17E Ka la 2a, Problems 5, 9

(a) (i) $\frac{d[P]}{dt} = k_b[A][B]$

$K_{eq} = \frac{[A]^2}{[A_2]} \Rightarrow [A] = \sqrt{K_{eq}[A_2]} = \sqrt{\frac{k_a}{k_a'}[A_2]}$

$\frac{d[P]}{dt} = k_b[B]\sqrt{\frac{k_a}{k_a'}[A_2]}$

(ii) $\frac{d[A]}{dt} = 2k_a[A_2] - 2k_a'[A]^2 - k_b[A][B]$

$k_b[A][B] = 2k_a[A_2] - 2k_a'[A]^2$

$[A](k_b[B] + 2[A]) = 2k_a[A_2]$

$[A] = \frac{2k_a[A_2]}{k_b[B] + 2[A]}$

$\frac{d[P]}{dt} = k_b[B]\left(\frac{2k_a[A_2]}{k_b[B] + 2[A]}\right)$

2a) $\frac{d[O_3]}{dt} = -k_a[O_3] - k_b[O][O_3] + k_a'[O_2][O]$

$K_{eq} = \frac{[O_2][O]}{[O_3]} \Rightarrow [O] = K_{eq}\frac{[O_3]}{[O_2]} = \frac{k_a[O_3]}{k_a'[O_2]}$

$\frac{d[O_3]}{dt} = -k_a[O_3] - k_b\left(\frac{k_a[O_3]}{k_a'[O_2]}\right)[O_3] + k_a'[O_2]\left(\frac{k_a[O_3]}{k_a'[O_2]}\right)$

$\frac{d[O_3]}{dt} = -k_a[O_3] - \frac{k_b k_a[O_3]^2}{k_a'[O_2]} + k_a[O_3]$

$= \frac{-k_b k_a[O_3]^2}{k_a'[O_2]}$

5. $\frac{d[D]}{dt^2} \quad \frac{d[C]}{dt} = k_2[C] \qquad [D]=0$

$$A \underset{k_1'}{\overset{k_1}{\rightleftarrows}} B \underset{k_2'}{\overset{k_2}{\rightleftarrows}} C \underset{k_3'}{\overset{k_3}{\rightleftarrows}} D$$

$$\frac{d[C]}{dt^2} \quad k_2[B] \qquad -k_3[C] - k_3'[C] = 0$$

$$[C] = \frac{k_2[B]}{k_3 + k_3'}$$

$$\frac{d[B]}{dt} = k_1[A] + k_2'[C] - k_1'[B] - k_2[B] = 0$$

$$[B] = \frac{k_1[A] + k_2[C]}{k_1' + k_2}$$

$$\Rightarrow [C] = k_2\left(\frac{k_1[A] + k_2[C]}{k_1' + k_2}\right) = \frac{k_2 k_1[A] + k_2^2[C]}{(k_1' + k_2)(k_3 + k_2')}$$

$$[C] = \frac{k_2 k_1[A]}{(k_1' + k_2)(k_3 + k_2') - k_2^2}$$

$$\frac{d[D]}{dt} = \frac{k_3 k_2 k_1[A]}{(k_1' + k_2)(k_3 + k_2') - k_2^2}$$

9. Intermediates: OF, F

$$\frac{d[OF]}{dt^2} \quad 2k_a[F_2O]^2 + k_b[F][F_2O] - 2k_3[OF]^2 = 0$$

$$\frac{d[F]}{dt^2} \quad 2k_a[F_2O]^2 - k_b[F][F_2O] + 2k_3[OF]^2 - 2k_4[F]^2[F_2O] = 0$$

$$[OF] = \frac{\sqrt{2k_a[F_2O]^2 + k_b[F][F_2O]}}{2k_3}$$

$$0 = 2k_a[F_2O]^2 - k_b[F][F_2O] + 2k_3\frac{\sqrt{2k_a[F_2O]^2 + k_b[F][F_2O]}}{2k_3} - 2k_4[F]^2[F_2O]$$

$$2k_4[F]^2[F_2O] = 4k_a[F_2O]^2$$

$2k_d[P]^2[F_2O]^2 = k_a[F_2O]^2$

$[P] = \sqrt{\frac{2k_a[F_2O]}{k_d}}$

$\frac{d[F_2O]}{dt} = -k_a[F_2O]^2 - k_b[P][F_2O]$

$= -k_a[F_2O]^2 - \sqrt{\frac{2k_a}{k_d}[F_2O]}[F_2O] \cdot k_b$

$-\frac{d[F_2O]}{dt} = k_a[F_2O]^2 + k_b\sqrt{\frac{2k_a}{k_d}}[F_2O]^{3/2}$

17P 4a) 5a)

4a) $v = \frac{V_{max}[S]}{[S]+K_m}$

$0.205\ \text{mmol dm}^{-3}\text{s}^{-1} = \frac{V_{max}(875\ \text{mmol dm}^{-3})}{32\ \text{mmol dm}^{-3} + 875\ \text{mmol dm}^{-3}}$

$V_{max} = 0.212\ \text{mmol dm}^{-3}\text{s}^{-1}$

5a) $k_b = k_{cat}$ $V_{max} = k_{cat}[E]$ $V_{max} = 0.250\ \text{mmol dm}^{-3}\text{s}^{-1}$

$[E] = 2.3\ \text{mmol dm}^{-3}$

$2.8\times10^5\ \text{mmol dm}^{-3}\text{s}^{-1} = k_{cat}(2.3\ \text{mmol dm}^{-3})$

$1.1\times10^5\ \text{s}^{-1} = k_{cat}$

$\frac{k_{cat}}{K_m} = \frac{1.1\times10^5\ \text{s}^{-1}}{1\times10^{-3}\ \text{mol/L}} = 1.1\times10^8\ \text{s}^{-1}\text{M}^{-1}$

1/7(3a) Problem 7

3a) $\frac{\phi_{F,0}}{\phi_F} = 1 + \tau_0 k_Q [Q]$

$\frac{1}{0.5} = 1 + 6.0\text{ns} (3.0\times10^{8} \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}) [Q]$

$2 = 1 + (6.0\times10^{-9} \text{s})(3.0\times10^{8} \text{dm}^3 \text{mol}^{-1} \text{s}^{-1})[Q]$

$2 = 1 + 1.8 \text{ dm}^3 \text{mol}^{-1} [Q]$

$\frac{1}{1.8} = [Q] = 0.55 \text{ M}$

7. $\tau_0 = 1\text{ns} \rightarrow 10\text{ps} \Rightarrow \tau_1 = 0.01\tau_0$

$R_0 = 5.6\text{nm}$ $\quad \eta_T = R_0^6/(R_0^6 + R^6)$

$\phi_{F,0} = k_F \tau_0$

$\phi_F = k_F \tau_1 = k_F\, 0.01\tau_0 \Rightarrow \phi_F = 0.01\, \phi_{F,0}$

$\frac{\phi_{F,0}}{\phi_F} = \frac{\phi_{F,0}}{0.01\phi_{F,0}} = 100 \Leftrightarrow \frac{\phi_F}{\phi_{F,0}} = 0.01$

$\eta_T = 1 - \frac{\phi_F}{\phi_{F,0}} = \frac{R_0^6}{R_0^6 + R}$

$1 - 0.01 = \frac{R_0^6}{R_0^6 + R^6}$

$0.99 = \frac{5.6^6}{5.6^6 + R^6} \Rightarrow 0.99(5.6)^6 + 0.99R^6 = 5.6^6$

$R = \sqrt[6]{\frac{5.6^6 - (0.99)(5.6)^6}{0.99}} = 2.6\text{nm}$

Bonus

E17E.1b) (i) $\frac{d[H]}{dt} = k_b[CI]$

$K = \frac{[CI]}{[A][B]}$ $[CI] = K[A][B]$

$= \frac{k_a}{k_a'}[A][B]$

$\frac{d[H]}{dt} = k_b \frac{k_a}{k_a'}[A][B]$

(ii) $\frac{d[CI]}{dt} = k_a[A][B] - k_a'[CI] - k_b[CI] = 0$

$[CI] = \frac{k_a[A][B]}{k_a' + k_b}$

$\frac{d[H]}{dt} = k_b\left(\frac{k_a[A][B]}{k_a' + k_b}\right)$

E17E.2b $K = \frac{[CH_2ClCH_2O^-]}{[CH_2ClCH_2OH][OH^-]}$

$[CH_2ClCH_2O^-] = K[CH_2ClCH_2OH][OH^-]$

$\frac{d[(CH_2CH_2)O]}{dt} = k_2[CH_2ClCH_2O^-]$

$\frac{d[(CH_2CH_2)O]}{dt} = k_2(K[CH_2ClCH_2OH][OH^-])$

P17E.6 $\frac{d[NO_2]}{dt} = 2k_b[N_2O_2][O_2]$

$\frac{d[N_2O_2]}{dt} = -k_b[N_2O_2][O_2] + k_a[NO]^2 - k_a'[N_2O_2] = 0$

$k_a'[N_2O_2] + k_b[N_2O_2][O_2] = k_a[NO]^2$

$[N_2O_2] = \frac{k_a[NO]^2}{k_a' + k_b[O_2]}$ $\rightarrow \frac{d[NO_2]}{dt} = 2k_b[O_2]\left(\frac{k_a[NO]^2}{k_a' + k_b[O_2]}\right)$

E17F.4(b) $V = \frac{V_{max}[S]}{[S]+K_m}$

$0.208\ mmol\ dm^{-3}s^{-1} = \frac{V_{max}[S_0]}{0.895\ mol\ dm^{-3} + 0.072\ mol\ dm^{-3}}$

$0.208\ mmol\ dm^{-3}s^{-1} = \frac{V_{max}[S_0]\ (0.895\ mol\ dm^{-3})}{0.907\ mmol\ dm^{-3}}$

$V_{max} = 0.212\ mmol\ dm^{-3}\ s^{-1}$

E17F.5b. $eff = \frac{k_b}{K_M}$ $k_b[E] = V_{max}$

$k_b \cdot 3.10\times10^{-9}\ mol\ dm^{-3} = 4.25\times10^{-4}\ mol\ dm^{-3}s^{-1}$

$k_b = 1.18\times10^{5}\ s^{-1}$

$\frac{1.18\times10^{5}\ s^{-1}}{0.032\ mol\ dm^{-3}} = 3.69\times10^{6}\ M^{-1}s^{-1}$

E17G.2(a). $\phi_{F,0} = k_F \tau_0$

$0.35 = k_F(5.6\ ns)$

$0.0625\ ns^{-1}$

E17G.3(b) $\frac{\phi_{F,0}}{\phi_F} = 1 + \tau_0 k_Q[Q]$

$\frac{1}{0.75} = 1 + (3.8\ ns)(2.5\times10^{9}\ dm^{3}mol^{-1}s^{-1})[Q]$

$\frac{1}{3} = (3.8\times10^{-9}\ s)(2.5\times10^{9}\ dm^{3}mol^{-1}s^{-1})[Q]$

$\frac{1}{3} = 8.75\ dm^{3}mol^{-1}[Q]$

$[Q] = 0.0381\ mol\ dm^{-3}$