. Linear least squares was then used to find the slope and intercept of the best straight line through the resulting data. The resulting Arrhenius plot is shown in Figure 1.

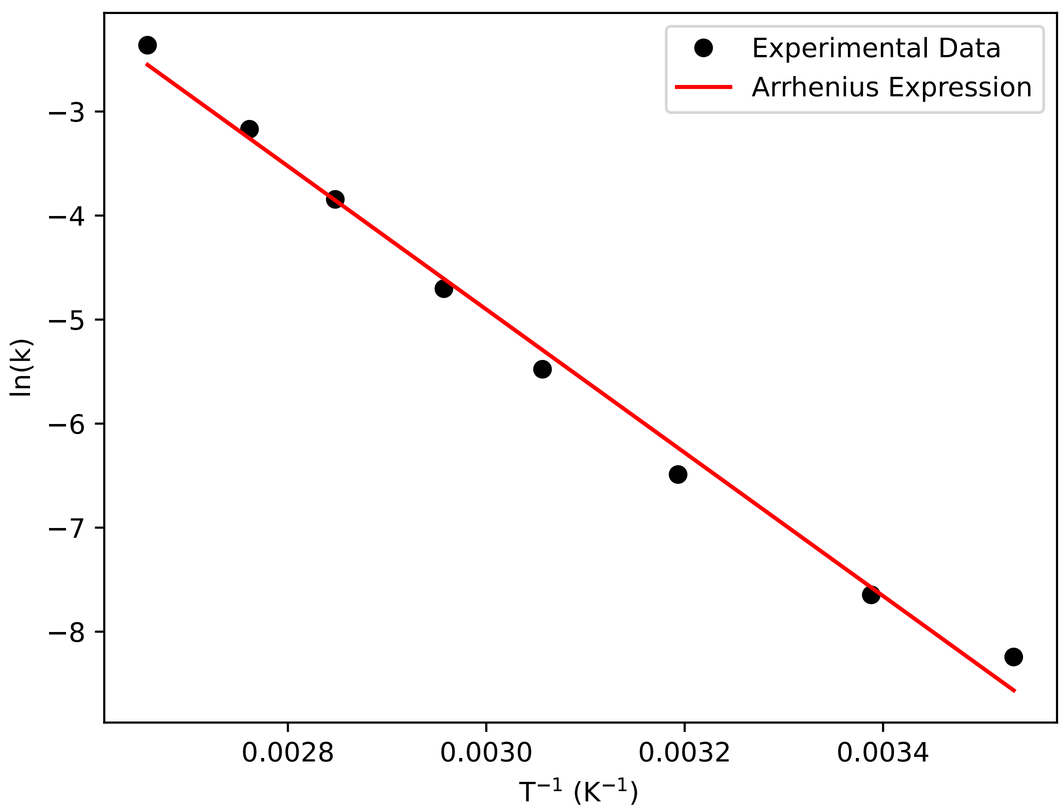

Figure 1. Arrhenius plot comparing the line obtained using linear least squares to the experimental data.

The linear least squares analysis yielded the coefficient of determination, R^2, the slope, m, the upper and lower limits of the 95% confidence interval for the slope, m_{CI_u}

and m_{CI_l}, the intercept, b, and the upper and lower limits of the 95% confidence interval for the intercept, b_{CI_u} and b_{CI_l}. Referring to equation (2), the activation energy, pre-exponential factor and their 95% confidence intervals were calculated using equations (3) through (8).

$$m = \frac{-E}{R} \qquad \Rightarrow \qquad E = -mR \tag{3}$$

$$E_{CI_u} = -m_{CI_u}R \tag{4}$$

$$E_{CI_l} = -m_{CI_l}R \tag{5}$$

$$b = \ln k_0 \qquad \Rightarrow \qquad k_0 = \exp\left(b\right) \tag{6}$$

$$k_{0,CI_u} = \exp\left(b_{CI_u}\right) \tag{7}$$

$$k_{0,CI_l} = \exp\left(b_{CI_l}\right) \tag{8}$$

Results and Discussion

The calculations were performed as described, yielding a coefficient of determination, R^2, equal to 0.992. The best estimate for k_0 is 6.97 × 10^6 L mol^{-1} min^{-1}, 95% CI [1.01 × 10^6, 4.79 × 10^7], and that for E is 57.3 kJ mol^{-1}, 95% CI [52, 62.5].

The upper and lower limits of the 95% confidence interval for k_0 are not particularly close to the estimated value, indicating significant uncertainty. However, estimated pre-exponential factors are often found to have large uncertainties. The uncertainty in the activation energy spans 10.5 kJ mol^{-1}, equal to 18% of the estimated value, 57.3 kJ mol^{-1}. The coefficient of determination is quite close to 1.0.

While the model plot shows good agreement between the experimental data and the model, there does appear to be a slight trend in the deviations. At low $(T)^{-1}$ the points fall above the line, at intermediate values they are below it, and at the the largest value it is again above the line. Nonetheless, the deviations are small, and it appears that the experimental data are consistent with the Arrhenius expression within the range of temperatures studied. In light of the slight apparent curvature seen in the data, however, the fitted Arrhenius expression should not be extrapolated to higher or lower temperatures than those used in the experiments.