CHAPTER 12

REVIEW PROBLEMS

1. Use the given data for the hypothetical reaction:

\[ 2A + B \rightarrow \text{products} \]

<table>
<thead>
<tr>
<th>Reaction #</th>
<th>[A]</th>
<th>[B]</th>
<th>Initial rate (mol/L s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.1</td>
<td>3.0 \times 10^{-2}</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>0.3</td>
<td>3.0 \times 10^{-2}</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
<td>0.3</td>
<td>6.0 \times 10^{-2}</td>
</tr>
</tbody>
</table>

(a) Determine the rate law for this reaction.

\[ \text{RATE} = k [A]^n [B]^m \]

\[
\frac{r_2}{r_1} = \frac{0.03}{0.03} = \frac{k(0.1)^n(0.3)^m}{k(0.1)^n(0.1)^m}
\]

\[ 1 = 3^m \]
\[ n = 0 \]

\[
\frac{r_3}{r_0} = \frac{0.06}{0.03} = \frac{k(0.2)^n(0.3)^m}{k(0.1)^n(0.3)^m}
\]

\[ 2 = 2^n \]
\[ n = 1 \]

(b) Calculate the value of the rate constant.

\[ k = \frac{\text{RATE}}{[A]} \]

\[ = \frac{3.0 \times 10^{-2}}{0.1} \]

\[ = 30 \text{ s}^{-1} \]
2. Given the following data for 15.0°C, derive the rate law expression and calculate the rate constant for the reaction:

\[ A + B + 3C \rightarrow \text{products} \]

<table>
<thead>
<tr>
<th>Reaction #</th>
<th>[A]</th>
<th>[B]</th>
<th>[C]</th>
<th>Initial rate (mol/L s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.4</td>
<td>0.1</td>
<td>0.1</td>
<td>6.0 \times 10^{-3}</td>
</tr>
<tr>
<td>2</td>
<td>0.4</td>
<td>0.2</td>
<td>0.1</td>
<td>6.0 \times 10^{-3}</td>
</tr>
<tr>
<td>3</td>
<td>0.4</td>
<td>0.3</td>
<td>0.2</td>
<td>1.2 \times 10^{-2}</td>
</tr>
<tr>
<td>4</td>
<td>1.2</td>
<td>0.4</td>
<td>0.2</td>
<td>0.11</td>
</tr>
</tbody>
</table>

(a) Determine the rate law for this reaction.

\[
\text{RATE} = k \left[ A \right]^m \left[ B \right]^n \left[ C \right]^\rho
\]

\[
\frac{\Gamma_4}{\Gamma_1} = \frac{0.4}{0.1} = \frac{k \left( 1.2 \right)^n \left( 1.2 \right)^m \left( 1 \right)^\rho}{k \left( 1 \right)^n \left( 1 \right)^m \left( 1 \right)^\rho}
\]

\[
1 = 3^m
\]

\[
m = 0
\]

\[
\frac{\Gamma_3}{\Gamma_1} = \frac{0.12}{0.1} = \frac{k \left( 1.4 \right)^n \left( 0.3 \right)^0 \left( 1 \right)^\rho}{k \left( 1 \right)^n \left( 1 \right)^0 \left( 1 \right)^\rho}
\]

\[
2 = 2^\rho
\]

\[
\rho = 1
\]

(b) Calculate the value of the rate constant

\[
k = \frac{\text{RATE}}{\left[ A \right]^m \left[ C \right]^\rho}
\]

\[
k = \frac{0.11}{(1.2)^0 (1.2)}
\]

\[
k = 0.38 \frac{L^2}{mol^2 s}
\]

\[
\text{RATE} = k \left[ A \right]^2 \left[ C \right]
\]
3. The following data were obtained for the reaction

\[ \text{OCI}^- (aq) + \Gamma^- (aq) \rightarrow \text{OI}^- (aq) + \text{Cl}^- (aq) \]

<table>
<thead>
<tr>
<th>Reaction #</th>
<th>[OCI]₀</th>
<th>[\Gamma]₀</th>
<th>Initial rate (mol/L s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0015</td>
<td>0.0015</td>
<td>1.36 \times 10^{-4}</td>
</tr>
<tr>
<td>2</td>
<td>0.0030</td>
<td>0.0015</td>
<td>2.72 \times 10^{-4}</td>
</tr>
<tr>
<td>3</td>
<td>0.0015</td>
<td>0.0030</td>
<td>2.72 \times 10^{-4}</td>
</tr>
</tbody>
</table>

(a) Determine the rate law for this reaction.

\[ \text{Rate} = [\text{OCI}^-]^n [\Gamma^-]^m \]

\[ \frac{\text{Rate}_2}{\text{Rate}_1} = \frac{2.72 \times 10^{-4}}{1.36 \times 10^{-4}} = \frac{k(.003)^n (.0015)^m}{k(.0015)^n (.0015)^m} \]

\[ a^n = 2 \]
\[ n = 1 \]

\[ \frac{\text{Rate}_3}{\text{Rate}_1} = \frac{2.72 \times 10^{-4}}{1.36 \times 10^{-4}} = \frac{k(.0015)^n (.003)^m}{k(.0015)^n (.0015)^m} \]

\[ a^m = 2 \]
\[ m = 1 \]

(b) Calculate the value of the rate constant.

\[ k = \frac{\text{Rate}}{[\text{OCI}^-][\Gamma^-]} = \frac{1.36 \text{ mol/L s}}{(.0015 \text{ mol/L})(.0015 \text{ mol/L})} \]

\[ = \frac{60.4 \text{ L}}{\text{mol \cdot s}} \]

(c) Calculate the rate when [OCI⁻] = 0.0020 mol/L and [\Gamma⁻] = 0.0050 mol/L.

\[ \text{Rate} = k[\text{OCI}^-][\Gamma^-] \]

\[ = (60.4 \text{ L/mol \cdot s})(.0020 \text{ mol/L})(.0050 \text{ mol/L}) \]

\[ = 6.0 \times 10^{-4} \text{ mol/L \cdot s} \]

OVER
4. The following data were measured for the reaction

\[
\text{BF}_3 (g) + \text{NH}_3 (g) \rightarrow \text{F}_2 \text{BNH}_3 (g)
\]

<table>
<thead>
<tr>
<th>Trial</th>
<th>[BF(_3)] (mol/L)</th>
<th>[NH(_3)] (mol/L)</th>
<th>Initial Rate (mol/L \cdot s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.250</td>
<td>0.250</td>
<td>0.2130</td>
</tr>
<tr>
<td>2</td>
<td>0.250</td>
<td>0.125</td>
<td>0.1065</td>
</tr>
<tr>
<td>3</td>
<td>0.200</td>
<td>0.100</td>
<td>0.0682</td>
</tr>
<tr>
<td>4</td>
<td>0.350</td>
<td>0.100</td>
<td>0.1193</td>
</tr>
<tr>
<td>5</td>
<td>0.175</td>
<td>0.100</td>
<td>0.0596</td>
</tr>
</tbody>
</table>

a. Determine the rate law for the reaction.

\[
\frac{\gamma_4}{\gamma_5} = \frac{0.2130}{0.1065} = \frac{k(0.250)^n(0.250)^m}{k(0.250)^n(0.125)^m}
\]

\[
2 = 2^n
\]

\[
m = 1
\]

b. Determine the overall order of the reaction.

SECOND

c. Determine the value of the rate constant.

\[
\text{RATE} = k [\text{BF}_3][\text{NH}_3]
\]

\[
0.130 = k (0.250)(0.250)
\]

\[
k = \frac{0.130}{(0.250)^2} = 3.41 \frac{\text{L}}{\text{mol} \cdot \text{s}}
\]

d. Determine the rate when [BF\(_3\)] = 0.100 mol/L and [NH\(_3\)] = 0.500 mol/L.

\[
\text{RATE} = k [\text{BF}_3][\text{NH}_3]
\]

\[
= (3.41 \frac{\text{L}}{\text{mol} \cdot \text{s}})(0.100 \frac{\text{mol}}{\text{L}})(0.500 \frac{\text{mol}}{\text{L}})
\]

\[
= 0.1704 \frac{\text{mol}}{\text{L} \cdot \text{s}}
\]

\[
= (0.170 \frac{\text{mol}}{\text{L} \cdot \text{s}})
\]
5. A certain reaction has the following general form:

\[ aA \rightarrow bB \]

At a particular temperature and \([A]_0 = 2.00 \times 10^{-2} \text{ M}\), concentration vs. time data were collected for this reaction, and a plot of \(\ln[A]\) versus time resulted in a straight line with a slope value of \(-2.97 \times 10^{-2} \text{ min}^{-1}\).

a. Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.

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

b. Determine the half-life for this reaction.

\[
t_{\frac{1}{2}} = \frac{0.693}{k} \\
= \frac{0.693}{2.97 \times 10^{-2} \text{ min}^{-1}} \\
= 23.3 \text{ min}
\]

c. How much time is required for the concentration of A to decrease to \(2.50 \times 10^{-3} \text{ M}\)?

\[
\ln \left( \frac{[A]_0}{[A]} \right) = kt \\
\ln \left( \frac{0.02}{0.0035} \right) = (2.97 \times 10^{-2})t \\
2.079741542 = (0.0297)t \\
t = 70.0 \text{ min}
\]
6. The reaction

\[ A \rightarrow B + C \]

is known to be zero order in A and to have a rate constant of \(5.0 \times 10^{-3}\) mol/L s at 25.0°C. An experiment was run at 25.0°C where \([A]_0 = 1.0 \times 10^{-3}\) M.

a. Write the integrated rate law for this reaction.

\[
[A] = \frac{[A]_0}{1 + \frac{[A]_0}{k_0 t}} = \frac{(1.0 \times 10^{-3}) \text{ mol L}^{-1}}{1 + \frac{(1.0 \times 10^{-3})}{5 \times 10^{-4} \text{ L s}^{-1} \cdot \text{mol}^{-1}}} \]

b. Calculate the half-life for this reaction.

\[
t_{1/2} = \frac{[A]_0}{2 k} = \frac{(1.0 \times 10^{-3})}{2 \times (5 \times 10^{-4} \text{ L s}^{-1} \cdot \text{mol}^{-1})} = 0.01 \text{ s}
\]

c. Calculate the concentration of B after \(5.0 \times 10^{-3}\) s has elapsed.

\[
[B] = 7.5 \times 10^{-4} \text{ mol L}^{-1}
\]

Since \(7.5 \times 10^{-4}\) mol of A remains it means \(2.5 \times 10^{-4}\) mol of A reacted. For every 1 mole of A that reacts 1 mole of B is produced.

7. The first order rate constant for the radioactive decay of radium-223 is \(0.0606\) day\(^{-1}\). What is the half-life of radium-223?

\[
t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0606} = 11.41 \text{ days}
\]
8. For the reaction: $A \rightarrow \text{products}$ successive half-lives are observed to be 10.0, 20.0, and 40.0 minutes for an experiment in which $[A]_0 = 0.10$ M. Assuming the reaction is second order, calculate the concentration of $A$ at the following times:

a. 80.0 min

\[
\frac{1}{[A]} = \frac{1}{k[A]_0} + \frac{1}{[A]_0} = (1.0)(80.0) + \frac{1}{1} = 90
\]

\[\frac{1}{[A]} = 1.1 \times 10^{-2} \text{ mol L}^{-1}\]

b. 30.0 min

\[
\frac{1}{[A]} = \frac{1}{k[A]_0} + \frac{1}{[A]_0} = (1.0)(30.0) + \frac{1}{1} = 90
\]

\[\frac{1}{[A]} = 0.025 \text{ mol L}^{-1}\]

9. For the reaction

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

The rate law is

\[\text{Rate} = (1.4 \times 10^{-10} \text{ L/mol} \cdot \text{s}) [\text{NO}_2]^2\]

(a) If 3.00 mol of NO$_2$ is initially present in a sealed 2.00 L container at 25.0°C, what is the half-life of the reaction?

\[
t_{\frac{1}{2}} = \frac{1}{k [A]_0} = \frac{1}{(1.4 \times 10^{-10})(1.50)} = 1.76 \times 10^9 \text{ y} = 151 \text{ yr}\]

(b) What concentration of NO$_2$ remains after 115 years?

\[
\frac{1}{[A]} = \frac{1}{k [A]_0} + \frac{1}{[A]_0} = (1.4 \times 10^{-10}) (3626640000) + \frac{1}{0.5} = 1.17 \times 10^7 \text{ mol L}^{-1}
\]

\[\boxed{[A] = 0.852 \text{ mol L}^{-1}}\]
10. For the reaction
\[ \text{Mo(CO)}_6 + \text{P(CH}_3)_3 \rightarrow \text{Mo(CO)}_3 \text{P(CH}_3)_3 + \text{CO} \]
the proposed mechanism is

(1) \[ \text{Mo(CO)}_6 \rightarrow \text{Mo(CO)}_3 + \text{CO} \]
(2) \[ \text{Mo(CO)}_3 + \text{P(CH}_3)_3 \rightarrow \text{Mo(CO)}_3 \text{P(CH}_3)_3 \]

a. Disregarding the absence of information regarding the rate law, is the proposed mechanism consistent with the equation for the overall reaction?

YES

b. What is the molecularity of each step of the mechanism?
1: \text{UNIMOLECULAR}
2: \text{BIMOLECULAR}

c. Identify the intermediate(s).
\[ \text{Mo(CO)}_5 \]

11. The decomposition of nitrous oxide, \( \text{N}_2\text{O} \), is believed to occur by a two-step mechanism:

\[ \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O} \] (slow)
\[ \text{N}_2\text{O} + \text{O} \rightarrow \text{N}_2 + \text{O}_2 \] (fast)

a. Write the equation for the overall reaction.
\[ 2 \text{N}_2\text{O} \rightarrow 2 \text{N}_2 + \text{O}_2 \]

b. Write the rate law for the overall reaction.
\[ \text{RATE} = k [\text{N}_2\text{O}] \]
12. Ozone reacts with nitrogen dioxide to produce Dinitrogen pentoxide and oxygen:

\[ \text{O}_3 (\text{g}) + 2 \text{NO}_2 (\text{g}) \rightarrow \text{N}_2\text{O}_5 (\text{g}) + \text{O}_2 (\text{g}) \]

The reaction is believed to occur in two steps:

\[ \text{O}_3 (\text{g}) + \text{NO}_2 (\text{g}) \rightarrow \text{NO}_3 (\text{g}) + \text{O}_2 (\text{g}) \]

\[ \text{NO}_3 (\text{g}) + \text{NO}_2 (\text{g}) \rightarrow \text{N}_2\text{O}_5 (\text{g}) \]

The experimental rate law is: \[ \text{rate} = k[\text{O}_3][\text{NO}_2] \]

What can you say about the relative rates of the two steps of the proposed mechanism?

Since the rate law conforms to the molecularity of the first step, it must be the rate determining step.

13. The gas phase reaction between methane and diatomic sulfur is given by the equation:

\[ \text{CH}_4 (\text{g}) + 2 \text{S}_2 (\text{g}) \rightarrow \text{CS}_2 (\text{g}) + 2 \text{H}_2\text{S} (\text{g}) \]

At 550°C the rate constant for this reaction is 1.1 L/mol s and at 625°C the rate constant is 6.4 L/mol s. Using these values, calculate \( E_a \) for this reaction.

\[
\ln \left( \frac{k_2}{k_1} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

\[
\ln \left( \frac{6.4}{1.1} \right) = \frac{E_a}{8.314} \left( \frac{1}{823} - \frac{1}{898} \right)
\]

\[
\ln \left( \frac{6.4}{1.1} \right) = E_a \left( \frac{1.014510^{26} \times 10^{-11}}{8.314} \right)
\]

\[
1.760787811 = E_a \left( 1.220531392 \times 10^{-5} \right)
\]

\[
E_a = 144 \, \text{kJ/mol}
\]

\[
E_a = \left[ \frac{144 \, \text{kJ}}{\text{mol}} \right]
\]

OVER
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. The rate constant at 302°C is \(2.45 \times 10^{-4}\) L/mol. What is the rate constant for this reaction at 205°C?

\[
\ln \left( \frac{k_2}{k_1} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

\[
\ln \left( \frac{k_2}{2.45 \times 10^{-4}} \right) = \frac{1.67 \times 10^{3}}{8.314} \left( \frac{1}{375} - \frac{1}{478} \right)
\]

\[
\ln \left( \frac{k_2}{2.45 \times 10^{-4}} \right) = -7.0853236
\]

\[
\frac{k_2}{2.45 \times 10^{-4}} = e^{-7.0853236}
\]

\[
k_2 = (2.45 \times 10^{-4})(8.346213909 \times 10^{-4}) = 2.04 \times 10^{-7} \text{ L/mol.s}
\]

15. The rate constants for the decomposition of acetaldehyde

\[ \text{CH}_3\text{CHO}(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{CO}(\text{g}) \]

were measured at five different temperatures. A plot of \(\ln(k)\) versus \(1/T\) produced a straight line with a slope of \(-2.09 \times 10^4\) K and a y-intercept of -0.45.

(a) Determine the activation energy for this reaction.

\[
\text{Slope} = -\frac{E_a}{R} = -2.09 \times 10^4 \text{ K}
\]

\[
E_a = (8.314 \text{ J/mol K}) (2.09 \times 10^4 \text{ K})
\]

\[
= 1.74 \times 10^5 \text{ J/mol} = 174 \text{ kJ/mol}
\]

(b) Determine the value of the frequency factor for this reaction.

\[
\ln A = -0.45
\]

\[
A = e^{-0.45} = 0.638 \text{ s}^{-1}
\]

(c) Calculate the value of the rate constant at 537°C.

\[
\ln k = (-\frac{E_a}{2})(\frac{1}{T}) + \ln A
\]

\[
= - (2.09 \times 10^4 \text{ K}) \left( \frac{1}{810 K} \right) + \ln (0.638)
\]

\[
= -25.33305314
\]

\[
k = \frac{3.83 \times 10^{-12}}{\text{mol.s}}
\]
16. What part of the energy profile of a reaction is affected by a catalyst?

A catalyst increases the rate of reaction by either decreasing the activation energy or by increasing the frequency factor.

17. What is the difference between a homogeneous and a heterogeneous catalyst?

A homogeneous catalyst is in the same phase as the reactants while a heterogeneous catalyst is in a different phase.