LECTURE 32

1. (a) Write the rate law that corresponds to the following reaction mechanism using the steady-state approximation. **Do not** make any assumptions about rates of step 1 and step 2.

\[
\begin{align*}
\text{Step 1} & \quad 2 \text{NO}_2\text{Cl} \rightleftharpoons \text{N}_2\text{O}_4 + \text{Cl}_2 \\
& \quad k_1 \\
\text{Step 2} & \quad \text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2 \\
& \quad k_2
\end{align*}
\]

(b) Write the rate law if the first step is in fast equilibrium and the second step is slow.

2. For the reaction: \(2\text{A} + \text{B}_2 \rightarrow 2\text{AB}\), a proposed mechanism is:

\[
\begin{align*}
\text{Step 1} & \quad \text{A} + \text{B}_2 \rightleftharpoons \text{AB}_2 \\
& \quad k_1 \\
\text{Step 2} & \quad \text{A} + \text{AB}_2 \rightarrow \text{AB} + \text{AB} \\
& \quad k_2
\end{align*}
\]

If the consumption of \(\text{AB}_2\) by reaction with \(\text{A}\) is slower than the decomposition of \(\text{AB}_2\), write the rate law for this mechanism using the steady-state approximation.

3. It has been experimentally determined that the rate law for the reaction, \(\text{O}_3 + \text{NO} \rightarrow \text{O}_2 + \text{NO}_2\), is rate = \(k_{\text{obs}}[\text{O}_3][\text{NO}]\). Write the rate law that corresponds to the following reaction mechanism, and state whether this reaction mechanism is consistent with the experimental rate law.

\[
\begin{align*}
\text{Step 1} & \quad \text{NO} + \text{NO} \rightleftharpoons \text{N}_2\text{O}_2 \\
& \quad \text{(fast, reversible)} \\
& \quad k_1 \\
\text{Step 2} & \quad \text{N}_2\text{O}_2 + 2\text{O}_3 \rightarrow 2\text{NO}_2 + 2\text{O}_2 \\
& \quad \text{(slow)} \\
& \quad k_2
\end{align*}
\]

**Additional Book Problems:**
Atkins and Jones, Chemical Principles, fifth edition:
Chapter 14.7 and 14.8, problem 14.48, 14.49
Chapter 14.7 and 14.8, problem 14.51, 14.52