

Chemistry 2000 Spring 2006 Test 1 Solutions

Marginal notes indicate problems assigned during the term which draw on similar themes.

1. (a) $[\text{S}_2\text{O}_8^{2-}]$ doubles from experiment 1 to experiment 2 while $[\text{I}^-]$ is held constant, causing the rate to double. The reaction is therefore first-order with respect to $[\text{S}_2\text{O}_8^{2-}]$. In experiments 2 and 3, $[\text{S}_2\text{O}_8^{2-}]$ is held constant while $[\text{I}^-]$ is doubled, causing a doubling of the rate. The reaction is therefore also first-order with respect to $[\text{I}^-]$. The rate law is

$$v = k[\text{S}_2\text{O}_8^{2-}][\text{I}^-].$$

- (b) We can use the data from any of the experiments. From experiment 1, we have

$$\begin{aligned} k &= \frac{v}{[\text{S}_2\text{O}_8^{2-}][\text{I}^-]} \\ &= \frac{1.4 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}}{(0.038 \text{ mol/L})(0.060 \text{ mol/L})} \\ &= 6.1 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}. \end{aligned}$$

- (c) i. For an elementary reaction, the rate law would agree with the molecularity. In this case, we would have a third-order reaction with respect to $[\text{I}^-]$. Since the order with respect to $[\text{I}^-]$ is first, this reaction cannot be elementary.
- ii. There are really too many reactants for it to be likely that this reaction is elementary.

Chapter 15 #47 and additional problems on elementary

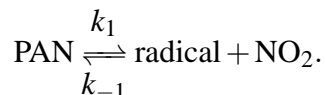
vs complex reactions

Chapter 15 #25 and 43

2. (a)

$$\begin{aligned} k &= Ae^{-E_a/(RT)} \\ &= (5.4 \times 10^{16} \text{ s}^{-1}) \exp\left(\frac{-114700 \text{ J/mol}}{(8.314472 \text{ J K}^{-1} \text{ mol}^{-1})(293.15 \text{ K})}\right) \\ &= 2.0 \times 10^{-4} \text{ s}^{-1}. \\ \therefore t_{1/2} &= \frac{\ln 2}{k} = \frac{\ln 2}{2.0 \times 10^{-4} \text{ s}^{-1}} = 3.5 \times 10^3 \text{ s}. \end{aligned}$$

(b) The reaction is



At equilibrium, the rates of the forward and reverse reactions are equal:

$$\begin{aligned} k_1[\text{PAN}] &= k_{-1}[\text{radical}][\text{NO}_2]. \\ \therefore K &= \frac{[\text{radical}][\text{NO}_2]}{[\text{PAN}]} = \frac{k_1}{k_{-1}} \\ &= \frac{2.0 \times 10^{-4} \text{ s}^{-1}}{5.74 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}} \\ &= 3.4 \times 10^{-14} \text{ mol/L}. \end{aligned}$$

Additional problems on the relationship between kinetics and equilibrium

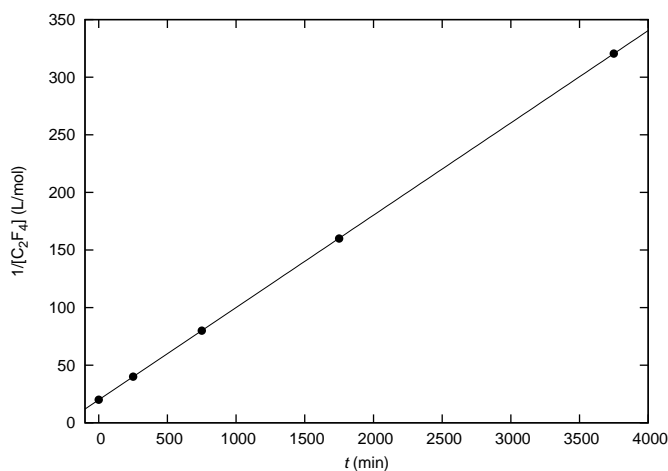
Chapter 15 #19

(c)

$$\begin{aligned} \ln x &= \ln x_0 - kt. \\ \therefore \ln(0.05 \text{ bar}) &= \ln(0.45 \text{ bar}) - (2.0 \times 10^{-4} \text{ s}^{-1})t. \\ \therefore t &= \frac{\ln(0.45 \text{ bar}) - \ln(0.05 \text{ bar})}{2.0 \times 10^{-4} \text{ s}^{-1}} \\ &= 1.1 \times 10^4 \text{ s} \\ &\equiv \frac{1.1 \times 10^4 \text{ s}}{3600 \text{ s/h}} \\ &= 3.1 \text{ h}. \end{aligned}$$

3. If the reaction is elementary, then according to the law of mass action it should follow the second-order rate law $v = k[\text{C}_2\text{F}_4]^2$. A plot of $1/[\text{C}_2\text{F}_4]$ vs t should be linear. Here is my graph:

Chapter 15 #47 and a second-order plot



The data fit the line nicely which supports the hypothesis that this is an elementary reaction.

The rate constant is equal to the slope of the graph. Using a couple of points on the graph, you should get (roughly)

$$k = 8.0 \times 10^{-2} \text{ L mol}^{-1} \text{ min}^{-1}.$$

4. (a) $\text{Hg}_{(\text{aq})}$

Chapter 15 #49

(b) The equilibrium approximation can be applied to the first step:

$$\begin{aligned} k_1[\text{Hg}_2^{2+}] &\approx k_{-1}[\text{Hg}^{2+}][\text{Hg}]. \\ \therefore [\text{Hg}] &\approx \frac{k_1[\text{Hg}_2^{2+}]}{k_{-1}[\text{Hg}^{2+}]}. \end{aligned}$$

The rate of reaction is

$$\begin{aligned} v &= k_2[\text{Hg}][\text{Ti}^{3+}] \\ &\approx \frac{k_1 k_2 [\text{Hg}_2^{2+}][\text{Ti}^{3+}]}{k_{-1}[\text{Hg}^{2+}]}. \end{aligned}$$

(c) According to our rate law, doubling the mercury (II) ion concentration cuts the rate in half.