Exercises

A. The graph below shows concentration versus time for the consecutive elementary reactions:

\[ A \rightarrow B \rightarrow C \rightarrow D \]

with rate constants \( k_a \ \ kb \ \ kc \)

Initial concentrations are \( [A]_o = 1 \text{ molar}, \) and \( [B]_o = [C]_o = [D]_o = 0 \)

Estimate the values of \( k_a, \) \( k_b, \) and \( k_c \) from the data in the graph.

![Graph showing concentration versus time for reactions A, B, C, and D.](image)

B. Given the information below, calculate \( [NO_3]_{ss} \):

\[
\begin{align*}
N_2O_5 &\rightarrow NO_2 + NO_3 \quad k_1 = 3.2 \times 10^{-4} \text{ sec}^{-1} \\
NO_2 + NO_3 &\rightarrow N_2O_5 \quad k_{-1} = 8.3 \times 10^{-13} \text{ cm}^3/(\text{molecules sec}) \\
NO_3 + NO &\rightarrow 2 NO_2 \quad k_2 = 3.3 \times 10^{-11} \text{ cm}^3/(\text{molecules sec}) \\
NO_2 + NO_3 &\rightarrow NO + O_2 + NO_2 \quad k_3 = 1.4 \times 10^{-16} \text{ cm}^3/(\text{molecules sec})
\end{align*}
\]

\( [NO_2] = [NO] = 1 \times 10^9 \quad [N_2O_5] = 1.0 \times 10^{10} \text{ molecules/cm}^3 \)

C. Consider the elementary reaction \( X \rightarrow Y \)

\( k_1 \)

\( E_a = 4.0 \text{ kcal/mole} \quad \Delta H^o_r = -5.0 \text{ kcal/mole} \quad \Delta S^o_r = -15 \text{ cal/(mole K)} \)

A-factor = \( 1.00 \times 10^{-11} \text{ cm}^3/(\text{molecules sec}) \)

For \( Y \rightarrow X \) (reaction -1), what is \( E_a \)? The A-factor?
Problems

1) Consider elementary reactions below and constant concentrations of Cl, CH₄, O₂, and NO.

\[
\begin{align*}
\text{Cl} + \text{CH}_4 & \rightarrow \text{HCl} + \cdot\text{CH}_3 & k_1 = 1.0 \times 10^{-13} \text{ cm}^3/(\text{molecules sec}) \\
\cdot\text{CH}_3 + \text{O}_2 & \rightarrow \text{CH}_3\text{OO}\cdot & k_2 = 3.5 \times 10^{-12} \text{ cm}^3/(\text{molecules sec}) \\
\text{CH}_3\text{OO}\cdot + \text{NO} & \rightarrow \text{CH}_3\text{O}\cdot + \text{NO}_2 & k_3 = 8.7 \times 10^{-12} \text{ cm}^3/(\text{molecules sec})
\end{align*}
\]

\[
\begin{align*}
[\text{CH}_4] &= 4.4 \times 10^{16} & [\text{Cl}] &= 1.0 \times 10^4 \text{ molecules/cm}^3 \\
[\text{O}_2] &= 5.0 \times 10^{18} & [\text{NO}] &= 1.0 \times 10^{10} \text{ molecules/cm}^3
\end{align*}
\]

What are the steady state concentrations of \(\cdot\text{CH}_3\) and \(\text{CH}_3\text{OO}\cdot\)?

Explain whether or not you have sufficient information to compute \([\text{CH}_3\text{O}\cdot]_{ss}\).

2) GIVEN: the two different expressions given below for the rate constant for the reaction:

\[
\text{\text{C}_4\text{H}_9\text{O}\cdot + \cdot\text{NO} \rightarrow \text{C}_4\text{H}_9\text{ONO}}
\]

\[
k = 7.8 \times 10^{-12} \exp(+2.85 \text{ kJ/mol}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.
\]

a) In the first expression, what, if anything, is the relationship between \(7.8 \times 10^{-12}\) and the rate constant for collisions?

b) In the first expression, what, if anything, is the relationship between \(2.85 \text{ kJ/mol}\) and the enthalpy barrier separating reactants and products?

3) Consider the elementary reactions at right and the data:

\[
k_2 = 1.8 \times 10^{13} \exp(-12.2 \text{ kcal/mole}/RT) \text{ s}^{-1}
\]

\[
\Delta H^o_r = +1.7 \text{ kcal/mole} \quad \Delta S^o_r = +11.5 \text{ cal/(mole K)}.
\]

What is the Arrhenius expression for \(k_2\)?

4) Explain why the reaction below could not be an elementary reactions:

A gas phase reaction \(\text{A} + \text{B} \rightarrow \text{products}\) follows the rate law \(v = k[A][B]\)

with \(k = 1.4 \times 10^{-11} \text{ e}^{-1000/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) and \(\Delta H^o_r = +20 \text{ kJ/mole}\)
5) The graph below shows concentration versus time for the elementary reactions:

\[ \text{A} \rightarrow \text{B} \quad \text{ka} \]
\[ \text{B} \rightarrow \text{C} \quad \text{kb} \]
\[ \text{C} \rightarrow \text{B} \quad \text{k}_{-b} \]

Initial concentrations are \([\text{A}]_0 = 1\) molar, and \([\text{B}]_0 = [\text{C}]_0 = [\text{D}]_0 = 0\)

**Estimate** the values of \(k_a\), \(k_b\), and \(k_{-b}\) from the data in the graph.

6. **This question does not count towards your grade.** Concentrations of \(\text{O}_2\) in the atmosphere are controlled by the following processes. \(\tau\), of \(\text{O}_2\) in the atmosphere is \(4.5 \times 10^3\) years

<table>
<thead>
<tr>
<th>Inputs (kg/year)</th>
<th>Removal (kg/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photosynthesis on land (1.65 \times 10^{14})</td>
<td>Aerobic Respiration (2.3 \times 10^{14})</td>
</tr>
<tr>
<td>Photosynthesis in ocean (1.35 \times 10^{14})</td>
<td>Microbial Oxidation (5.1 \times 10^{13})</td>
</tr>
<tr>
<td>Fuel combustion (1.2 \times 10^{13})</td>
<td>Other (0.7 \times 10^{13})</td>
</tr>
</tbody>
</table>

a) Show from this data that \([\text{O}_2]\) in the atmosphere is at (or close to) steady state.

b) Calculate the mass of \(\text{O}_2\) in the atmosphere.