Chapter 11 Homework Solutions

11.1 The first step is the rate determining step. Therefore, the rate law is: rate = k[H_2O_2][Br^-]

This reaction is first-order with respect to [H_2O_2], first-order with respect to [Br^-], and second order overall.

11.2 A_2 = A + A : Fast pre-equilibrium with equil. constant, K.
A + B $\rightarrow$ P : Slow rate-determining step with rate constant, k.

$$K = \frac{[A]^2}{[A_2]} \rightarrow [A] = K^{1/2}[A_2]^{1/2}$$

$$rate = \frac{d[P]}{dt} = k[A][B] = kK^{1/2}[A_2]^{1/2}[B] = k_{eff}[A_2]^{1/2}[B]\ ,\ where\ k_{eff} = kK^{1/2}$$

11.3

$$2A \overset{K}{=} A_2 \quad \text{(fast pre-equilbrium)}$$

$$A_2 + B \overset{k_2}{\rightarrow} \text{Products} \quad \text{(slow)}$$

$$K = \frac{[A_2]}{[A]^2} \quad \rightarrow \quad [A_2] = K[A]^2$$

rate = $k_2[A_2][B] = k_2K[A]^2[B]$

11.4 Mechanism:

$$O_3 \overset{k_1}{\rightarrow} O_2 + O$$

$$O_2 + O \overset{k_1'}{\rightarrow} O_3$$

$$O + O_3 \overset{k_2}{\rightarrow} O_2 + O_2$$

Steady-State on [O]: $\frac{d[O]}{dt} = 0 = k_1[O_3] - k_1'[O][O_2] - k_2[O][O_3]$

Therefore: $[O]\{k_1'[O_2] + k_2[O_3]\} = k_1[O_3] \quad \rightarrow \quad [O] = \frac{k_1[O_3]}{k_1'[O_2] + k_2[O_3]}$

$$rate = -\frac{d[O_3]}{kt} = -\{-k_1[O_3] + k_1'[O_2][O] - k_2[O_3][O]\} = k_1[O_3] - k_1'[O_2][O] + k_2[O_3][O]$$

Substitute for [O]

$$rate = -\frac{d[O_3]}{kt} = k_1[O_3] - k_1'[O_2]\frac{k_1[O_3]}{k_1'[O_2]+k_2[O_3]} + k_2[O_3]\frac{k_1[O_3]}{k_1'[O_2]+k_2[O_3]}$$

$$= \frac{k_1[O_3]\{k_1'[O_2]+k_2[O_3]\} - k_1k_1'[O_2][O_3] + k_1k_2[O_3]^2}{k_1'[O_2]+k_2[O_3]}$$

$$= \frac{k_1k_1'[O_2][O_3] + k_1k_2[O_3]^2 - k_1k_1'[O_2][O_3] + k_1k_2[O_3]^2}{k_1'[O_2]+k_2[O_3]}$$

$$= \frac{2k_1k_2[O_3]^2}{k_1'[O_2]+k_2[O_3]}$$

If the k_2 step is slow (i.e. $k_2[O_3] << k_1'[O_2]$), then

$$rate = \frac{2k_1k_2[O_3]^2}{k_1'[O_2]} = k_{eff}\frac{[O_3]^2}{[O_2]}$$ and the reaction orders are: 2 with respect to $[O_3]$

-1 with respect to $[O_2]$

11.5 Mechanism:

$$AH + B \xrightarrow{k_1} BH^+ + A^-$$

$$A^- + BH^+ \xrightarrow{k_2} AH + B$$

$$A^- + AH \xrightarrow{k_3} \text{Product}$$

Steady-State on $[A^-]$: $\frac{d[A^-]}{dt} = 0 = k_1[AH][B] - k_2[A^-][BH^+] - k_3[A^-][AH]$

Therefore: $[A^-]\{k_2[BH^+] + k_3[AH]\} = k_1[AH][B] \quad \rightarrow \quad [A^-] = \frac{k_1[AH][B]}{k_2[BH^+]+k_3[AH]}$

$$rate = \frac{d[\text{Product}]}{dt} = k_3[A^-][AH] = k_3\frac{k_1[AH][B]}{k_2[BH^+]+k_3[AH]}[AH] = \frac{k_1k_3[AH]^2[B]}{k_2[BH^+]+k_3[AH]}$$

11.6

$$A + B \underset{k_{-1}}{\overset{k_1}{=}} I$$

$$I + C \xrightarrow{k_2} P$$

Steady-State Approx. on [I]: $\frac{d[I]}{dt} = 0 = k_1[A][B] - k_{-1}[I] - k_2[I][C]$

Therefore: $[I]\{k_{-1} + k_2[C]\} = k_1[A][B] \quad \rightarrow \quad [I] = \frac{k_1[A][B]}{k_{-1} + k_2[C]}$

$$rate = \frac{d[P]}{dt} = k_2[I][C] = k_2\left\{\frac{k_1[A][B]}{k_{-1} + k_2[C]}\right\}[C] = \frac{k_1 k_2[A][B][C]}{k_{-1} + k_2[C]}$$

11.7 $K_M = 0.045$ M v = 1.15 mM/s = $1.15\text{x}10^{-3}$ M/s [S] = 0.111 M

$$v_o = \frac{k_2[E]_o[S]}{K_M + [S]} = \frac{V_m[S]}{K_M + [S]} \qquad \rightarrow$$

$$V_m = v_o\frac{K_M + [S]}{[S]} = (1.15x10^{-3}\ M/s)\cdot\frac{0.045M + 0.111M}{0.111M}$$

$$= (1.15x10^{-3}\ M/s)\cdot(1.405) = 1.62x10^{-3}\ M/s\ (or\ 1.62\ mM/s)$$

11.8 $(v_o)_1 = 3.7\text{x}10^{-8}$ M/s when $[S]_1 = 2.5\text{x}10^{-4}$ M $[E]_o = 4.0\text{x}10^{-6}$ M
$(v_o)_2 = 9.8\text{x}10^{-8}$ M/s when $[S]_2 = 1.0\text{x}10^{-3}$ M

$$v_o = \frac{V_m[S]}{K_M + [S]} \rightarrow \frac{1}{v_o} = \frac{K_M + [S]}{V_M[S]} = \frac{K_M}{V_M}\frac{1}{[S]} + \frac{1}{V_m} = slope\cdot\frac{1}{[S]} + Int$$

$$slope = \frac{K_M}{V_m} \quad and \quad Int = \frac{1}{V_m}$$

$$slope = \frac{\frac{1}{(v_o)_2} - \frac{1}{(v_o)_1}}{\frac{1}{[S]_2} - \frac{1}{[S]_1}} = \frac{\frac{1}{9.8x10^{-8}\ M/s} - \frac{1}{3.7x10^{-8}\ M/s}}{\frac{1}{1.0x10^{-3}\ M} - \frac{1}{2.5x10^{-4}\ M}} = 5.61x10^3\ s$$

$$Int = \frac{1}{(v_o)_1} - slope\cdot\frac{1}{[S]_1} = \frac{1}{3.7x10^{-8}\ M/s} - (5.61x10^3\ s)\cdot\frac{1}{2.5x10^{-4}\ M} = 4.59x10^6\ s/M$$

$$V_m = \frac{1}{Int} = \frac{1}{4.59x10^{6}\ s/M} = 2.18x10^{-7}\ M/s$$

$$K_M = slope \cdot V_m = (5.61x10^{3}\ s)(2.18x10^{-7}\ M/s) = 1.22x10^{-3}\ M$$

$$V_m = k_2[E]_o \quad \rightarrow \quad k_2 = \frac{V_m}{[E]_o} = \frac{2.18x10^{-7}\ M/s}{4.0x10^{-6}\ M} = 5.45x10^{-2}\ s^{-1}$$

11.9 K_M = 2.8x10^{-5} M V_m = 53 μM/min
[S] = 7.5x10^{-5} M [I] = 4.8x10^{-4} M K_I = 1.7x10^{-4} M

No Inhibitor: $$v_o = \frac{V_m[S]}{K_M + [S]} = \frac{(53\,\mu M/\min)(7.5x10^{-5}\ M)}{2.8x10^{-5}\ M + 7.5x10^{-5}\ M} = 38.6\,\mu M/\min$$

$$1 + \frac{[I]}{K_I} = 1 + \frac{4.8x10^{-4}\ M}{1.7x10^{-4}\ M} = 3.82$$

(a) Competitive Inhibition

$$(v_o)_{inh} = \frac{V_m[S]}{K_M\left(1 + \frac{[I]}{K_I}\right) + [S]} = \frac{(53\,\mu M/\min)(7.5x10^{-5}\ M)}{(2.8x10^{-5}\ M)(3.82) + 7.5x10^{-5}\ M} = 21.8\mu M/\min$$

$$i\% = 100 \cdot \left(1 - \frac{(v_o)_{inh}}{v_o}\right) = 100 \cdot \left(1 - \frac{21.8\,\mu M/\min}{38.6\,\mu M/\min}\right) = 43.5\%$$

(b) Uncompetitive Inhibition

$$(v_o)_{inh} = \frac{V_m[S]}{K_M + [S]\left(1 + \frac{[I]}{K_I}\right)} = \frac{(53\,\mu M/\min)(7.5x10^{-5}\ M)}{2.8x10^{-5}\ M + (7.5x10^{-5}\ M)(3.82)} = 12.6\mu M/\min$$

$$i\% = 100 \cdot \left(1 - \frac{(v_o)_{inh}}{v_o}\right) = 100 \cdot \left(1 - \frac{12.6\,\mu M/\min}{38.6\,\mu M/\min}\right) = 67.4\%$$

(c) Noncompetitive Inhibition

$$(v_o)_{inh} = \frac{V_m[S]}{\left(K_M + [S]\right)\left(1 + \frac{[I]}{K_I}\right)} = \frac{(53\,\mu M/\min)(7.5x10^{-5}\,M)}{(2.8x10^{-5}\,M + 7.5x10^{-5}\,M)(3.82)} = 10.1\mu M/\min$$

$$i\% = 100\cdot\left(1 - \frac{(v_o)_{inh}}{v_o}\right) = 100\cdot\left(1 - \frac{10.1\,\mu M/\min}{38.6\,\mu M/\min}\right) = 73.8\%$$

11.10 $K_M = 2.7x10^{-3}$ M [S] = $3.6x10^{-4}$ M $K_I = 3.1x10^{-5}$ M

$$i\% = 100\left(1 - \frac{(v_o)_{inh}}{v_o}\right) = 65\% \rightarrow 1 - \frac{(v_o)_{inh}}{v_o} = 0.65 \rightarrow \frac{(v_o)_{inh}}{v_o} = 0.35 \rightarrow \frac{v_o}{(v_o)_{inh}} = \frac{1}{0.35} = 2.86$$

No Inhibitor: $v_o = \frac{V_m[S]}{K_M + [S]}$

Competitive Inhibitor: $(v_o)_{inh} = \frac{V_m[S]}{K_M\left(1 + \frac{[I]}{K_I}\right) + [S]}$

$$\frac{v_o}{(v_o)_{inh}} = \frac{\dfrac{V_m[S]}{K_M + [S]}}{\dfrac{V_m[S]}{K_M\left(1 + \frac{[I]}{K_I}\right) + [S]}} = \frac{K_M\left(1 + \frac{[I]}{K_I}\right) + [S]}{K_M + [S]} = \frac{K_M + [S] + \frac{K_M}{K_I}[I]}{K_M + [S]} = 1 + \frac{\frac{K_M}{K_I}[I]}{K_M + [S]}$$

$$2.86 = 1 + \frac{\dfrac{2.7x10^{-3}\,M}{3.1x10^{-5}\,M}[I]}{2.7x10^{-3}\,M + 3.6x10^{-4}\,M} = 1 + \left(2.85x10^{4}\,M^{-1}\right)[I]$$

$$[I] = \frac{2.86 - 1}{2.85x10^{4}\,M^{-1}} = 6.53x10^{-5}\,M$$

11.11 Two points on Graph: $\left(\frac{1}{v_o}\right)_1 = 0.06\,s/mM \quad at \quad \left(\frac{1}{[S]}\right)_1 = 2.0\,mM^{-1}$

$$\left(\frac{1}{v_o}\right)_2 = 0.10\,s/mM \quad at \quad \left(\frac{1}{[S]}\right)_2 = 5.0\,mM^{-1}$$

$$v_o = \frac{V_m[S]}{K_M + [S]} \quad \rightarrow \quad \frac{1}{v_o} = \frac{K_M + [S]}{V_M[S]} = \frac{K_M}{V_M}\frac{1}{[S]} + \frac{1}{V_m} = slope \cdot \frac{1}{[S]} + Int$$

$$slope = \frac{K_M}{V_m} \quad and \quad Int = \frac{1}{V_m}$$

$$slope = \frac{\left(\frac{1}{v_o}\right)_2 - \left(\frac{1}{v_o}\right)_1}{\left(\frac{1}{[S]}\right)_2 - \left(\frac{1}{[S]}\right)_1} = \frac{0.10\,s/mM - 0.06\,s/mM}{5.0\,mM^{-1} - 2.0\,mM^{-1}} = 0.0133\,s$$

$$Int = \left(\frac{1}{v_o}\right)_1 - slope \cdot \left(\frac{1}{[S]}\right)_1 = 0.06\,s/mM - (0.0133\,s)(2.0\,mM^{-1}) = 0.0334\,s/mM$$

$$V_m = \frac{1}{Int} = \frac{1}{0.0334\,s/mM} = 30.0\,mM/s$$

$$K_M = slope \cdot V_m = (0.0133\,s)(30.0\,mM/s) = 0.40\,mM$$