

## Chapter 11 Homework Solutions

**11.1** The first step is the rate determining step. Therefore, the rate law is:  $\text{rate} = k[\text{H}_2\text{O}_2][\text{Br}^-]$

This reaction is first-order with respect to  $[\text{H}_2\text{O}_2]$ , first-order with respect to  $[\text{Br}^-]$ , and second order overall.

**11.2**  $\text{A}_2 = \text{A} + \text{A}$  : Fast pre-equilibrium with equil. constant,  $K$ .  
 $\text{A} + \text{B} \rightarrow \text{P}$  : Slow rate-determining step with rate constant,  $k$ .

$$K = \frac{[\text{A}]^2}{[\text{A}_2]} \rightarrow [\text{A}] = K^{1/2}[\text{A}_2]^{1/2}$$

$$\text{rate} = \frac{d[\text{P}]}{dt} = k[\text{A}][\text{B}] = kK^{1/2}[\text{A}_2]^{1/2}[\text{B}] = k_{\text{eff}}[\text{A}_2]^{1/2}[\text{B}], \text{ where } k_{\text{eff}} = kK^{1/2}$$

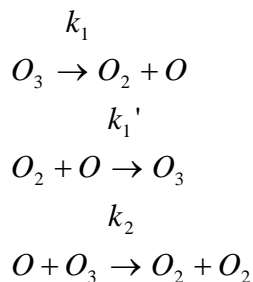
**11.3**  $\text{K}$   
 $2\text{A} = \text{A}_2$  (fast pre-equilibrium)

$k_2$   
 $\text{A}_2 + \text{B} \rightarrow \text{Products}$  (slow)

$$K = \frac{[\text{A}_2]}{[\text{A}]^2} \rightarrow [\text{A}_2] = K[\text{A}]^2$$

$$\text{rate} = k_2[\text{A}_2][\text{B}] = k_2K[\text{A}]^2[\text{B}]$$

**11.4** Mechanism:



Steady-State on  $[\text{O}]$ :  $\frac{d[\text{O}]}{dt} = 0 = k_1[\text{O}_3] - k_1'[\text{O}][\text{O}_2] - k_2[\text{O}][\text{O}_3]$

Therefore:  $[\text{O}]\{k_1'[\text{O}_2] + k_2[\text{O}_3]\} = k_1[\text{O}_3] \rightarrow [\text{O}] = \frac{k_1[\text{O}_3]}{k_1'[\text{O}_2] + k_2[\text{O}_3]}$

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

Substitute for [O]

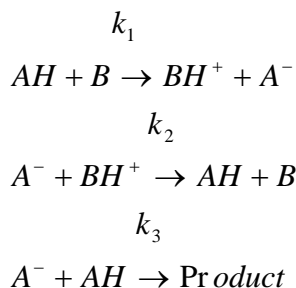
$$\begin{aligned} rate &= -\frac{d[O_3]}{dt} = k_1[O_3] - k_1'[O_2] \frac{k_1[O_3]}{k_1'[O_2] + k_2[O_3]} + k_2[O_3] \frac{k_1[O_3]}{k_1'[O_2] + k_2[O_3]} \\ &= \frac{k_1[O_3]\{k_1'[O_2] + k_2[O_3]\} - k_1k_1'[O_2][O_3] + k_1k_2[O_3]^2}{k_1'[O_2] + k_2[O_3]} \\ &= \frac{k_1k_1'[O_2][O_3] + k_1k_2[O_3]^2 - k_1k_1'[O_2][O_3] + k_1k_2[O_3]^2}{k_1'[O_2] + k_2[O_3]} \\ &= \frac{2k_1k_2[O_3]^2}{k_1'[O_2] + k_2[O_3]} \end{aligned}$$

If the  $k_2$  step is slow (i.e.  $k_2[O_3] \ll k_1'[O_2]$ , 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:

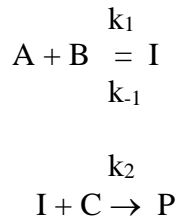


Steady-State on  $[A^-]$ :  $\frac{d[A^-]}{dt} = 0 = k_1[AH][B] - k_2[A^-][BH^+] - k_3[A^-][AH]$

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

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

11.6



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

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

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

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

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

$$\begin{aligned}
 V_m &= v_o \frac{K_M + [S]}{[S]} = (1.15 \times 10^{-3} \text{ M/s}) \cdot \frac{0.045 \text{ M} + 0.111 \text{ M}}{0.111 \text{ M}} \\
 &= (1.15 \times 10^{-3} \text{ M/s}) \cdot (1.405) = 1.62 \times 10^{-3} \text{ M/s (or } 1.62 \text{ mM/s)}
 \end{aligned}$$

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

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

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

$$\text{slope} = \frac{\frac{1}{(v_o)_2} - \frac{1}{(v_o)_1}}{\frac{1}{[S]_2} - \frac{1}{[S]_1}} = \frac{\frac{1}{9.8 \times 10^{-8} \text{ M/s}} - \frac{1}{3.7 \times 10^{-8} \text{ M/s}}}{\frac{1}{1.0 \times 10^{-3} \text{ M}} - \frac{1}{2.5 \times 10^{-4} \text{ M}}} = 5.61 \times 10^3 \text{ s}$$

$$\text{Int} = \frac{1}{(v_o)_1} - \text{slope} \cdot \frac{1}{[S]_1} = \frac{1}{3.7 \times 10^{-8} \text{ M/s}} - (5.61 \times 10^3 \text{ s}) \cdot \frac{1}{2.5 \times 10^{-4} \text{ M}} = 4.59 \times 10^6 \text{ s/M}$$

$$V_m = \frac{1}{\text{Int}} = \frac{1}{4.59 \times 10^6 \text{ s/M}} = 2.18 \times 10^{-7} \text{ M/s}$$

$$K_M = \text{slope} \cdot V_m = (5.61 \times 10^3 \text{ s})(2.18 \times 10^{-7} \text{ M/s}) = 1.22 \times 10^{-3} \text{ M}$$

$$V_m = k_2[E]_o \rightarrow k_2 = \frac{V_m}{[E]_o} = \frac{2.18 \times 10^{-7} \text{ M/s}}{4.0 \times 10^{-6} \text{ M}} = 5.45 \times 10^{-2} \text{ s}^{-1}$$

**11.9**  $K_M = 2.8 \times 10^{-5} \text{ M}$        $V_m = 53 \text{ } \mu\text{M/min}$   
 $[S] = 7.5 \times 10^{-5} \text{ M}$        $[I] = 4.8 \times 10^{-4} \text{ M}$        $K_I = 1.7 \times 10^{-4} \text{ M}$

**No Inhibitor:**  $v_o = \frac{V_m[S]}{K_M + [S]} = \frac{(53 \text{ } \mu\text{M/min})(7.5 \times 10^{-5} \text{ M})}{2.8 \times 10^{-5} \text{ M} + 7.5 \times 10^{-5} \text{ M}} = 38.6 \text{ } \mu\text{M/min}$

$$1 + \frac{[I]}{K_I} = 1 + \frac{4.8 \times 10^{-4} \text{ M}}{1.7 \times 10^{-4} \text{ M}} = 3.82$$

**(a) Competitive Inhibition**

$$(v_o)_{inh} = \frac{V_m[S]}{K_M \left(1 + \frac{[I]}{K_I}\right) + [S]} = \frac{(53 \text{ } \mu\text{M/min})(7.5 \times 10^{-5} \text{ M})}{(2.8 \times 10^{-5} \text{ M})(3.82) + 7.5 \times 10^{-5} \text{ M}} = 21.8 \text{ } \mu\text{M/min}$$

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

**(b) Uncompetitive Inhibition**

$$(v_o)_{inh} = \frac{V_m[S]}{K_M + [S] \left(1 + \frac{[I]}{K_I}\right)} = \frac{(53 \text{ } \mu\text{M/min})(7.5 \times 10^{-5} \text{ M})}{2.8 \times 10^{-5} \text{ M} + (7.5 \times 10^{-5} \text{ M})(3.82)} = 12.6 \text{ } \mu\text{M/min}$$

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

(c) **Noncompetitive Inhibition**

$$(v_o)_{inh} = \frac{V_m[S]}{(K_M + [S])\left(1 + \frac{[I]}{K_I}\right)} = \frac{(53 \mu\text{M} / \text{min})(7.5 \times 10^{-5} \text{ M})}{(2.8 \times 10^{-5} \text{ M} + 7.5 \times 10^{-5} \text{ M})(3.82)} = 10.1 \mu\text{M} / \text{min}$$

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

**11.10**  $K_M = 2.7 \times 10^{-3} \text{ M}$      $[S] = 3.6 \times 10^{-4} \text{ M}$      $K_I = 3.1 \times 10^{-5} \text{ M}$

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

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

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

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

$$2.86 = 1 + \frac{\frac{2.7 \times 10^{-3} \text{ M}}{3.1 \times 10^{-5} \text{ M}}[I]}{2.7 \times 10^{-3} \text{ M} + 3.6 \times 10^{-4} \text{ M}} = 1 + (2.85 \times 10^4 \text{ M}^{-1})[I]$$

$$[I] = \frac{2.86 - 1}{2.85 \times 10^4 \text{ M}^{-1}} = 6.53 \times 10^{-5} \text{ M}$$

**11.11** Two points on Graph:  $\left(\frac{1}{v_o}\right)_1 = 0.06 \text{ s/mM}$  at  $\left(\frac{1}{[S]}\right)_1 = 2.0 \text{ mM}^{-1}$   
 $\left(\frac{1}{v_o}\right)_2 = 0.10 \text{ s/mM}$  at  $\left(\frac{1}{[S]}\right)_2 = 5.0 \text{ mM}^{-1}$

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

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

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

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

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

$$K_M = \text{slope} \cdot V_m = (0.0133 \text{ s})(30.0 \text{ mM/s}) = 0.40 \text{ mM}$$