REB, The Course
Class 4 Practice Assignment Calculations

Equation numbers correspond to Practice Assignment 4 Solution.

Rate expressions for the mechanistic steps:

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

$$r_2 = k_{2,f} \left[\mathrm{Cl_2}\right] - k_{2,r} [\mathrm{Cl}]^2 \tag{5}$$

$$r_3 = k_{3,f} [\mathrm{Cl}] \left[\mathrm{Cl_2}\right] - k_{3,r} \left[\mathrm{Cl_3}\right] \tag{6}$$

$$r_4 = k_{4,f} [\mathrm{CO}] \left[\mathrm{Cl_3}\right] \tag{7}$$

Expression for the non-elementary reaction in terms of the rates of the mechanistic steps:

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

$$r_1 = \frac{r_{\mathrm{COCl_2},1}}{\nu_{\mathrm{COCl_2},1}} = \frac{r_4}{1} = r_4 \tag{8}$$

Bodenstein steady-state approximations for Cl and Cl_3:

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

$$0 = 2\, r_2 - r_3 + r_4 \tag{9}$$

$$0 = r_3 - r_4 \tag{10}$$

To solve equations (9) and (10) for $\left[Cl\right]$ and $\left[Cl_3\right]$, first substitute equations (5) through (7) into equations (9) and (10).

$$0 = 2k_{2,f}\left[\mathrm{Cl_2}\right] - 2k_{2,r}\left[\mathrm{Cl}\right]^2 - k_{3,f}\left[\mathrm{Cl}\right]\left[\mathrm{Cl_2}\right] \\ +k_{3,r}\left[\mathrm{Cl_3}\right] + k_{4,f}\left[\mathrm{CO}\right]\left[\mathrm{Cl_3}\right] \tag{A}$$

$$0 = k_{3,f}\left[\mathrm{Cl}\right]\left[\mathrm{Cl_2}\right] - k_{3,r}\left[\mathrm{Cl_3}\right] - k_{4,f}\left[\mathrm{CO}\right]\left[\mathrm{Cl_3}\right] \tag{B}$$

Adding equations (A) and (B) yields equation (C), and rearranging the result yields an expression for $\left[Cl\right]$, equation (11).

$$0 = 2k_{2,f}\left[\mathrm{Cl_2}\right] - 2k_{2,r}\left[\mathrm{Cl}\right]^2 \tag{C}$$

$$\left[\mathrm{Cl}\right] = \sqrt{\frac{k_{2,f}\left[\mathrm{Cl_2}\right]}{k_{2,r}}} \tag{11}$$

Substitution of equation (14) into equation (B) yields equation (D). Combining the last two terms yields equation (E), which can be rearranged to obtain an expression for $\left[Cl_3\right]$, equation (12).

$$0 = k_{3,f}\sqrt{\frac{k_{2,f}\left[\mathrm{Cl_2}\right]}{k_{2,r}}}\left[\mathrm{Cl_2}\right] - k_{3,r}\left[\mathrm{Cl_3}\right] - k_{4,f}\left[\mathrm{CO}\right]\left[\mathrm{Cl_3}\right] \tag{D}$$

$$0 = k_{3,f}\sqrt{\frac{k_{2,f}\left[\mathrm{Cl_2}\right]}{k_{2,r}}}\left[\mathrm{Cl_2}\right] - \left(k_{3,r} - k_{4,f}\left[\mathrm{CO}\right]\right)\left[\mathrm{Cl_3}\right] \tag{E}$$

$$\left[\mathrm{Cl_3}\right] = \frac{k_{3,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}}\left[\mathrm{Cl_2}\right]^{\frac{3}{2}}}{k_{3,r} + k_{4,f}\left[\mathrm{CO}\right]} \tag{12}$$

Substitute equation (7) into equation (8).

$$r_1 = k_{4,f}\left[\mathrm{CO}\right]\left[\mathrm{Cl_3}\right] \tag{F}$$

Substituting equation (12) into equation (F) yields equation (G). The rate expression has three terms, a numerator and a two term denominator. The minimum number of apparent rate coefficients will result if the equation is rearranged so that one of the three terms does not contain a rate coefficient. It is preferable for that term to be in the denominator. One way of accomplishing that is shown in equation (13) which resulted from dividing both the numerator and denominator by $k_{4,f}$.

$$r_1 = k_{4,f}\,[\mathrm{CO}]\,\frac{k_{3,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}}\,\left[\mathrm{Cl_2}\right]^{\frac{3}{2}}}{k_{3,r} + k_{4,f}\,[\mathrm{CO}]} \tag{G}$$

$$r_1 = \frac{k_{3,f}k_{4,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}}\,[\mathrm{CO}]\,\left[\mathrm{Cl_2}\right]^{\frac{3}{2}}}{k_{3,r} + k_{4,f}\,[\mathrm{CO}]}$$

$$r_1 = \frac{k_{3,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}}\,[\mathrm{CO}]\,\left[\mathrm{Cl_2}\right]^{\frac{3}{2}}}{\frac{k_{3,r}}{k_{4,f}} + [\mathrm{CO}]} \tag{13}$$