CHAPTER 12

PROBLEMS

1. Thiosulfate ion is oxidized by iodine according to the following reaction:

\[ 2S_2O_3^{2-} (aq) + I_2 (aq) \rightarrow S_4O_6^{2-} (aq) + 2I^- (aq) \]

If 0.0080 mol of \( S_2O_3^{2-} \) is consumed in 1.0 L of solution each second, what is the rate of consumption of \( I_2 \)? At what rates are \( S_4O_6^{2-} \) and \( I^- \) produced?

2. The decomposition of hydrogen iodide on finely divided gold at 150°C is zero order with respect to HI. The rate defined below is constant at 1.20 \( \times \) \( 10^{-4} \) mol/L s.

\[ 2HI (g) \rightarrow H_2 (g) + I_2 (g) \]

\[ \text{Rate} = -\frac{\Delta [HI]}{\Delta t} = k = 1.20 \times 10^{-4} \text{ mol/L s} \]

a. If an experiment has an initial HI concentration of 0.250 M, what is the concentration of HI after 25.0 minutes?

b. How long will it take for all of the HI to decompose?

c. Give the rates of formation of \( H_2 \) and \( I_2 \).

3. The reaction

\[ 2NO (g) + Cl_2 (g) \rightarrow 2NOCl (g) \]

was studied at -10°C. The following results were obtained where

\[ \text{Rate} = -\frac{\Delta [Cl_2]}{\Delta t} \]

<table>
<thead>
<tr>
<th>([NO]_0)</th>
<th>([Cl_2]_0)</th>
<th>Initial rate (mol/L min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.10</td>
<td>0.18</td>
</tr>
<tr>
<td>0.10</td>
<td>0.20</td>
<td>0.35</td>
</tr>
<tr>
<td>0.20</td>
<td>0.20</td>
<td>1.45</td>
</tr>
</tbody>
</table>

a. What is the rate law?

b. What is the value of the rate constant?

4. Hydrogen reacts with nitric oxide to form nitrous oxide (laughing gas), according to the equation

\[ H_2 (g) + NO (g) \rightarrow N_2O (g) + H_2O (g) \]

Determine the rate equation and the rate constant for the reaction from the following data

<table>
<thead>
<tr>
<th>([NO])</th>
<th>([H_2])</th>
<th>Rate (mol/L s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.30</td>
<td>0.35</td>
<td>(2.835 \times 10^{-3})</td>
</tr>
<tr>
<td>0.60</td>
<td>0.35</td>
<td>(1.134 \times 10^{-2})</td>
</tr>
<tr>
<td>0.60</td>
<td>0.70</td>
<td>(2.268 \times 10^{-2})</td>
</tr>
</tbody>
</table>
5. The dimerization of butadiene was studied at 500 K.

\[ 2\text{C}_4\text{H}_6 (g) \rightarrow \text{C}_8\text{H}_{12} (g) \]

The following data were obtained where

\[ \text{Rate} = -\frac{\Delta [\text{C}_4\text{H}_6]}{\Delta t} \]

<table>
<thead>
<tr>
<th>time (s)</th>
<th>[C\text{H}_6]</th>
</tr>
</thead>
<tbody>
<tr>
<td>195</td>
<td>1.6 \times 10^{-2}</td>
</tr>
<tr>
<td>604</td>
<td>1.5 \times 10^{-2}</td>
</tr>
<tr>
<td>1246</td>
<td>1.3 \times 10^{-2}</td>
</tr>
<tr>
<td>2180</td>
<td>1.1 \times 10^{-2}</td>
</tr>
<tr>
<td>6210</td>
<td>6.8 \times 10^{-3}</td>
</tr>
</tbody>
</table>

Determine the form of the integrated rate law and the rate constant for this reaction. Write the rate law for the reaction.

6. The decomposition of hydrogen peroxide was studied and the data in the table were obtained at a particular temperature where

\[ \text{Rate} = -\frac{\Delta [\text{H}_2\text{O}_2]}{\Delta t} \]

<table>
<thead>
<tr>
<th>time (s)</th>
<th>[H\text{O}_2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>120 ± 1</td>
<td>0.91</td>
</tr>
<tr>
<td>300 ± 1</td>
<td>0.78</td>
</tr>
<tr>
<td>600 ± 1</td>
<td>0.59</td>
</tr>
<tr>
<td>1200 ± 1</td>
<td>0.37</td>
</tr>
<tr>
<td>1800 ± 1</td>
<td>0.22</td>
</tr>
<tr>
<td>2400 ± 1</td>
<td>0.13</td>
</tr>
<tr>
<td>3000 ± 1</td>
<td>0.082</td>
</tr>
<tr>
<td>3600 ± 1</td>
<td>0.050</td>
</tr>
</tbody>
</table>

Determine the integrated rate law and the value of the rate constant. Also write the rate law.

7. The decomposition of SO\textsubscript{2}Cl\textsubscript{2}, according to the equation:

\[ \text{SO}_2\text{Cl}_2 (g) \rightarrow \text{SO}_2 (g) + \text{Cl}_2 (g) \]

has been found to be a first-order chemical reaction. At 602 K, 2.00% of the SO\textsubscript{2}Cl\textsubscript{2} initially present had decomposed at the end of 6.72 min.

a. What is the rate constant, k, at this temperature?

b. What is the half-life of the reaction?
8. In 0.0400 M NaOH at 20°C, the decomposition of H$_2$O$_2$ by the reaction
\[ \text{H}_2\text{O}_2 \text{ (l)} \rightarrow 2\text{H}_2\text{O (l)} + \text{O}_2 \text{ (g)} \]
has been shown to be first-order in H$_2$O$_2$ only.
   a. If the half-life is found to be 654 min., what fraction of the original H$_2$O$_2$ remains after exactly 100 min have elapsed?
   b. What is the initial rate of reaction in a 0.0200 M solution of H$_2$O$_2$?

9. The rate constant at 45°C for the decomposition of dinitrogen pentoxide, N$_2$O$_5$, dissolved in chloroform, CHCl$_3$,
is $6.2 \times 10^{-4}$ min$^{-1}$. The reaction can be written:
\[ 2\text{N}_2\text{O}_5 \text{ (g)} \rightarrow 4\text{NO}_2 \text{ (g)} + \text{O}_2 \]
The decomposition is first-order in N$_2$O$_5$.
   a. What is the rate of the reaction when [N$_2$O$_5$] = 0.40?
   b. What is the concentration of N$_2$O$_5$ remaining at the end of one hour if the initial concentration of N$_2$O$_5$ was 0.40 M?

10. It took 143 s for 50% of a particular substance to decompose. If the initial concentration was 0.060 M and the decomposition reaction follows second-order kinetics, what is the value of the rate constant?

11. Write the rate laws for the following elementary reactions:
   a. CH$_3$NC (g) $\rightarrow$ CH$_3$CN (g)
   b. O$_3$ (g) + NO (g) $\rightarrow$ O$_2$ (g) + NO$_2$ (g)

12. The rate constant at 325 °C for the reaction
\[ \text{C}_4\text{H}_8 \text{ (g)} \rightarrow 2\text{C}_2\text{H}_4 \text{ (g)} \]
is $6.1 \times 10^{-8}$ sec$^{-1}$, and the activation energy is 261 kJ per mole of C$_4$H$_8$. Determine the frequency factor for the reaction.

13. The hydrolysis of the sugar sucrose to the sugars glucose and fructose
\[ \text{C}_{12}\text{H}_{22}\text{O}_{11} \text{ (s)} + \text{H}_2\text{O (l)} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 \text{ (s)} + \text{C}_6\text{H}_{12}\text{O}_6 \text{ (s)} \]
follows a first-order rate equation:
\[ \text{Rate} = k[\text{C}_{12}\text{H}_{22}\text{O}_{11}] \]
The products have the same molecular formulas but differ in the arrangement of the atoms in their molecules. In neutral solution, $k = 2.1 \times 10^{-11}$ sec$^{-1}$ at 27°C and $8.5 \times 10^{-11}$ sec$^{-1}$ at 37°C. Determine the activation energy, the frequency factor, and the rate constant for this reaction at 47°C.

14. The activation energy for the reaction
\[ \text{H}_2 \text{ (g)} + \text{I}_2 \text{ (g)} \rightarrow 2\text{HI} \text{ (g)} \]
is 167 kJ/mol and $\Delta E$ for the reaction is +28 kJ/mol. What is the activation energy for the decomposition of HI?

15. Chemists commonly use a rule of thumb that an increase of 10 K in temperature doubles the rate of a reaction. What must the activation energy be for this statement to be true for a temperature increase from 25°C to 35°C?

16. If the rate of a reaction doubles for every 10°C rise in temperature, how much faster would the reaction proceed at 55°C than at 25°C and at 100°C than at 25°C?
17. The reaction

\[ 2\text{NO} (g) + \text{O}_2 (g) \rightarrow 2\text{NO}_2 (g) \]

exhibits the rate law

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

Which of the following mechanisms is consistent with this rate law?

a. \( \text{NO} + \text{O}_2 \rightarrow \text{NO}_2 + \text{O} \) Slow
   \( \text{O} + \text{NO} \rightarrow \text{NO}_2 \) Fast
b. \( \text{NO} + \text{O}_2 \rightleftharpoons \text{NO}_3 \) Both fast with equal rates
   \( \text{NO}_3 + \text{NO} \rightarrow 2\text{NO}_2 \) Slow
c. \( 2\text{NO} \rightarrow \text{N}_2\text{O}_2 \) Slow
   \( \text{N}_2\text{O}_2 + \text{O}_2 \rightarrow \text{N}_2\text{O}_4 \) Fast
   \( \text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2 \) Fast
d. \( 2\text{NO} \rightleftharpoons \text{N}_2\text{O}_2 \) Both fast with equal rates
   \( \text{N}_2\text{O}_2 \rightarrow \text{NO}_2 + \text{N} \) Slow
   \( \text{N} + \text{O}_2 \rightarrow \text{NO}_2 \) Fast

18. The reaction

\[ 2\text{NO}_2\text{Cl} \rightarrow 2\text{NO}_2 + \text{Cl}_2 \]

follows the rate law

\[ \text{Rate} = k [\text{NO}_2\text{Cl}] \]

The mechanism is

Step 1 \( \text{NO}_2\text{Cl} \rightarrow \text{NO}_2 + \text{Cl} \)
Step 2 \( \text{NO}_2\text{Cl} + \text{Cl} \rightarrow \text{NO}_2 + \text{Cl}_2 \)

Which is the rate-determining step?

19. Most of the 15.7 billion pounds of HNO\textsubscript{3} produced in the United States during 1977 was prepared by the following sequence of reactions:

Step 1 \( 4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O} \)
Step 2 \( 2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \)
Step 3 \( 3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO} \)

The first reaction is run by burning ammonia in air over a platinum catalyst. This reaction is fast. Reaction (3) is also fast. The second reaction limits the rate at which nitric acid can be prepared from ammonia. If Reaction (2) is second order in NO and first order in O\textsubscript{2}, what is the rate of formation of NO\textsubscript{2} when the oxygen concentration is 0.50 M and the nitric oxide concentration is 0.75 M? The rate constant for the reaction is \( 5.8 \times 10^{-6} \text{ L}^2/\text{mol}^2 \text{ s}^{-1} \)