REB, The Course
Class 3 Learning Activity Solution

Reversible reaction (1) is elementary and the forward rate coefficient obeys the Arrhenius expression with a pre-exponential factor equal to 6.97 x 10^6 L mol^{-1} min^{-1} and an activation energy equal to 57.3 kJ mol^{-1}. Use the ideal gas law to replace the concentrations in the rate expression with partial pressures in atm, and combine the terms involving temperature into apparent forward and reverse rate coefficients.

$$A + B \rightleftarrows Y + Z \qquad (1)$$

Write a utility function that takes the ideal gas constant and equal-sized arrays of absolute temperatures and rate coefficients as arguments and returns the pre-exponential factor and activation energy, their 95% confidence intervals (CIs), and the coefficient of determination. Add the function to reb_utils.py and use it to determine whether the apparent forward rate coefficient displays Arrhenius temperature dependence, and, if so, what are the best estimates for the pre-exponential factor and the activation energy at temperatures between 0 and 100 °C?

A utility function named Arrhenius_parameters was written and added to reb_utils.py. The arguments are an array of k values, and array of T values in absolute units, and the ideal gas constant in the same temperature units as in $\underline{T}$ and with whatever energy units are desired for the activation energy. The algorithm is straightforward. The k and T vectors are used to create arrays of $\ln k$ as $\underline{y}$, and T^{-1} values as $\underline{x}$. Least squares parameter estimation is used to estimate the slope and intercept, their 95% CIs, and the coefficient of determination. The activation energy and its 95% CI are calculated from the estimated slope, and the pre-exponential factor and its 95% CI are calculated from the intercept.

Knowing that reaction (1) is elementary, the rate expression is given in equation (2). Using the ideal gas law to replace the concentrations with partial pressures gives equation (3).

$$r_1 = k_{1,f} C_A C_B - k_{1,r} C_y C_Z \tag{2}$$

$$r_1 = \frac{k_{1,f}}{(RT)^2} P_A P_B - \frac{k_{1,r}}{(RT)^2} P_Y P_Z \tag{3}$$

Combining the terms involving temperature yields apparent rate coefficients as defined in equations (4) and (5), with the rate expression given by equation (6).

$$k'_{1,f} = \frac{k_{1,f}}{(RT)^2} \tag{4}$$

$$k'_{1,r} = \frac{k_{1,r}}{(RT)^2} \tag{5}$$

$$r_1 = k'_{1,f} P_A P_B - k'_{1,r} P_Y P_Z \tag{6}$$

Substitution of the Arrhenius expression for the true forward rate coefficient into equation (4) yields equation (7). The pre-exponential factor and activation energy in equation (7) are given in the problem narrative as $k_{0,1,f}$ = 6.97 x 10^6 L mol^{-1} min^{-1} and $E_{1,f}$ = 57.3 kJ mol^{-1}.

$$k'_{1,f} = \frac{k_{0,1,f}}{(RT)^2} \exp\left(\frac{-E_{1,f}}{RT}\right) \tag{7}$$

A range of temperature values between 273 and 373 K (0 and 100 °C) was chosen, and equation (7) was used to calculate values of $k'_{1,f}$ corresponding to each value of T in that range. It should be noted that the ideal gas constant in the exponential term must have units of kJ mol^{-1} K^{-1}, while the ideal gas constant in the denominator of the pre-exponential term must have units of L atm mol^{-1} K^{-1}.

If the apparent forward rate coefficient displays Arrhenius temperature dependence, a plot of $\ln k'_{1,f}$ *vs.* $\frac{1}{T}$ will yield a straight line. Accordingly the $\underline{k}'_{1,f}$ *vs.* $\underline{T}$ data were used to generate a corresponding set of $\ln k'_{1,f}$ *vs.* $\frac{1}{T}$ data, and linear least

squares was used to fit a straight line to the $\ln k'_{1,f}$ *vs.* $\frac{1}{T}$ data. The resulting Arrhenius plot is shown in Figure 1.

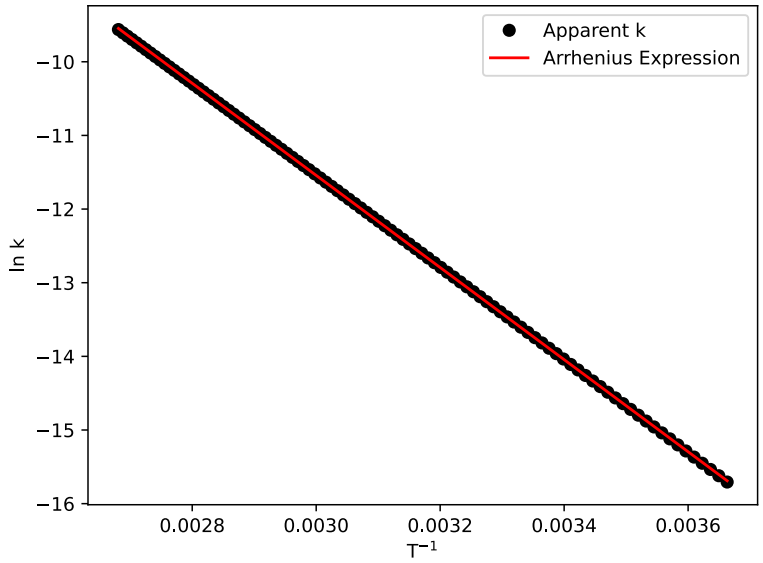

Figure 1. Arrhenius plot using rate coefficients calculated from collision theory.

The data fall nearly perfectly on the least squares line. The activation energy was found to equal 52 kJ mol^{-1}, 95% CI [51.96, 52.04], and the pre-exponential factor, 1367 mol L^{-1} atm^{-2} min^{-1}, 95% CI [1345, 1389]. The coefficient of determination was 1.

Discussion

The Arrhenius plot convincingly shows that despite the T^{-2} in the pre-exponential factor, the apparent rate coefficient does exhibit Arrhenius temperature dependence. This is because the change in the T^{-2} with temperature is negligibly small compared to the change in the exponential term. The accuracy with which the Arrhenius expression captures the temperature dependence is evidenced not only by how close to the Arrhenius line the data fall in Figure 1, but also by the coefficient of determination being equal to 1 and the upper and lower limits of the 95% CI for the estimated parameters being nearly equal to the estimated values.

This result suggests that the rate expression for an elementary reaction can be written using either concentrations or partial pressures, and in both cases the rate coefficients can be assumed to have Arrhenius temperature dependence. Of course, the pre-exponential factors will have different values and units, and the present results suggest that the activation energies will be different (57.3 *vs*. 52 kJ mol^{-1} here)