REB, The Book
Example 4.8.4 Calculations

Equation numbers match those in the Example 4.8.4 Solution.

Rate expressions for the mechanistic steps:

$$r_j = k_{j,f}\prod_{i_r}[i_r]^{-\nu_{i_r,j}} - k_{j,r}\prod_{i_p}[i_p]^{\nu_{i_p,j}}$$

$$r_2 = k_{2,f}[E]\left[S\right] - k_{2,r}\left[E{-}S\right] \tag{5}$$

$$r_3 = k_{3,f}[E][I] - k_{3,r}[E{-}I] \tag{6}$$

$$r_4 = k_{4,f}\left[E{-}S\right] \tag{7}$$

Expression for the apparent rate of generation of P in terms of the rates of the mechanistic steps:

$$r_{i,j_{non}} = \sum_{j'}\nu_{i,j'}r_{j'}$$

$$r_1 = \frac{r_{P,1}}{\nu_{P,1}} = \frac{r_{P,1}}{1} = r_{P,1} \tag{8}$$

Bodenstein steady-state approximations for E, E-S and E-I:

$$0 = \sum_{j'}\nu_{i_{RI},j'}r_{j'}$$

$$0 = -r_2 - r_3 + r_4 \tag{9}$$

$$0 = r_2 - r_4 \tag{10}$$

$$0 = r_3 \tag{11}$$

Expression for the conservation of enzyme

$$C_{cat,0} = C_{cat,free} + \sum_{i_c} \kappa_{i_c} C_{i_c}$$

$$E_0 = [E] + [E{-}S] + [E{-}I] \tag{12}$$

Substitution of equation (6) in equation (10) and solving for the concentration of E-I yields equation (12).

$$0 = k_{3,f}[E][I] - k_{3,r}[E{-}I]$$

$$[E{-}I] = \frac{k_{3,f}[I]}{k_{3,r}}[E] \tag{A}$$

Substitution of equations (5) and (7) into equation (9) and solving for the concentration of E-S yields equation (13).

$$0 = k_{2,f}[E][S] - k_{2,r}[E{-}S] - k_{4,f}[E{-}S]$$

$$[E{-}S] = \frac{k_{2,f}[S]}{k_{2,r} + k_{4,f}}[E] \tag{B}$$

Substitution of equations (12) and (13) into equation (11) and solving for the concentration of E yields equation (14).

$$E_0 = [E] + \frac{k_{2,f}[S]}{k_{2,r} + k_{4,f}}[E] + \frac{k_{3,f}[I]}{k_{3,r}}[E]$$

$$[E] = \frac{E_0}{1 + \frac{k_{2,f}[S]}{k_{2,r} + k_{4,f}} + \frac{k_{3,f}[I]}{k_{3,r}}} \tag{15}$$

Substitution of equation (15) into equation (B) yields equation (14) for the concentration of E-S.

$$\left[E{-}S\right] = \frac{k_{2,f}\left[S\right]}{k_{2,r}+k_{4,f}} \frac{E_0}{1+\frac{k_{2,f}[S]}{k_{2,r}+k_{4,f}}+\frac{k_{3,f}[I]}{k_{3,r}}}$$

$$\left[E{-}S\right] = \frac{k_{2,f}E_0\left[S\right]}{k_{2,r}+k_{4,f}+k_{2,f}\left[S\right]+\frac{k_{3,f}\left(k_{2,r}+k_{4,f}\right)[I]}{k_{3,r}}}$$

$$\left[E{-}S\right] = \frac{k_{2,f}k_{3,r}E_0\left[S\right]}{k_{2,r}k_{3,r}+k_{4,f}k_{3,r}+k_{2,f}k_{3,r}\left[S\right]+k_{3,f}\left(k_{2,r}+k_{4,f}\right)[I]} \quad (14)$$

Substitution of equation (7) into equation (8) followed by substitution of equation (14) yields the rate expression, equation (16).

$$r_1 = \frac{k_{2,f}k_{4,f}k_{3,r}E_0\left[S\right]}{k_{2,r}k_{3,r}+k_{4,f}k_{3,r}+k_{2,f}k_{3,r}\left[S\right]+k_{3,f}\left(k_{2,r}+k_{4,f}\right)[I]} \quad (16)$$