Determining the Rate Law with Average Initial Rate

Problem 14-42

Ammonia decomposes on the surface of a hot tungsten wire. Following are the half-lives that were obtained at 1100°C for different initial concentrations of NH_3: $[NH_3]_o$ = 0.0031 M, $t_{1/2}$ = 7.6 min; 0.0015 M, 3.7 min; 0.00068 M, 1.7 min. For this decomposition reaction, what is **(a)** the order of the reaction; **(b)** the rate constant, *k*?

Solution

For this problem, we need to calculate the average initial rate at each concentration. Usually, average rate is calculated from a change in concentration for a fixed amount of time. In this case, the time to reduce the concentration by one-half is calculated.

$$\text{Rate}_1 = \frac{\frac{1}{2}[\text{NH}_3]_\text{o}}{t_{1/2}} = \frac{\frac{1}{2}\left(0.0031\text{ M}\right)}{7.6\text{ min}} = 2.039\times10^{-4}\ \text{M}/\text{min}$$

$$\text{Rate}_2 = \frac{\frac{1}{2}\left(0.0015\text{ M}\right)}{3.7\text{ min}} = 2.027\times10^{-4}\ \text{M}/\text{min}$$

$$\text{Rate}_3 = \frac{\frac{1}{2}\left(0.00068\text{ M}\right)}{1.7\text{ min}} = 2.000\times10^{-4}\ \text{M}/\text{min}$$

The rate law can be written:

Rate = k[NH3]^a

(a) So, using the method of initial rates we can write for a pair of reactions

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k[\text{NH}_3]_1^a}{k[\text{NH}_3]_2^a} = \frac{2.039\times10^{-4}\ \text{M}/\text{min}}{2.027\times10^{-4}\ \text{M}/\text{min}} = \left(\frac{0.0031\text{ M}}{0.0015\text{ M}}\right)^a$$

$$1.006 = 2.07^a$$

$$a = 0$$

Try a different pair of reactions:

$$\frac{\text{Rate}_2}{\text{Rate}_3} = \frac{k[\text{NH}_3]_2^a}{k[\text{NH}_3]_3^a} = \frac{2.027\times10^{-4}\ \text{M}/\text{min}}{2.000\times10^{-4}\ \text{M}/\text{min}} = \left(\frac{0.0015\text{ M}}{0.00068\text{ M}}\right)^a$$

$$1.0135 = 2.21^a$$

$$a = 0$$

(b) Since the reaction order is zero, Rate = k

$$\text{Average Rate} = \text{average } k = 2.02\ \text{M}/\text{min}$$