REB, The Course
Example 4.8.6 Calculations

Equation numbers correspond to those in Example 4.8.6 Solution.

Apparent Rate of the Non-Elementary Reaction

$$r_1 = k_{6,f}\theta_{CO_2} - k_{6,r}\left[CO_2\right]\theta_v \tag{7}$$

Quasi-Equilibrium Expressions

$$K_2 = \frac{\theta_{O_2}}{\left[O_2\right]\theta_v} \tag{8}$$

$$K_3 = \frac{\theta_{CO_3}}{\left[CO\right]\theta_{O_2}} \tag{9}$$

$$K_4 = \frac{\left[CO_2\right]\theta_O}{\theta_{CO_3}} \tag{10}$$

$$K_5 = \frac{\theta_{CO_2}}{\left[CO\right]\theta_O} \tag{11}$$

Site Conservation Equation

$$1 = \theta_v + \theta_{O_2} + \theta_{CO_3} + \theta_O + \theta_{CO_2} \tag{12}$$

Solving (8) for the O_2 coverage yields equation (A)

$$\theta_{O_2} = K_2\theta_v\left[O_2\right] \tag{A}$$

Solving (9) for the CO_3 coverage and substituting (A) yields equation (B)

$$\theta_{CO_3} = K_3\theta_{O_2}\left[CO\right] = K_2K_3\left[O_2\right]\left[CO\right]\theta_v \tag{B}$$

Solving (10) for the O coverage and substituting (B) yields equation (C)

$$\theta_O = \frac{K_4\theta_{CO_3}}{[CO_2]} = \frac{K_2K_3K_4\,[O_2]\,[CO]}{[CO_2]}\theta_v \qquad \text{(C)}$$

Solving (11) for the CO_2 coverage and substituting (C) yields equation (C)

$$\theta_{CO_2} = K_5\theta_O\,[CO] = K_5\frac{K_2K_3K_4\,[O_2]\,[CO]^2}{[CO_2]}\theta_v \qquad \text{(D)}$$

Substitution of (A) through (D) into (12) and solving for the vacant site coverage yields (13).

$$\theta_v = \frac{1}{\left(\begin{array}{c}1 + K_2\,[O_2] + K_2K_3\,[CO]\,[O_2] \\ +\frac{K_2K_3K_4[CO][O_2]}{[CO_2]} + \frac{K_2K_3K_4K_5[CO]^2[O_2]}{[CO_2]}\end{array}\right)} \qquad (13)$$

Substitution of equation (13) into equations (A) through (D) yields equations (14) through (17).

$$\theta_{O_2} = \frac{K_2\,[O_2]}{\left(\begin{array}{c}1 + K_2\,[O_2] + K_2K_3\,[CO]\,[O_2] \\ +\frac{K_2K_3K_4[CO][O_2]}{[CO_2]} + \frac{K_2K_3K_4K_5[CO]^2[O_2]}{[CO_2]}\end{array}\right)} \qquad (14)$$

$$\theta_{CO_3} = \frac{K_2K_3\,[CO]\,[O_2]}{\left(\begin{array}{c}1 + K_2\,[O_2] + K_2K_3\,[CO]\,[O_2] \\ +\frac{K_2K_3K_4[CO][O_2]}{[CO_2]} + \frac{K_2K_3K_4K_5[CO]^2[O_2]}{[CO_2]}\end{array}\right)} \qquad (15)$$

$$\theta_O = \frac{\frac{K_2 K_3 K_4 [CO][O_2]}{[CO_2]}}{\left(\begin{array}{c} 1 + K_2[O_2] + K_2 K_3 [CO][O_2] \\ + \frac{K_2 K_3 K_4 [CO][O_2]}{[CO_2]} + \frac{K_2 K_3 K_4 K_5 [CO]^2 [O_2]}{[CO_2]} \end{array}\right)} \tag{16}$$

$$\theta_{CO_2} = \frac{\frac{K_2 K_3 K_4 K_5 [CO]^2 [O_2]}{[CO_2]}}{\left(\begin{array}{c} 1 + K_2[O_2] + K_2 K_3 [CO][O_2] \\ + \frac{K_2 K_3 K_4 [CO][O_2]}{[CO_2]} + \frac{K_2 K_3 K_4 K_5 [CO]^2 [O_2]}{[CO_2]} \end{array}\right)} \tag{17}$$

Substitution of equations (13) and (17) into equation (7) gives the requested rate expression, equation (18).

$$r_1 = k_{6,f} \frac{\frac{K_2 K_3 K_4 K_5 [CO]^2 [O_2]}{[CO_2]}}{\left(\begin{array}{c} 1 + K_2[O_2] + K_2 K_3 [CO][O_2] \\ + \frac{K_2 K_3 K_4 [CO][O_2]}{[CO_2]} + \frac{K_2 K_3 K_4 K_5 [CO]^2 [O_2]}{[CO_2]} \end{array}\right)} - k_{6,r}[CO_2] \frac{1}{\left(\begin{array}{c} 1 + K_2[O_2] + K_2 K_3 [CO][O_2] \\ + \frac{K_2 K_3 K_4 [CO][O_2]}{[CO_2]} + \frac{K_2 K_3 K_4 K_5 [CO]^2 [O_2]}{[CO_2]} \end{array}\right)}$$

$$r_1 = k_{6,f}\frac{K_2K_3K_4K_5\left[CO\right]^2\left[O_2\right]}{\left[CO_2\right]\left(\begin{array}{c}1+K_2\left[O_2\right]+K_2K_3\left[CO\right]\left[O_2\right]\\+\frac{K_2K_3K_4[CO]\left[O_2\right]}{[CO_2]}+\frac{K_2K_3K_4K_5[CO]^2[O_2]}{[CO_2]}\end{array}\right)} - \frac{k_{6,r}\left[CO_2\right]}{\left(\begin{array}{c}1+K_2\left[O_2\right]+K_2K_3\left[CO\right]\left[O_2\right]\\+\frac{K_2K_3K_4[CO]\left[O_2\right]}{[CO_2]}+\frac{K_2K_3K_4K_5[CO]^2[O_2]}{[CO_2]}\end{array}\right)}$$

$$r_1 = k_{6,f}\frac{K_2K_3K_4K_5\left[CO\right]^2\left[O_2\right]}{\left[CO_2\right]\left(\begin{array}{c}1+K_2\left[O_2\right]+K_2K_3\left[CO\right]\left[O_2\right]\\+\frac{K_2K_3K_4[CO]\left[O_2\right]}{[CO_2]}+\frac{K_2K_3K_4K_5[CO]^2[O_2]}{[CO_2]}\end{array}\right)} - \frac{k_{6,r}\left[CO_2\right]^2}{\left[CO_2\right]\left(\begin{array}{c}1+K_2\left[O_2\right]+K_2K_3\left[CO\right]\left[O_2\right]\\+\frac{K_2K_3K_4[CO]\left[O_2\right]}{[CO_2]}+\frac{K_2K_3K_4K_5[CO]^2[O_2]}{[CO_2]}\end{array}\right)}$$

$$r_1 = k_{6,f}\frac{K_2K_3K_4K_5\left[CO\right]^2\left[O_2\right]}{\left(\begin{array}{c}\left[CO_2\right]+K_2\left[O_2\right]\left[CO_2\right]+K_2K_3\left[CO\right]\left[O_2\right]\left[CO_2\right]\\ +K_2K_3K_4\left[CO\right]\left[O_2\right]+K_2K_3K_4K_5\left[CO\right]^2\left[O_2\right]\end{array}\right)}$$

$$-\frac{k_{6,r}\left[CO_2\right]^2}{\left(\begin{array}{c}\left[CO_2\right]+K_2\left[O_2\right]\left[CO_2\right]+K_2K_3\left[CO\right]\left[O_2\right]\left[CO_2\right]\\ +K_2K_3K_4\left[CO\right]\left[O_2\right]+K_2K_3K_4K_5\left[CO\right]^2\left[O_2\right]\end{array}\right)}$$

$$r_1 = \frac{k_{6,f}K_2K_3K_4K_5\left[CO\right]^2\left[O_2\right]-k_{6,r}\left[CO_2\right]^2}{\left(\begin{array}{c}\left[CO_2\right]+K_2\left[O_2\right]\left[CO_2\right]+K_2K_3\left[CO\right]\left[O_2\right]\left[CO_2\right]\\ +K_2K_3K_4\left[CO\right]\left[O_2\right]+K_2K_3K_4K_5\left[CO\right]^2\left[O_2\right]\end{array}\right)} \qquad (18)$$