REB, The Book
Example 4.8.1 Calculations

Rates of the mechanistic steps:

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

$$r_2 = k_{2,f} \left[O_2\right] - k_{2,r} \left[O\cdot\right]^2 \tag{6}$$

$$r_3 = k_{3,f}[O\cdot][N_2] - k_{3,r}[NO][N\cdot] \tag{7}$$

$$r_4 = k_{4,f}[N\cdot][O_2] \tag{8}$$

$$r_5 = 0 \tag{9}$$

Rate of generation of NO:

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

$$r_{NO,1} = r_3 + r_4 \tag{10}$$

Bodenstein steady state approximations for O· and N·:

$$0 = \sum_{j_{step}} \nu_{i_{RI},j_{step}} r_{j_{step}}$$

$$0 = 2r_2 - r_3 + r_4 \tag{11}$$

$$0 = r_3 - r_4 - 2r_5 \tag{12}$$

To solve equations (11) and (12) for $[O\cdot]$ and $[N\cdot]$, start by adding equations (11) and (12). Substituting equations (6) and (9), and solving for $[O\cdot]$ gives equation (13).

$$0 = 2r_2 - 2r_5$$

$$0 = 2k_{2,f}[O_2] - 2k_{2,r}[O\cdot]^2$$

$$[O\cdot] = \sqrt{\frac{k_{2,f}}{k_{2,r}}[O_2]} \tag{13}$$

Substituting equations (7), (8), and (9) into equation (12) and solving for $[N\cdot]$ gives equation (14).

$$0 = k_{3,f}[O\cdot][N_2] - k_{3,r}[NO][N\cdot] - k_{4,f}[N\cdot][O_2]$$

$$k_{3,r}[NO][N\cdot] + k_{4,f}[N\cdot][O_2] = k_{3,f}[O\cdot][N_2]$$

$$[N\cdot]\left(k_{3,r}[NO] + k_{4,f}[O_2]\right) = k_{3,f}[O\cdot][N_2]$$

$$[N\cdot] = \frac{k_{3,f}[O\cdot][N_2]}{k_{3,r}[NO] + k_{4,f}[O_2]} \tag{14}$$

Substituting equation (13) into equation (14) gives equation (15).

$$[N\cdot] = \frac{k_{3,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}[O_2]}\,[N_2]}{\left(k_{3,r}[NO] + k_{4,f}[O_2]\right)} \tag{15}$$

Substitute equations (7) and (8) into equation (10).

$$r_{NO,1} = k_{3,f}[O\cdot][N_2] - k_{3,r}[NO][N\cdot] + k_{4,f}[N\cdot][O_2]$$

$$r_{NO,1} = k_{3,f}[O\cdot][N_2] - \left(k_{3,r}[NO] - k_{4,f}[O_2]\right)[N\cdot]$$

Substitute equation (14).

$$r_{NO,1} = k_{3,f}[O\cdot][N_2] - \left(k_{3,r}[NO] - k_{4,f}[O_2]\right)\frac{k_{3,f}[O\cdot][N_2]}{k_{3,r}[NO] + k_{4,f}[O_2]}$$

$$r_{NO,1} = k_{3,f}[O\cdot][N_2]\left(1 - \frac{k_{3,r}[NO] - k_{4,f}[O_2]}{k_{3,r}[NO] + k_{4,f}[O_2]}\right)$$

$$r_{NO,1} = k_{3,f}[O\cdot][N_2]\left(\frac{k_{3,r}[NO] + k_{4,f}[O_2] - k_{3,r}[NO] + k_{4,f}[O_2]}{k_{3,r}[NO] + k_{4,f}[O_2]}\right)$$

$$r_{NO,1} = k_{3,f}[O\cdot][N_2]\left(\frac{2k_{4,f}[O_2]}{k_{3,r}[NO] + k_{4,f}[O_2]}\right)$$

Substitute equation (13) and rearrange to get the rate expression, equation (16).

$$r_{NO,1} = k_{3,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}\left[O_2\right]}\,[N_2]\left(\frac{2k_{4,f}[O_2]}{k_{3,r}[NO] + k_{4,f}[O_2]}\right)$$

$$r_{NO,1} = \left(\frac{2k_{3,f}k_{4,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}}\left[O_2\right]^{\frac{3}{2}}[N_2]}{k_{3,r}[NO] + k_{4,f}[O_2]}\right) \tag{16}$$