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.

Step 1 $$2\,NO_2Cl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_4 + Cl_2$$

Step 2 $$N_2O_4 \xrightarrow{k_2} 2NO_2$$

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

(a) $$\text{rate} = \frac{2k_2k_1[NO_2Cl]^2}{(k_{-1}[Cl_2]+k_2)}$$

(b) $$\text{rate} = \frac{2k_2k_1[NO_2Cl]^2}{(k_{-1}[Cl_2])}$$ **or** $$\text{rate} = \frac{2k_2K_1[NO_2Cl]^2}{[Cl_2]}$$

2. For the reaction: $2A + B_2 \rightarrow 2AB$, a proposed mechanism is:

Step 1 $$A + B_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB_2$$

Step 2 $$A + AB_2 \xrightarrow{k_2} AB + AB$$

If the consumption of AB_2 by reaction with A is slower than the decomposition of AB_2, write the rate law for this mechanism using the steady-state approximation.

$2k_2K_1[A]^2[B_2]$ or $2k_2k_1[A]^2[B_2]/k_{-1}$

3. It has been experimentally determined that the rate law for the reaction,

$$O_3 + NO \rightarrow O_2 + NO_2, \text{ is rate} = k_{obs}[O_3][NO].$$

Write the rate law that corresponds to the following reaction mechanism, and state whether this reaction mechanism is consistent with the experimental rate law.

Step 1 (fast, reversible) $$NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$$

Step 2 (slow) $$N_2O_2 + 2O_3 \xrightarrow{k_2} 2NO_2 + 2O_2$$

rate = $k_2K_1[O_3]^2[NO]^2$ or $k_{obs}[O_3]^2[NO]^2$
No the above mechanism is not consistent with the experimental rate law.

LECTURE 32

<u>Additional Book Problems</u>:
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

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