Problem 3.7.3 (a)

$$S + E \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} P + E$$

$$\frac{d}{dt} s(t) = -k_1 s(t) e(t) + k_{-1} c(t)$$

$$\frac{d}{dt} e(t) = -k_1 s(t) e(t) + k_{-1} c(t) + k_2 c(t) - k_{-2} p(t) e(t)$$

$$\frac{d}{dt} c(t) = k_1 s(t) e(t) - k_{-1} c(t) - k_2 c(t) + k_{-2} p(t) e(t)$$

$$\frac{d}{dt} p(t) = k_2 c(t) - k_{-2} p(t) e(t)$$

$$e(t) = e_T - c(t) \qquad c(t) = c^{qss}(t)$$

$$0 = k_1 s(t) \left(e_T - c^{qss}(t)\right) - k_{-1} c^{qss}(t) - k_2 c^{qss}(t) + k_{-2} p(t) \left(e_T - c^{qss}(t)\right)$$

$$\left[k_1 s(t) + k_{-1} + k_2 + k_{-2} p(t)\right] c^{qss}(t) = k_1 s(t) e_T + k_{-2} p(t) e_T$$

$$c^{qss}(t) = \frac{k_1 e_T s + k_{-2} e_T p}{k_1 s + k_{-1} + k_2 + k_{-2} p}$$

$$\frac{d}{dt} p(t) = k_2 c^{qss}(t) - k_{-2} p(t) \left(e_T - c^{qss}(t)\right)$$

$$\frac{d}{dt} p(t) = \frac{k_2 k_1 e_T s + \cancel{k_{-2} k_2 e_T p} - k_{-2} p e_T (\cancel{k_1 s} + k_{-1} + \cancel{k_2} + \cancel{k_{-2} p}) + \cancel{k_{-2} p k_1 e_T s} + \cancel{k_{-2}^2 p^2 e_T}}{k_1 s + k_{-1} + k_2 + k_{-2} p}$$

$$= \frac{k_2 k_1 e_T s - k_{-2} k_{-1} e_T p}{k_1 s + k_{-1} + k_2 + k_{-2} p}$$

*

Problem 3.7.3 (b)

$$\frac{d}{dt}P(t) = \frac{k_2 k_1 e_T s - k_{-2} k_{-1} e_T p}{k_1 s + k_{-1} + k_2 + k_{-2} p} \qquad @\ C^{qss}$$

$$\text{net rate of } s \to p = \frac{V_f \frac{s}{K_s} - V_r \frac{p}{K_p}}{1 + \frac{s}{K_s} + \frac{p}{K_p}}$$

$$\frac{d}{dt}p(t) = \frac{k_2 k_1 e_T s - k_{-2} k_{-1} e_T p}{k_1 s + k_{-2} p + k_{-1} + k_2}$$

$$\boxed{\div k_1} \Rightarrow \frac{k_2 e_T s - \frac{k_{-2} k_{-1}}{k_1} e_T p}{s + \frac{k_{-2}}{k_1} p + \frac{k_{-1}}{k_1} + \frac{k_2}{k_1}}$$

$$\boxed{\div k_{-2}} \Rightarrow \frac{\frac{k_2}{k_{-2}} e_T s - \frac{k_{-1}}{k_1} e_T p}{\frac{s}{k_{-2}} + \frac{p}{k_1} + \frac{k_{-1} + k_2}{k_1 k_{-2}}}$$

$$\boxed{\div \frac{k_{-1} + k_2}{k_1 k_{-2}}} \Rightarrow \frac{\frac{k_2}{\cancel{k_{-2}}} \times \frac{k_1 \cancel{k_{-2}}}{k_{-1} + k_2} e_T s - \frac{k_{-1}}{\cancel{k_1}} \times \frac{\cancel{k_1} k_{-2}}{k_{-1} + k_2} e_T p}{\frac{s}{\cancel{k_{-2}}} \times \frac{k_1 \cancel{k_{-2}}}{k_{-1} + k_2} + \frac{p}{\cancel{k_1}} \times \frac{\cancel{k_1} k_{-2}}{k_{-1} + k_2} + 1}$$

$$\Rightarrow \frac{\left[\frac{k_1 k_2 e_T}{k_{-1} + k_2}\right] s - \left[\frac{k_{-1} k_{-2} e_T}{k_{-1} + k_2}\right] p}{1 + \frac{k_1}{k_{-1} + k_2} s + \frac{k_{-2}}{k_{-1} + k_2} p} \Leftrightarrow \frac{V_f \frac{s}{K_s} - V_r \frac{p}{K_p}}{1 + \frac{s}{K_s} + \frac{p}{K_p}}$$

$$K_s = \frac{k_{-1} + k_2}{k_1} \ \# \qquad V_f = k_2 e_T \ \#$$

$$K_p = \frac{k_{-1} + k_2}{k_{-2}} \ \# \qquad V_r = k_{-1} e_T \ \#$$

Problem 3.7.3 (c)

irreversible ver. $\frac{d}{dt} p(t) = \frac{k_2 k_1 e_T s(t)}{k_{-1} + k_2 + k_1 s(t)}$

@ C^{qss}

reversible ver. $\frac{d}{dt} p(t) = \frac{k_2 k_1 e_T s - k_{-2} k_{-1} e_T p}{k_1 s + k_{-1} + k_2 + k_{-2} p}$

@ C^{qss}

if $k_{-2} = 0$:

reversible ver. $\frac{d}{dt} p(t) = \frac{k_2 k_1 e_T s - \cancel{k_{-2} k_{-1} e_T p}}{k_1 s + k_{-1} + k_2 + \cancel{k_{-2} p}}$

@ C^{qss}

$= \frac{k_2 k_1 e_T s}{k_1 s + k_{-1} + k_2}$ *

compare with

irreversible ver. $\frac{d}{dt} p(t) = \frac{k_2 k_1 e_T s(t)}{k_{-1} + k_2 + k_1 s(t)}$

@ C^{qss}

Same !

$\Rightarrow$ if $k_{-2} = 0$, irreversible Michaelis–Menten rate law is recovered. *

Problem 3.7.5 (b)

$$\xrightarrow{v_0} S_1 \xrightarrow{v_1} S_2 \xrightarrow{v_2} S_3 \xrightarrow{v_3}$$

$$v_i = \frac{V_{\max}^i s_i}{K_{Mi} + s_i},$$

$$\frac{d}{dt} s_1(t) = V_0 - \frac{V_{max}^1 S_1}{K_{m1} + S_1}$$

$$\frac{d}{dt} S_2(t) = \frac{V_{max}^1 S_1}{K_{m1} + S_1} - \frac{V_{max}^2 S_2}{K_{m2} + S_2}$$

$$\frac{d}{dt} S_3(t) = \frac{V_{max}^2 S_2}{K_{m2} + S_2} - \frac{V_{max}^3 S_3}{K_{m3} + S_3}$$

$V_0 = 2$

$V_{max}^1 = 9 \qquad K_{m1} = 1$

$V_{max}^2 = 12 \qquad K_{m2} = 0.4$

$V_{max}^3 = 15 \qquad K_{m3} = 3$

$$\begin{cases} S_1 = 0.3 \\ S_2 = 0.2 \\ S_3 = 0.1 \end{cases} \qquad \begin{cases} S_1 = 6 \\ S_2 = 4 \\ S_3 = 4 \end{cases}$$

from 3.1.2 (b)

when s is small compare to K_m, $K_m + s \approx K_m$

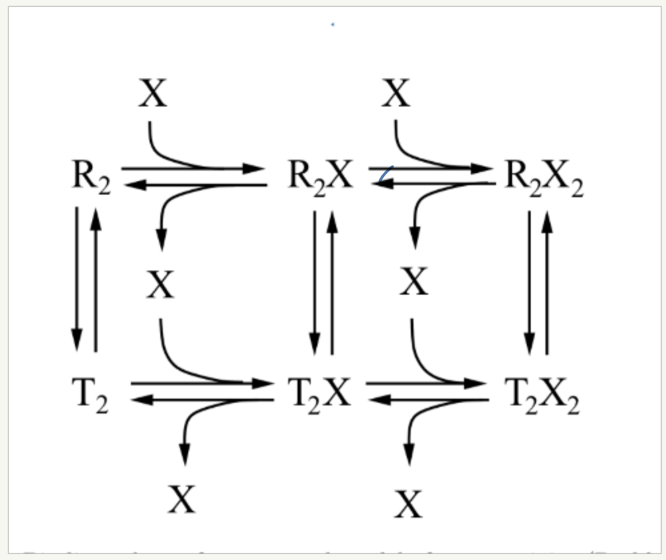
$$\frac{V_{max} s}{K_m + s} \Rightarrow \frac{V_{max}}{K_m} s \quad (\text{ first order kinetics form } v = ks)$$

$$k_1 = \frac{V_{max}^1}{K_{m1}} = \frac{9}{1} = 9$$

$$k_2 = \frac{V_{max}^2}{K_{m2}} = \frac{12}{0.4} = 30$$ ← 選 30 因為反應越快越接近完整反應

$$K_3 = \frac{V_{max}^3}{K_{m3}} = \frac{15}{3} = 5$$

Problem. 3.7.11 (a)



$$[R_2] = \frac{[T_2]}{K} \qquad [R_2X_1] = \frac{2[X][R_2]}{K_R} \qquad [R_2X_2] = \frac{[X][R_2X_1]}{2K_R}$$

$$[T_2X_1] = \frac{2[X][T_2]}{K_T} \qquad [T_2X_2] = \frac{[X][T_2X_1]}{2K_T}.$$

$$[R_2X_2] = \frac{[x]}{\cancel{2}K_R} \cdot \frac{\cancel{2}[X][R_2]}{K_R} = \frac{[x]^2[R_2]}{K_R^2}$$

$$[T_2X_2] = \frac{[x]}{\cancel{2}K_T} \cdot \frac{\cancel{2}[X][T_2]}{K_T} = \frac{[x]^2[T_2]}{K_T^2}$$

$$R_2X + X \underset{2K_{-R}}{\overset{K_R}{\rightleftharpoons}} R_2X_2$$

$$R_2 + X \underset{K_{-R}}{\overset{2K_R}{\rightleftharpoons}} R_2X$$

$$T_2 + X \underset{K_{-T}}{\overset{2K_T}{\rightleftharpoons}} T_2X$$

$$T_2X + X \underset{2K_{-T}}{\overset{K_T}{\rightleftharpoons}} T_2X_2$$

$$R_2 \rightleftharpoons T_2$$

$$R_2X_2 \rightleftharpoons T_2X_2$$

$$R_2X \rightleftharpoons T_2X$$

$$Y = \frac{2[R_2X_2] + [R_2X] + 2[T_2X_2] + [T_2X]}{2[R_2X_2] + 2[R_2X] + 2[R_2] + 2[T_2X_2] + 2[T_2X] + 2[T_2]}$$

$$= \frac{\frac{\cancel{2}[x]^2\cancel{[R_2]}}{K_R^2} + \frac{\cancel{2}[x]\cancel{[R_2]}}{K_R} + \frac{\cancel{2}[x]^2\cancel{[R_2]}K}{K_T^2} + \frac{\cancel{2}[x]\cancel{[R_2]}K}{K_T}}{\frac{\cancel{2}[x]^2\cancel{[R_2]}}{K_R^2} + \frac{\overset{2}{\cancel{4}}[x]\cancel{[R_2]}}{K_R} + \cancel{2[R_2]} + \frac{\cancel{2}[x]^2\cancel{[R_2]}K}{K_T^2} + \frac{\overset{2}{\cancel{4}}[x]\cancel{[R_2]}K}{K_T} + \cancel{2[R_2]}K}$$

$$= \frac{\frac{[x]^2}{K_R^2} + \frac{[x]}{K_R} + \frac{[x]^2K}{K_T^2} + \frac{[x]K}{K_T}}{\underbrace{\boxed{\frac{[x]^2}{K_R^2} + \frac{2[x]}{K_R} + 1}}_{(a+b)^2} + \frac{[x]^2K}{K_T^2} + \frac{2[x]K}{K_T} + K}$$

$$= \frac{\frac{[x]}{K_R}\left(1 + \frac{[x]}{K_R}\right) + K\frac{[x]}{K_T}\left(1 + \frac{[x]}{K_T}\right)}{\left(1 + \frac{[x]}{K_R}\right)^2 + K\left(1 + \frac{[x]}{K_T}\right)^2}$$

Problem 3.7.11 (b)

$$Y = \frac{K \frac{[x]}{K_T}\left(1+\frac{[x]}{K_T}\right) + \frac{[x]}{K_R}\left(1+\frac{[x]}{K_R}\right)}{K\left(1+\frac{[x]}{K_T}\right)^2 + \left(1+\frac{[x]}{K_R}\right)^2}$$

myoglobin oxygen-binding behaviour

$\Rightarrow$ hyperbolic

if $K = 0$:

$$Y = \frac{\cancelto{0}{K \frac{[x]}{K_T}\left(1+\frac{[x]}{K_T}\right)} + \frac{[x]}{K_R}\left(1+\frac{[x]}{K_R}\right)}{\cancel{K\left(1+\frac{[x]}{K_T}\right)^2} + \left(1+\frac{[x]}{K_R}\right)^2} = \frac{\frac{[x]}{K_R}\cancel{\left(1+\frac{[x]}{K_R}\right)}}{\left(1+\frac{[x]}{K_R}\right)^{\cancel{2}\,1}} = \frac{[x]}{K_R+[x]}$$

if $K_R = K_T$:

$$Y = \frac{K \frac{[x]}{K_T}\left(1+\frac{[x]}{K_T}\right) + \frac{[x]}{\cancel{K_R}\,K_T}\left(1+\frac{[x]}{\cancel{K_R}\,K_T}\right)}{K\left(1+\frac{[x]}{K_T}\right)^2 + \left(1+\frac{[x]}{\cancel{K_R}\,K_T}\right)^2}$$

same behaviour when $K = 0$

$$= \frac{\cancel{(K+1)}\frac{[x]}{K_T}\cancel{\left(1+\frac{[x]}{K_T}\right)}}{\cancel{(K+1)}\left(1+\frac{[x]}{K_T}\right)^{\cancel{2}\,1}} = \frac{\frac{[x]}{K_T}}{1+\frac{[x]}{K_T}} = \frac{[x]}{K_T+[x]}$$

Problem 3.7.11 (c)

$$R_4 + X \underset{k_{-R}}{\overset{4k_R}{\rightleftharpoons}} R_4X \Rightarrow [R_4X] = \frac{4}{1}\frac{[R_4][X]}{K_R}$$

$$R_4X + X \underset{2k_{-R}}{\overset{3k_R}{\rightleftharpoons}} R_4X_2 \Rightarrow [R_4X_2] = \frac{3}{2}\frac{[R_4X][X]}{K_R} = \frac{3}{\cancel{2}}\frac{[X]}{K_R}\frac{\cancel{4}^{2}}{1}\frac{[R_4][X]}{K_R} = \frac{6[R_4][X]^2}{K_R^2}$$

$$R_4X_2 + X \underset{3k_{-R}}{\overset{2k_R}{\rightleftharpoons}} R_4X_3 \Rightarrow [R_4X_3] = \frac{2}{3}\frac{[R_4X_2][X]}{K_R} = \frac{2}{\cancel{3}}\frac{[X]}{K_R}\frac{\cancel{6}^{2}[R_4][X]^2}{K_R^2} = \frac{4[R_4][X]^3}{K_R^3}$$

$$R_4X_3 + X \underset{4k_{-R}}{\overset{k_R}{\rightleftharpoons}} R_4X_4 \Rightarrow [R_4X_4] = \frac{1}{4}\frac{[R_4X_3][X]}{K_R} = \frac{1}{\cancel{4}}\frac{[X]}{K_R}\frac{\cancel{4}[R_4][X]^3}{K_R^3} = \frac{[R_4][X]^4}{K_R^4}$$

$$T_4 + X \rightleftharpoons T_4X \Rightarrow [T_4X] = \frac{4}{1}\frac{[T_4][X]}{K_T}$$

$$T_4X + X \rightleftharpoons T_4X_2 \Rightarrow [T_4X_2] = \frac{6}{1}\frac{[T_4][X]^2}{K_T^2}$$

$$T_4X_2 + X \rightleftharpoons T_4X_3 \Rightarrow [T_4X_3] = \frac{4}{1}\frac{[T_4][X]^3}{K_T^3}$$

$$T_4X_3 + X \rightleftharpoons T_4X_4 \Rightarrow [T_4X_4] = \frac{[T_4][X]^4}{K_T^4}$$

$$R_4 \rightleftharpoons T_4$$

$$R_4X \rightleftharpoons T_4X \qquad R_4 = \frac{T_4}{K}$$

$$R_4X_2 \rightleftharpoons T_4X_2$$

$$R_4X_3 \rightleftharpoons T_4X_3$$

$$R_4X_4 \rightleftharpoons T_4X_4$$

Problem 3.7.11 (c) — Continue

$R_4 + X \underset{K_{-R}}{\overset{4K_R}{\rightleftharpoons}} R_4X \Rightarrow [R_4X] = \frac{4}{1}\frac{[R_4][X]}{K_R}$

$R_4X + X \underset{2K_{-R}}{\overset{3K_R}{\rightleftharpoons}} R_4X_2 \Rightarrow [R_4X_2] = \frac{6[R_4][X]^2}{K_R^2}$

$R_4X_2 + X \underset{3K_{-R}}{\overset{2K_R}{\rightleftharpoons}} R_4X_3 \Rightarrow [R_4X_3] = \frac{4[R_4][X]^3}{K_R^3}$

$R_4X_3 + X \underset{4K_{-R}}{\overset{K_R}{\rightleftharpoons}} R_4X_4 \Rightarrow [R_4X_4] = \frac{[R_4][X]^4}{K_R^4}$

$T_4 + X \rightleftharpoons T_4X \Rightarrow [T_4X] = \frac{4}{1}\frac{[T_4][X]}{K_T}$

$T_4X + X \rightleftharpoons T_4X_2 \Rightarrow [T_4X_2] = \frac{6}{1}\frac{[T_4][X]^2}{K_T^2}$

$T_4X_2 + X \rightleftharpoons T_4X_3 \Rightarrow [T_4X_3] = \frac{4}{1}\frac{[T_4][X]^3}{K_T^3}$

$T_4X_3 + X \rightleftharpoons T_4X_4 \Rightarrow [T_4X_4] = \frac{[T_4][X]^4}{K_T^4}$

$R_4 \rightleftharpoons T_4$, $R_4X \rightleftharpoons T_4X$, $R_4X_2 \rightleftharpoons T_4X_2$, $R_4X_3 \rightleftharpoons T_4X_3$, $R_4X_4 \rightleftharpoons T_4X_4$, $R_4 = \frac{T_4}{K}$

$$Y = \frac{[R_4X] + 2[R_4X_2] + 3[R_4X_3] + 4[R_4X_4] + [T_4X] + 2[T_4X_2] + 3[T_4X_3] + 4[T_4X_4]}{4[R_4] + 4[R_4X] + 4[R_4X_2] + 4[R_4X_3] + 4[R_4X_4] + 4[T_4] + 4[T_4X] + 4[T_4X_2] + 4[T_4X_3] + 4[T_4X_4]}$$

$\boxed{\text{解 } R_4\text{，} T_4 \text{ 項在分子、分母與 } R_4 \text{ 項皆差 } K \text{ 倍.}}$

$$\Rightarrow \frac{\frac{\cancel{4}\cancel{[R_4]}[X]}{K_R} + \frac{\cancel{12}^{3}\cancel{[R_4]}[X]^2}{K_R^2} + \frac{\cancel{12}^{3}\cancel{[R_4]}[X]^3}{K_R^3} + \frac{\cancel{4}\cancel{[R_4]}[X]^4}{K_R^4}}{\cancel{4}\cancel{[R_4]} + \frac{\cancel{16}^{4}\cancel{[R_4]}[X]}{K_R} + \frac{\cancel{24}^{6}\cancel{[R_4]}[X]^2}{K_R^2} + \frac{\cancel{16}^{4}\cancel{[R_4]}[X]^3}{K_R^3} + \frac{\cancel{4}\cancel{[R_4]}[X]^4}{K_R^4}}$$

$\boxed{\text{化簡 } R_4 \text{ 項}}$

$$\Rightarrow \frac{\frac{[X]}{K_R}\boxed{\left(1 + \frac{3[X]}{K_R} + \frac{3[X]^2}{K_R^2} + \frac{[X]^3}{K_R^3}\right)}}{\boxed{1 + \frac{4[X]}{K_R} + \frac{6[X]^2}{K_R^2} + \frac{4[X]^3}{K_R^3} + \frac{[X]^4}{K_R^4}}}$$

$\Rightarrow (a+b)^3$ when $a = 1$, $b = \frac{[X]}{K_R}$

$\Rightarrow (a+b)^4$ when $a = 1$, $b = \frac{[X]}{K_R}$

$$\Rightarrow Y = \frac{K\frac{[X]}{K_T}\left(1 + \frac{[X]}{K_T}\right)^3 + \frac{[X]}{K_R}\left(1 + \frac{[X]}{K_R}\right)^3}{K\left(1 + \frac{[X]}{K_T}\right)^4 + \left(1 + \frac{[X]}{K_R}\right)^4}$$ #