A First Course on Kinetics and Reaction Engineering

Example 4.5

Problem Purpose

This example illustrates some uses of the Arrhenius equation for the temperature dependence of a rate coefficient.

Problem Statement

At 50 °C, the rate coefficient for a reaction is equal to 1.08 x 10^{-4} h^{-1}. The activation energy is equal to 95.3 kJ mol^{-1}. Assuming Arrhenius temperature dependence, evaluate all the constants appearing in the Arrhenius expression and use the result to compare the increase in the rate coefficient when the temperature increases from 25 °C to 35 °C to the increase in rate coefficient when the temperature increases from 70 °C to 80 °C.

Problem Analysis

This problem clearly involves the use of the Arrhenius expression for the temperature dependence of a rate coefficient. The only "trick" here is to realize that while the problem statement gives the activation energy, it does *not* provide the value of the pre-exponential factor. Instead, it gives the value of the rate coefficient at a temperature of 50 °C (323 K). That is, the quantity 1.08 x 10^{-4} h^{-1}, given in the problem statement is $k(323\ K)$, not k_0.

Problem Solution

According to the Arrhenius expression, the rate coefficient will depend upon the temperature according to equation (1).

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

The problem provides two pieces of information: the value of E_j (95.3 kJ mol−1) and the value of k_j at 50 °C (323 K). Substitution of these values into equation (1) permits calculation of the pre-exponential factor.

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

$$k_{0,j} = k_j\left(T\right)\exp\left\{\frac{E_j}{RT}\right\} = 1.08\times10^{-4}\exp\left\{\frac{95,300}{\left(8.3144\left(323\right)\right)}\right\}\ \text{h}^{-1}$$

$$k_{0,j} = 2.79 \text{ x } 10^{11}\ \text{h}^{-1}$$

According to the Arrhenius expression, the ratio of the rate coefficient at one temperature (T_1) to the rate coefficient at a second temperature (T_2) is given by equation (2).

$$\frac{k_j\left(T_1\right)}{k_j\left(T_2\right)} = \frac{k_{0,j}\exp\left\{\dfrac{-E_j}{RT_1}\right\}}{k_{0,j}\exp\left\{\dfrac{-E_j}{RT_2}\right\}} = \exp\left\{\frac{E_j}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\right\} \tag{2}$$

In the first case, T_2 = 35 °C (308 K) and T_1 = 25 °C (298 K); substituting these values shows that the rate increases by a factor of 3.49 when the temperature increases from 25 to 35 °C.

$$\frac{k_j\left(T_1\right)}{k_j\left(T_2\right)} = \exp\left\{\frac{95,300}{8.3144}\left(\frac{1}{308}-\frac{1}{298}\right)\right\} = 2.87\times 10^{-1}$$

$$k_j\left(308\right) = 3.49 k_j\left(298\right)$$

In the second case, T_2 = 80 °C (353 K) and T_1 = 70 °C (343 K); substituting these values shows that the rate increases by a factor of 2.58 when the temperature increases from 70 to 80 °C.

$$\frac{k_j\left(T_1\right)}{k_j\left(T_2\right)} = \exp\left\{\frac{95,300}{8.3144}\left(\frac{1}{353}-\frac{1}{343}\right)\right\} = 3.88\times 10^{-1}$$

$$k_j\left(353\right) = 2.58 k_j\left(343\right)$$

Notice that a 10 degree change in temperature causes a larger ***relative*** increase in the rate coefficient at low temperature than at high temperature. However, as shown in the video solution, the ***absolute*** increase is smaller at the lower temperature.

The problem could have been solved without using equation (2). To do so, substitute the pre-exponential factor found when answering the first question into equation (1). The only unknown in the resulting equation is the temperature, so the resulting equation can then be used to calculate the rate coefficient at each of the four temperatures of interest. The requested ratios can then be calculated. Doing this will allow you to see that while the relative increase is greater at low temperature, the absolute increase is greater at high temperature.