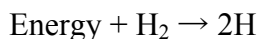


Homework 1

14. Some energy must be added to get the reaction started, that is, to overcome the activation energy barrier. Chemically, what happened is:



The hydrogen atoms initiate a chain reaction that proceeds very rapidly. Collisions of H₂ and O₂ molecules at room temperature do not have sufficient kinetic energy to form hydrogen atoms and initiate the reaction.

$$18. \quad \frac{\Delta[\text{H}_2]}{\Delta t} = 3 \frac{\Delta[\text{N}_2]}{\Delta t} \quad \text{and} \quad \frac{\Delta[\text{NH}_3]}{\Delta t} = -2 \frac{\Delta[\text{N}_2]}{\Delta t}$$

$$\text{so } -\frac{1}{3} \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NH}_3]}{\Delta t}$$

$$\text{or } \frac{\Delta[\text{NH}_3]}{\Delta t} = -\frac{2}{3} \frac{\Delta[\text{H}_2]}{\Delta t}$$

Ammonia is produced at a rate equal to 2/3 of the rate of consumption of hydrogen.

$$22. \text{ a. } \text{Rate} = k[\text{I}^-]^x[\text{S}_2\text{O}_8^{2-}]^y; \quad \frac{12.5 \times 10^{-6}}{6.25 \times 10^{-6}} = \frac{k(0.080)^x(0.040)^y}{k(0.080)^x(0.040)^y}, \quad 2.00 = 2.0^x, \quad x = 1$$

$$\frac{12.5 \times 10^{-6}}{6.25 \times 10^{-6}} = \frac{k(0.080)^x(0.040)^y}{k(0.080)^x(0.020)^y}, \quad 2.00 = 2.0^x, \quad x = 1$$

b. For the first experiment:

$$\frac{12.5 \times 10^{-6} \text{ mol}}{\text{L s}} = k \left(\frac{0.080 \text{ mol}}{\text{L}} \right) \left(\frac{0.040 \text{ mol}}{\text{L}} \right), \quad k = 3.9 \times 10^{-3} \text{ l/mol}\cdot\text{s}$$

Each of the other experiments also gives $k = 3.9 \times 10^{-3} \text{ L/mol}\cdot\text{s}$, so

$$k_{\text{mean}} = 3.9 \times 10^{-3} \text{ L/mol}\cdot\text{s}$$

28. a. Since the $\ln[\text{A}]$ vs. time plot was linear, the reaction is first order in A. The slope of the $\ln[\text{A}]$ vs. time plot equals $-k$. Therefore, the rate law, the integrated rate law and the rate constant values are:

$$\text{Rate} = k[\text{A}]; \quad \ln[\text{A}] = -kt + \ln[\text{A}]_0; \quad k = 2.97 \times 10^{-2} \text{ min}^{-1}$$

b. The half life expression for a first-order law is:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{k}, \quad t_{1/2} = \frac{0.6931}{2.97 \times 10^{-2} \text{ min}^{-1}} = 23.3 \text{ min}$$

c. 2.50×10^{-3} is 1/8 of the original amount of A present initially, so the reaction is 87.5% complete. When a first-order reaction is 87.5% complete (or 12.5% remains), the reaction has gone through 3 half-lives:

$$100\% \rightarrow 50.5\% \rightarrow 25\% \rightarrow 12.5\%; \quad t = 3 \times t_{1/2} = 3 \times 23.3 \text{ min} = 69.9 \text{ min}$$

$t_{1/2} \qquad \qquad t_{1/2} \qquad \qquad t_{1/2}$

Or we can use the integrated rate law:

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt, \quad \ln\left(\frac{2.50 \times 10^{-3} \text{ M}}{2.00 \times 10^{-2} \text{ M}}\right) = -(2.97 \times 10^{-2} \text{ min}^{-1}) t, \quad t = \frac{\ln(0.125)}{-2.97 \times 10^{-2} \text{ min}^{-1}} = 70.0 \text{ min}$$

44. Since $[B]_0 \gg [A]_0$, the B concentration is essentially constant during the experiment, so rate = $k'[A]$ where $k' = k[B]^2$. For this experiment, the reaction is a pseudo-first-order reaction in A.

a. $\ln([A]/[A]_0) = -k't$, $\ln(3.8 \cdot 10^{-3} \text{ M}/1.0 \cdot 10^{-2} \text{ M}) = -k' \cdot 8.0 \text{ s}$, $k' = 0.12 \text{ s}^{-1}$
 for the reaction: $k' = k[B]^2$, $k = 0.12 \text{ s}^{-1}/(3.0 \text{ mol/L})^2 = 1.3 \cdot 10^{-2} \text{ L}^2/\text{mol}^2 \cdot \text{s}$

b. $t_{1/2} = \ln 2/k' = 0.693/0.12 \text{ s}^{-1} = 5.8 \text{ s}$

c. $\ln([A]/1.0 \cdot 10^{-2} \text{ M}) = -0.12 \text{ s}^{-1} \times 13.0 \text{ s}$, $[A]/1.0 \cdot 10^{-2} = e^{-0.12(13.0)} = 0.21$,
 $[A] = 2.1 \cdot 10^{-3} \text{ M}$

d. $[A]_{\text{reacted}} = 0.010 \text{ M} - 0.0021 \text{ M} = 0.008 \text{ M}$, $[C]_{\text{reacted}} = 0.008 \text{ M} \cdot (2 \text{ mol C}/1 \text{ mol A})$
 $= 0.016 \text{ M} \approx 0.02 \text{ M}$

$[C]_{\text{remaining}} = 2.0 \text{ M} - 0.02 \text{ M} = 2.0 \text{ M}$; As expected, the concentration of C basically remains constant during this experiment since $[C]_0 \gg [A]_0$.

46. The observed rate law for this reaction is: Rate = $k[\text{NO}]^2[\text{H}_2]$. For a mechanism to be plausible, the sum of all the steps must give the overall balanced equation (true for all the proposed mechanisms in this problem), and the rate law derived from the mechanism must agree with the observed mechanism. In each mechanism (I – III), the first elementary step is the rate-determining step (the slow step), so the derived rate law for each mechanism will be the rate of the first step. The derived rate laws follow:

Mechanism I: Rate = $k[\text{H}_2]^2[\text{NO}]^2$

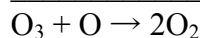
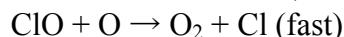
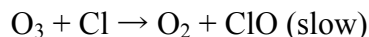
Mechanism II: Rate = $k[\text{H}_2][\text{NO}]$

Mechanism III: Rate = $k[\text{H}_2][\text{NO}]^2$

Only in Mechanism III does the derived rate law agree with the observed rate law. Thus, only Mechanism III is a plausible mechanism for this reaction.

58. $\ln(k_2/k_1) = E_a/R(1/T_1 - 1/T_2)$; Since the rate doubles, the $k_2 = 2k_1$.
 $\ln(2.000) = E_a/8.3145 \text{ J/mol}\cdot\text{K}(1/298 \text{ K} - 1/308 \text{ K})$, $E_a = 5.3 \cdot 10^4 \text{ J/mol} = 53 \text{ kJ/mol}$

62. The mechanism for the chlorine catalyzed destruction of ozone is:



Since the chlorine atom catalyzed reaction has a lower activation energy, then the Cl-catalyzed rate is faster. Hence, Cl is a more effective catalyst. Using the activation energy we can estimate the efficiency with which Cl atoms destroy ozone as compared to NO molecules (see Exercise 12.61 c).

$$\text{At } 25^\circ\text{C: } \frac{k_{\text{Cl}}}{k_{\text{NO}}} = \exp\left(\frac{-E_a(\text{Cl})}{RT} + \frac{E_a(\text{NO})}{RT}\right) = \exp\left(\frac{(-2100 - 11,900) \text{ J/mol}}{(8.3145 \times 298) \text{ J/mol}}\right) = e^{3.96} = 52$$

At 25°C , the Cl-catalyzed reaction is roughly 52 times faster than the NO-catalyzed reaction, assuming the frequency factor A is the same for each reaction.

76. We need the value of k at 500. K.

$$\ln(k_2/k_1) = E_a/R(1/T_1 - 1/T_2)$$

$$\ln(k_2/2.3 \times 10^{-12} \text{ L/mol}\cdot\text{s}) = (1.11 \times 10^5 \text{ J/mol})/8.3145 \text{ J/K}\cdot\text{mol}(1/273 \text{ K} - 1/500 \text{ K}) = 22.2$$

$$k_2/2.3 \times 10^{-12} = e^{22.2}, k_2 = 1.0 \times 10^{-2} \text{ L/mol}\cdot\text{s}$$

Since the decomposition reaction is an elementary reaction, then the rate law can be written using the coefficients in the balanced equation. For this reaction:

$$\text{Rate} = k[\text{NO}_2]^2.$$

To solve for the time, we must use the integrated rate law for second-order kinetics.

The major problem now is converting units so they match. Rearranging the ideal gas law gives $n/V = P/RT$. Substituting P/RT for concentration units in the second-order integrated rate law equation:

$$\frac{1}{[\text{NO}_2]} = kt + \frac{1}{[\text{NO}_2]_0}, \frac{1}{P/RT} = kt + \frac{1}{P_0/RT}, \frac{RT}{P} - \frac{RT}{P_0} = kt, t = \frac{RT}{k} \left(\frac{P_0 - P}{P \times P_0} \right)$$

$$t = \frac{(0.08206 \text{ L}\cdot\text{atm/K}\cdot\text{mol})(500 \text{ K})}{1.0 \times 10^{-2} \text{ L/mol}\cdot\text{s}} \times \left(\frac{2.5 \text{ atm} - 1.5 \text{ atm}}{1.5 \text{ atm} \times 2.5 \text{ atm}} \right) = 1.1 \times 10^3 \text{ s}$$