REB, The Course
Class 5 Learning Activity Calculations

Equation number correspond to the Class 5 Learning Activity Solution.

Case (a)

Rate of the apparent reaction:

$$r_{j_{non}} = r_{j_{rds}} = k_{j_{rds},f} \prod_{i_r} [i_r]^{-\nu_{i_r,j_{rds}}} - k_{j_{rds},r} \prod_{i_p} [i_p]^{\nu_{i_p,j_{rds}}}$$

$$r_1 = r_3 = k_{3,f} \left[H_2\right] \left[N_2O_2\right] - k_{3,r} \left[N_2\right] \left[H_2O_2\right] \tag{8}$$

Quasi-equilibrium expressions:

$$K_{j_{nrd}} = \prod_i [i]^{\nu_{i,j_{nrd}}}$$

$$K_2 = \frac{\left[N_2O_2\right]}{\left[NO\right]^2} \tag{9}$$

$$K_4 = \frac{\left[H_2O\right]^2}{\left[H_2\right] \left[H_2O_2\right]} \tag{10}$$

Start by solving equations (6) and (7) for $[N_2O_2]$ and $[H_2O_2]$.

$$\left[N_2O_2\right] = K_2 \left[NO\right]^2 \tag{13}$$

$$\left[H_2O_2\right] = \frac{\left[H_2O\right]^2}{\left[H_2\right] K_4} \tag{14}$$

Substitute equations (8) and (9) in equation (5) to get the mechanistic rate expression, equation (10).

$$r_1 = k_{3,f}\left[H_2\right] K_2 \left[NO\right]^2 - k_{3,r}\left[N_2\right] \frac{\left[H_2O\right]^2}{\left[H_2\right] K_4} \tag{15}$$

Case (b)

Rate expressions for the mechanistic steps:

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

$$r_2 = k_{2,f}[NO]^2 - k_{2,r}[N_2O_2] \tag{5}$$

$$r_3 = k_{3,f}[H_2][N_2O_2] \tag{6b}$$

$$r_4 = k_{4,f}[H_2][H_2O_2] - k_{4,r}[H_2O]^2 \tag{17}$$

Expression for r_1 in terms of the rates of the mechanistic steps:

$$r_{i,j} = \nu_{i,j} r_j$$

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

$$r_1 = \frac{r_{N_2,1}}{\nu_{N_2,1}} = \frac{r_{N_2,1}}{1} = r_{N_2,1} = r_3 \tag{8}$$

Bodenstein steady-state approximations for N_2O_2 and H_2O_2:

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

$$0 = r_2 - r_3 \tag{11}$$

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

Substituting equations (5) and (6b) into equation (11) yields equation (A), which can be solved for the concentration of N_2O_2, equation (16).

$$0 = k_{2,f}[NO]^2 - k_{2,r}[N_2O_2] - k_{3,f}[H_2][N_2O_2] \quad \text{(A)}$$

$$[N_2O_2] = \frac{k_{2,f}[NO]^2}{k_{2,r} + k_{3,f}[H_2]} \quad (16)$$

Substitution of equation (16) into equation (8) yields the desired mechanistic rate expression, equation (17).

$$r_1 = r_3 = k_{3,f}[H_2][N_2O_2] = k_{3,f}[H_2]\frac{k_{2,f}[NO]^2}{k_{2,r} + k_{3,f}[H_2]}$$

$$r_1 = \frac{k_{2,f}k_{3,f}[H_2][NO]^2}{k_{2,r} + k_{3,f}[H_2]} \quad (17)$$