REB, The Course
Class 6 Practice Assignment Calculations

Equation numbers correspond to Class 6 Practice Assignment Solution

Rate expressions for the mechanistic steps:

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

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

$$r_3 = k_{3,f} \left[E\text{-}S\right] \tag{6}$$

$$r_4 = k_{4,f} [E\text{-}P] - k_{4,r} [E] [P] \tag{7}$$

Rate expression for the non-elementary reaction:

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

$$r_1 = r_P = r_4 \tag{8}$$

Bodenstein steady-state approximations:

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

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

$$0 = r_2 - r_3 \tag{10}$$

$$0 = r_3 - r_4 \tag{11}$$

Conservation of enzyme:

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

$$E_0 = [E] + \left[E\text{-}S\right] + [E\text{-}P] \tag{12}$$

Substitution of equations ((5) through (7) into equations (8), (10), and (11) yields equations (A) - (C).

$$r_P = k_{4,f}\,[E\text{-}P] - k_{4,r}\,[E]\,[P] \tag{A}$$

$$0 = k_{2,f}\,[E]\,\left[S\right] - k_{2,r}\,\left[E\text{-}S\right] - k_{3,f}\left[E\text{-}S\right] \tag{B}$$

$$0 = k_{3,f}\left[E\text{-}S\right] - k_{4,f}\,[E\text{-}P] + k_{4,r}\,[E]\,[P] \tag{C}$$

Solving equation (B) yields equation (D).

$$\left[E\text{-}S\right] = \frac{k_{2,f}\left[S\right]}{k_{2,r} + k_{3,f}}\,[E] \tag{D}$$

Solving equation (C) yields equation (E).

$$[E\text{-}P] = \frac{k_{3,f}\left[E\text{-}S\right] + k_{4,r}\,[E]\,[P]}{k_{4,f}} \tag{E}$$

Substitution of equation (D) into equation (E) leads to equation (F).

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

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

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

$$[E\text{-}P] = \frac{k_{2,f}k_{3,f}\left[S\right] + k_{4,r}\left(k_{2,r} + k_{3,f}\right)[P]}{k_{4,f}\left(k_{2,r} + k_{3,f}\right)}[E] \tag{F}$$

Substitution of equations (D) and (F) into equation (12) leads to an expression for the concentration of E.

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

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

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

$$E = \frac{k_{4,f}\left(k_{2,r} + k_{3,f}\right)E_0}{\left(\begin{array}{c} k_{4,f}\left(k_{2,r} + k_{3,f}\right) + k_{2,f}\left(k_{3,f} + k_{4,f}\right)\left[S\right] \\ + k_{4,r}\left(k_{2,r} + k_{3,f}\right)[P] \end{array}\right)} \tag{13}$$

Substitution of equation (13) into equation (F) yields an expression for the concentration of E-P.

$$[E\text{-}P] = \frac{k_{2,f}k_{3,f}\left[S\right] + k_{4,r}\left(k_{2,r} + k_{3,f}\right)[P]}{k_{4,f}\left(k_{2,r} + k_{3,f}\right)} \frac{k_{4,f}\left(k_{2,r} + k_{3,f}\right)E_0}{\left(\begin{array}{c} k_{4,f}\left(k_{2,r} + k_{3,f}\right) + k_{2,f}\left(k_{3,f} + k_{4,f}\right)\left[S\right] \\ + k_{4,r}\left(k_{2,r} + k_{3,f}\right)[P] \end{array}\right)}$$

$$[E\text{-}P] = \frac{k_{2,f}k_{3,f}E_0\left[S\right] + k_{4,r}\left(k_{2,r} + k_{3,f}\right)E_0\left[P\right]}{\begin{pmatrix} k_{4,f}\left(k_{2,r} + k_{3,f}\right) + k_{2,f}\left(k_{3,f} + k_{4,f}\right)\left[S\right] \\ +k_{4,r}\left(k_{2,r} + k_{3,f}\right)\left[P\right] \end{pmatrix}} \tag{14}$$

Substitution of equations (13) and (14) in equation (A) leads to an acceptable form of the rate expression.

$$r_P = k_{4,f}\frac{k_{2,f}k_{3,f}E_0\left[S\right] + k_{4,r}\left(k_{2,r} + k_{3,f}\right)E_0\left[P\right]}{\begin{pmatrix} k_{4,f}\left(k_{2,r} + k_{3,f}\right) + k_{2,f}\left(k_{3,f} + k_{4,f}\right)\left[S\right] \\ +k_{4,r}\left(k_{2,r} + k_{3,f}\right)\left[P\right] \end{pmatrix}} - k_{4,r}\frac{k_{4,f}\left(k_{2,r} + k_{3,f}\right)E_0}{\begin{pmatrix} k_{4,f}\left(k_{2,r} + k_{3,f}\right) + k_{2,f}\left(k_{3,f} + k_{4,f}\right)\left[S\right] \\ +k_{4,r}\left(k_{2,r} + k_{3,f}\right)\left[P\right] \end{pmatrix}}\left[P\right]$$

$$r_P = \frac{k_{2,f}k_{3,f}k_{4,f}E_0\left[S\right] + k_{4,r}k_{4,f}\left(k_{2,r} + k_{3,f}\right)E_0\left[P\right] - k_{4,r}k_{4,f}\left(k_{2,r} + k_{3,f}\right)E_0\left[P\right]}{\begin{pmatrix} k_{4,f}\left(k_{2,r} + k_{3,f}\right) + k_{2,f}\left(k_{3,f} + k_{4,f}\right)\left[S\right] \\ +k_{4,r}\left(k_{2,r} + k_{3,f}\right)\left[P\right] \end{pmatrix}}$$

$$r_P = \frac{k_{2,f}k_{3,f}k_{4,f}E_0\left[S\right]}{\begin{pmatrix} k_{4,f}\left(k_{2,r} + k_{3,f}\right) + k_{2,f}\left(k_{3,f} + k_{4,f}\right)\left[S\right] \\ +k_{4,r}\left(k_{2,r} + k_{3,f}\right)\left[P\right] \end{pmatrix}} \tag{15}$$