REB, The Book
Example 3.6.4 Solution

The decomposition of HI, equation (1), is elementary. Collision theory predicts the rate coefficient to depend upon temperature as shown in equation (2) where N_{av} is Avogadro's number and k_B is the Boltzmann constant. The collision cross-section, σ_{HI-HI}, is 38.5 Å, the reduced mass, μ, is 1.063 x 10^{-22} g, and the activation energy, E, is 184.1 kJ mol^{-1}.

$$2\ HI \rightleftarrows H_2 + I_2 \tag{1}$$

$$k = N_{av}\sigma_{HI-HI}\sqrt{\frac{2k_BT}{\pi\mu}}\exp\left(\frac{-E}{RT}\right) \tag{2}$$

Use equation (2) to calculate the rate coefficient at several temperatures between 300 and 400 K. Then use the resulting k *vs.* T data to assess how well the Arrhenius expression describes the rate coefficient.

A range of temperature values between 300 and 400 K was chosen, and equation (2) was used to calculate corresponding values of k. The linearized Arrhenius expression indicates that a plot of $\ln k$ *vs.* $\frac{1}{T}$ will yield a straight line if the Arrhenius expression describes the data accurately. So the k *vs.* T data were used to generate a corresponding set of $\ln k$ *vs.* $\frac{1}{T}$ data, and linear least squares was used to fit a straight line to the data. The resulting Arrhenius plot is shown in Figure 1.

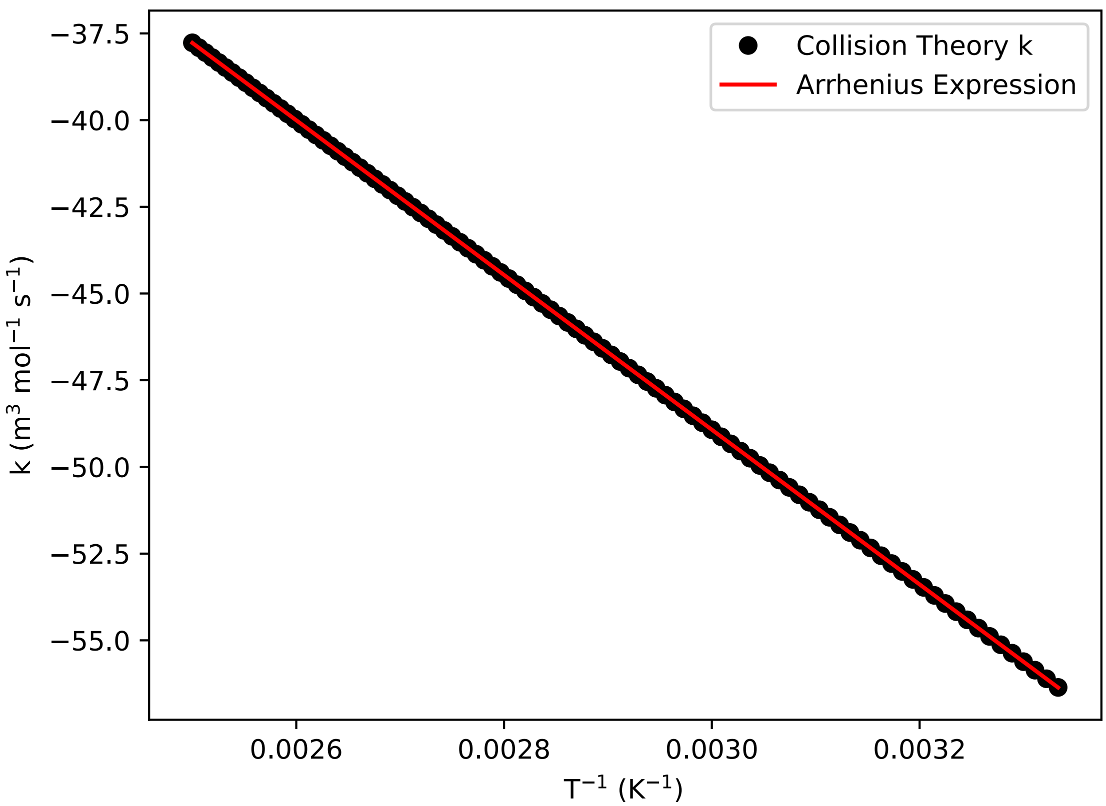

Figure 1. Arrhenius plot using rate coefficients calculated from collision theory.

The figure shows that the data fall nearly perfectly on the least squares line. The activation energy (R times the negative of the slope) and pre-exponential factor (exponential of the y-intercept) and their 95% confidence intervals were calculated, along with the coefficient of determination. The activation energy was found to equal 185 kJ mol^{-1}, 95% CI [185, 185], and the pre-exponential factor, 6.48×10^7 m^3 mol^{-1} s^{-1}, 95% CI [6.45×10^7, 6.5×10^7]. The coefficient of determination was 1.

Discussion

The Arrhenius plot convincingly shows that the Arrhenius expression offers an extremely accurate representation of the temperature dependence of the collision theory rate coefficient. This is because the temperature dependence is dominated by the exponential term. The error introduced by ignoring the $\sqrt{T}$ in the pre-exponential term is negligible. This is evident in Figure 1 and supported by the results that R^2 is equal to 1.0, the upper and lower limits of the 95% confidence interval for the activation energy equal the activation energy, and the upper and lower limits of the 95% confidence interval for the pre-exponential factor differ from the estimated value by 0.31%.