Homework #13-5: Ch. 13.5-13.6: Reaction Mechanisms & Catalysis
Problems pg. 577-578 #46, 47, 49, 51-55, 61, 62, pg. 581 #102

13.46 Reactions can be classified as unimolecular, bimolecular, and so on. Why are there no zero-molecular reactions? Explain why termolecular reactions are rare.

13.47 Determine the molecularity and write the rate law for each of the following elementary steps:
a) $X \rightarrow$ products
b) $X + Y \rightarrow$ products
c) $X + Y + Z \rightarrow$ products
d) $X + X \rightarrow$ products
e) $X + 2Y \rightarrow$ products

13.49 The equation for the combustion of ethane (C_2H_6) is:

$$2\ C_2H_6(g) + 7\ O_2(g) \rightarrow 4\ CO_2(g) + 6\ H_2O(l)$$

Explain why it is unlikely that this equation also represents the elementary step for the reaction.

13.51 The rate law for the reaction $2\ NO(g) + Cl_2(g) \rightarrow 2\ NOCl(g)$ is rate = $k[NO][Cl_2]$
(a) What is the order of the reaction?

(b) The proposed mechanism for this reaction is:

$$NO + Cl_2 \rightarrow NOCl_2$$
$$NOCl_2 + NO \rightarrow 2\ NOCl$$

What does the above mechanism imply about the relative rates of the two steps?

13.52 For the reaction $X_2 + Y + Z \rightarrow XY + XZ$, doubling X_2 doubles the reaction rate, tripling Y triples the rate, and doubling Z has no effect.
(a) What is the rate law?

(b) Why does the change in Z have no effect?

(c) Suggest a consistent mechanism

13.53 **The rate law for decomposition of ozone, $2\ O_3(g) \rightarrow 3\ O_2(g)$, is $k\dfrac{[O_3]^2}{[O_2]}$**

The proposed mechanism for the reaction is: $O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O + O_2$

$$O + O_3 \xrightarrow{k_2} 2O_2$$

where $k_1 \approx k_{-1} \gg k_2$. Derive the rate law from these elementary steps. Explain why the rate *decreases* with increasing O_2 concentration.

13.54 **The rate law for $2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$ is $\text{rate} = k[H_2][NO]^2$. Which of the following mechanisms can be ruled out on the basis of the observed rate law? Explain each choice.**

Mech I: $H_2 + NO \rightarrow H_2O + N$ **(slow)**
$N + NO \rightarrow N_2 + O$ **(fast)**
$O + H_2 \rightarrow H_2O$ **(fast)**

Mech II: $H_2 + 2NO \rightarrow N_2O + H_2O$ **(slow)**
$N_2O + H_2 \rightarrow N_2 + H_2O$ **(fast)**

Mech III: $2NO \rightleftharpoons N_2O_2$ **(fast equilibrium)**
$N_2O_2 + H_2 \rightarrow N_2O + H_2O$ **(slow)**
$N_2O + H_2 \rightarrow N_2 + H_2O$ **(fast)**

13.55 How does a catalyst increase the rate of a reaction?

13.61 Most reactions, including enzyme-catalyzed reactions, proceed faster at higher temperatures. However, for a given enzyme, the rate drops off abruptly at a certain temperature. Account for this behavior.

13.62 Consider the following mechanism for enzyme-catalyzed reaction:

$$\mathbf{E + S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{ES} \qquad \textbf{(fast equilibrium)}$$

$$\mathbf{ES} \xrightarrow{k_2} \mathbf{E + P} \qquad \textbf{(slow)}$$

Derive an expression for the rate law of the reaction in terms of the concentrations of E and S. (*Hint:* To solve for [ES], make use of the fact that, at equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction.

The rate law for step 2, the RDS, is: rate = k_2[ES]

13.102 Thallium(I) is oxidized by cerium(IV) as follows:

$$\mathbf{Tl^+ + 2\ Ce^{4+} \rightarrow Tl^{3+} + 2\ Ce^{3+}}$$

Mech: $\mathbf{Ce^{4+} + Mn^{2+} \rightarrow Ce^{3+} + Mn^{3+}}$

$\mathbf{Ce^{4+} + Mn^{3+} \rightarrow Ce^{3+} + Mn^{4+}}$

$\mathbf{Tl^+ + Mn^{4+} \rightarrow Tl^{3+} + Mn^{2+}}$

(a) Identify the catalyst, intermediates, and the rate-determining step if the rate law is rate = k[Ce^{4+}][Mn^{2+}].

(b) Explain why the reaction is slow without the catalyst.

(c) Classify the type of catalysis (homogeneous or heterogeneous).