Reaction Mechanisms/Kinetics In-Class Practice Problems

1. Nitrogen pentoxide reacts with nitric oxide in the gas phase according to the stoichiometric equation

$$N_2O_5 + NO \rightarrow 3NO_2$$

The following mechanism has been proposed.

$$N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$$

$$NO + NO_3 \xrightarrow{k_2} 2NO_2$$

(a) Assume that the steady-state approximation can be applied to NO_3 and derive an equation for the rate of production of NO_2.

(b) How does the rate of production of NO_2 relate to the rate of consumption of N_2O_5?

2. A. Lindemann (Trans Faraday Soc., 17, 598(1922)) proposed the following mechanism for a unimolecular gas reaction

$$A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + A$$

$$A^* \xrightarrow{k_2} Y + Z$$

The species A* is an enegized molecule that is present in low concentrations.

(a) Apply the steady-state approximation to A* and obtain an expression for the rate (i.e., d[Y]/dt or d[Z]/dt) in terms of [A], k_1, k_{-1}, and k_2.

(b) Identify the conditions under which the rate is first order and those under which it is second order, and give expressions for the observed first and second order rate constants in terms of k_1, k_{-1} and k_2.

3. The rate law for the reaction of para-hydrogen to ortho-hydrogen

$$para - H_2(g) \xrightarrow{k_{obs}} ortho - H_2(g)$$

is

$$\frac{d[ortho - H_2]}{dt} = k_{obs}[para - H_2]^{3/2}$$

Show that the following mechanism is consistent with this rate law and express k_{obs} in terms of the rate constants for the individual steps of the reaction mechanism.

$$para - H_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2H(g) \qquad \text{fast equilibrium}$$

$$H(g) + para - H_2 \xrightarrow{k_e} ortho - H_2(g) + H(g)$$