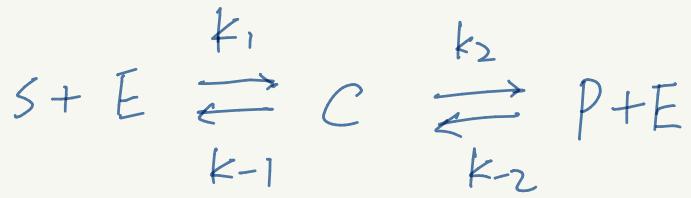


Problem 3.7.3 (a)



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

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

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

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

$$e(t) = e_T - C(t) \quad C(t) = C^{qss}(t)$$

$$0 = k_1 S(t) (e_T - C^{qss}(t)) - k_{-1} C^{qss}(t) - k_2 C^{qss}(t) + k_{-2} p(t) (e_T - C^{qss}(t))$$

$$[k_1 S(t) + k_{-1} + k_2 + k_{-2} p(t)] C^{qss}(t) = k_1 S(t) e_T + k_{-2} p(t) e_T$$

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

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

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

Problem 3.7.3 (b)

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

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

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

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

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

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

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

$$K_s = \frac{k_1 + k_2}{k_1} \quad V_f = k_2 e_T$$

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

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^{4ss}

reversible ver.
 @ C^{4ss} $\frac{d}{dt} P(t) = \frac{k_2 k_1 e_T s - k_{-2} k_{-1} e_T p}{k_1 s + k_{-1} + k_2 + k_{-2} p}$

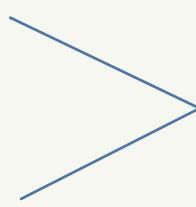
if $k_{-2} = 0$:

reversible ver.
 @ C^{4ss}
$$\frac{d}{dt} P(t) = \frac{k_2 k_1 e_T s - \cancel{k_{-2} k_{-1} e_T p}}{k_1 s + k_{-1} + k_2 + \cancel{k_{-2} p}}$$

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

Compare with

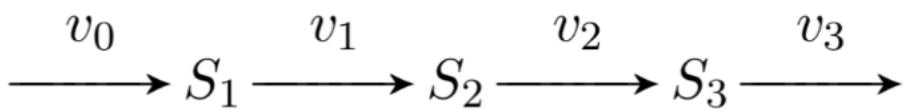
irreversible ver. $\frac{d}{dt} P(t) = \frac{k_2 k_1 e_T s(t)}{k_{-1} + k_2 + k_1 s(t)}$



Same !

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

Problem 3.7.5 (b)



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

$$\frac{d}{dt} S_1(t) = V_0 - \frac{V_{\max}^1 S_1}{K_{M_1} + S_1}$$

$$V_0 = 2$$

$$V_{\max}^1 = 9 \quad K_{M_1} = 1$$

$$\frac{d}{dt} S_2(t) = \frac{V_{\max}^1 S_1}{K_{M_1} + S_1} - \frac{V_{\max}^2 S_2}{K_{M_2} + S_2}$$

$$V_{\max}^2 = 12 \quad K_{M_2} = 0.4$$

$$\frac{d}{dt} S_3(t) = \frac{V_{\max}^2 S_2}{K_{M_2} + S_2} - \frac{V_{\max}^3 S_3}{K_{M_3} + S_3}$$

$$V_{\max}^3 = 15 \quad K_{M_3} = 3$$

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

from 3.1.2(b)

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

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

$$\Rightarrow \text{ODEs} \quad \begin{cases} \frac{d}{dt} S_1(t) = 2 - 9S_1 \\ \frac{d}{dt} S_2(t) = 9S_1 - 30S_2 \\ \frac{d}{dt} S_3(t) = 30S_2 - 5S_3 \end{cases}$$

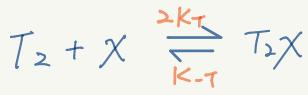
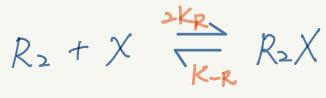
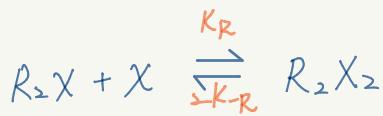
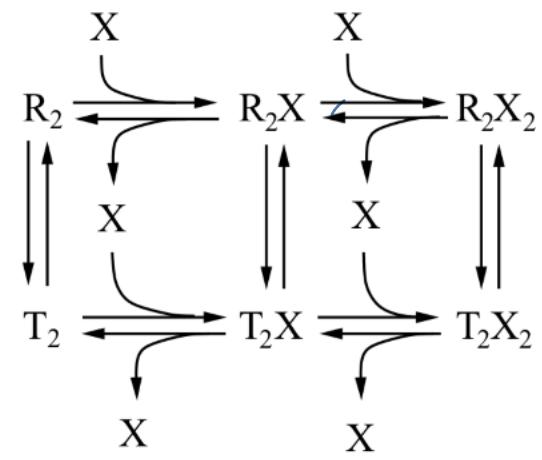


Problem. 3.7.11 (a)

$$\begin{aligned}[R_2] &= \frac{[T_2]}{K} & [R_2X_1] &= \frac{2[X][R_2]}{K_R} & [R_2X_2] &= \frac{[X][R_2X_1]}{2K_R} \\ [T_2X_1] &= \frac{2[X][T_2]}{K_T} & [T_2X_2] &= \frac{[X][T_2X_1]}{2K_T}. \end{aligned}$$

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

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



$$\begin{aligned} Y &= \frac{2[R_2X_2] + [R_2X] + 2[T_2X_2] + [T_2X]}{2[R_2X_2] + 2[R_2X] + 2[R_2] + 2[T_2X_2] + 2[T_2X] + 2[T_2]} \\ &= \frac{\cancel{2[X]^2[R_2]} + \cancel{2[X][R_2]} + \cancel{2[X]^2[R_2]}K + \cancel{2[X][R_2]}K}{K_R^2 + K_R + K_T^2 + K_T} \\ &= \frac{\cancel{2[X]^2[R_2]} + \cancel{2[X][R_2]} + \cancel{2[R_2]} + \cancel{2[X]^2[R_2]}K + \cancel{2[X][R_2]}K + \cancel{2[R_2]}K}{K_R^2 + K_R + K_T^2 + K_T} \\ &= \frac{\frac{[X]^2}{K_R^2} + \frac{[X]}{K_R} + \frac{[X]^2K}{K_T^2} + \frac{[X]K}{K_T}}{\boxed{\frac{[X]^2}{K_R^2} + \frac{2[X]}{K_R} + 1} + \frac{[X]^2K}{K_T^2} + \frac{2[X]K}{K_T} + K} \\ &= -\frac{\frac{[X]}{K_R} \left(1 + \frac{[X]}{K_R} \right) + K \frac{[X]}{K_T} \left(1 + \frac{[X]}{K_T} \right)}{\left(1 + \frac{[X]}{K_R} \right)^2 + K \left(1 + \frac{[X]}{K_T} \right)^2} \quad * \end{aligned}$$

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
⇒ hyperbolic

if $K=0$:

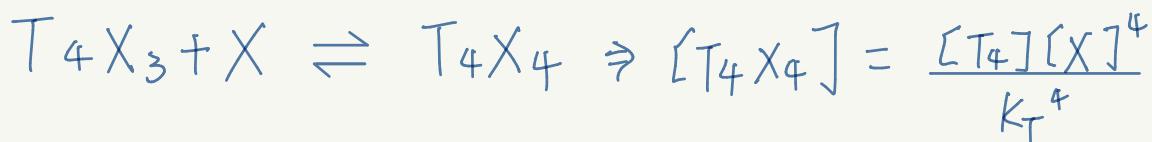
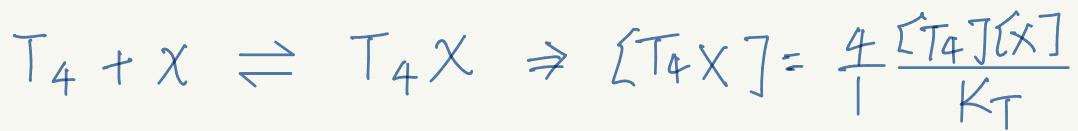
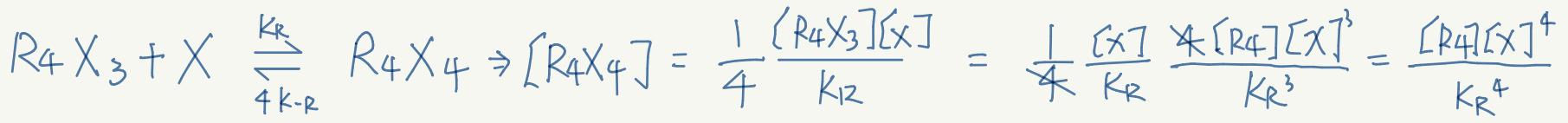
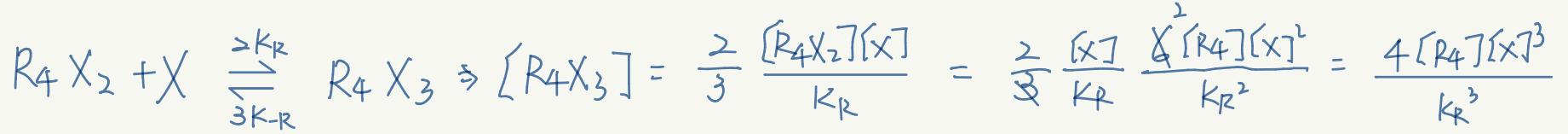
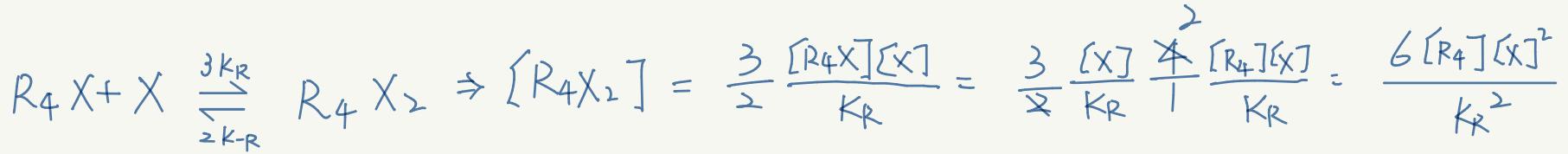
$$Y = \frac{\cancel{K} \frac{[X]}{K_T} \left(1 + \frac{[X]}{K_T} \right) + \frac{[X]}{K_R} \left(1 + \frac{[X]}{K_R} \right)}{\cancel{K} \left(1 + \frac{[X]}{K_T} \right)^2 + \left(1 + \frac{[X]}{K_R} \right)^2} = \frac{\frac{[X]}{K_R} \left(1 + \frac{[X]}{K_R} \right)}{\left(1 + \frac{[X]}{K_R} \right)^2}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

if $K_R = K_T$:

$$\begin{aligned} Y &= \frac{K \frac{[X]}{K_T} \left(1 + \frac{[X]}{K_T} \right) + \frac{[X]}{K_R} \left(1 + \frac{[X]}{K_T} \right)}{K \left(1 + \frac{[X]}{K_T} \right)^2 + \left(1 + \frac{[X]}{K_T} \right)^2} \\ &= \frac{(K+1) \frac{[X]}{K_T} \left(1 + \frac{[X]}{K_T} \right)}{(K+1) \left(1 + \frac{[X]}{K_T} \right)^2} = \frac{\frac{[X]}{K_T}}{1 + \frac{[X]}{K_T}} = \frac{[X]}{K_T + [X]} \end{aligned}$$

same behaviour when $K=0$

Problem 3.7.11 (c)



Problem 3.7.11(c) — Continue

$$R_4 + X \xrightleftharpoons[K_R]{4K_R} R_4 X \Rightarrow [R_4 X] = \frac{4}{1} \frac{[R_4][X]}{K_R}$$

$$R_4 X + X \xrightleftharpoons[2K_R]{3K_R} R_4 X_2 \Rightarrow [R_4 X_2] = \frac{6[R_4][X]^2}{K_R^2}$$

$$R_4 X_2 + X \xrightleftharpoons[3K_R]{2K_R} R_4 X_3 \Rightarrow [R_4 X_3] = \frac{4[R_4][X]^3}{K_R^3}$$

$$R_4 X_3 + X \xrightleftharpoons[4K_R]{K_R} R_4 X_4 \Rightarrow [R_4 X_4] = \frac{[R_4][X]^4}{K_R^4}$$

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

$$T_4 X + X \rightleftharpoons T_4 X_2 \Rightarrow [T_4 X_2] = \frac{6[T_4][X]^2}{K_T^2}$$

$$T_4 X_2 + X \rightleftharpoons T_4 X_3 \Rightarrow [T_4 X_3] = \frac{4[T_4][X]^3}{K_T^3}$$

$$T_4 X_3 + X \rightleftharpoons T_4 X_4 \Rightarrow [T_4 X_4] = \frac{[T_4][X]^4}{K_T^4}$$

$$R_4 \rightleftharpoons T_4, R_4 X \rightleftharpoons T_4 X, R_4 X_2 \rightleftharpoons T_4 X_2, R_4 X_3 \rightleftharpoons T_4 X_3, R_4 X_4 \rightleftharpoons T_4 X_4, R_4 = \frac{T_4}{K}$$

$$Y = \frac{[R_4 X] + 2[R_4 X_2] + 3[R_4 X_3] + 4[R_4 X_4] + [T_4 X] + 2[T_4 X_2] + 3[T_4 X_3] + 4[T_4 X_4]}{4[R_4] + 4[R_4 X] + 4[R_4 X_2] + 4[R_4 X_3] + 4[R_4 X_4] + 4[T_4] + 4[T_4 X] + 4[T_4 X_2] + 4[T_4 X_3] + 4[T_4 X_4]}$$

解 R_4 ,
 T_4 項在分子、
分母與 R_4
項皆差 K_R 倍。

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

$$\frac{[X]}{K_R} \left(1 + \frac{3[X]}{K_R} + \frac{3[X]^2}{K_R^2} + \frac{[X]^3}{K_R^3} \right) \Rightarrow (a+b)^3 \text{ when } a=1, b=\frac{[X]}{K_R}$$

化簡 R_4 項

$$\Rightarrow \frac{1 + \frac{4[X]}{K_R} + \frac{6[X]^2}{K_R^2} + \frac{4[X]^3}{K_R^3} + \frac{[X]^4}{K_R^4}}{1 + \frac{4[X]}{K_R} + \frac{6[X]^2}{K_R^2} + \frac{4[X]^3}{K_R^3} + \frac{[X]^4}{K_R^4}} \Rightarrow (a+b)^4$$

$$\text{when } a=1, b=\frac{[X]}{K_R}$$

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