REB, The Course
Class 6 Learning Activity Calculations

Equation numbers correspond to the Class 6 Learning Activity Solution

The rate expressions for the mechanistic steps are known since the steps are elementary.

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

$$r_2 = k_{2,f}[A][Ni] - k_{2,r}[A{-}Ni] \tag{5}$$

$$r_3 = k_{3,f}[A{-}Ni][H_2] \tag{6}$$

$$r_4 = k_{4,f}[Z{-}Ni] - k_{4,r}[Ni][Z] \tag{7}$$

The apparent rate of generation of Z by reaction (1) is equal to the sum of its rate of generation in each of the mechanistic steps.

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

$$r_{Z,1} = r_4 = k_{4,f}[Z{-}Ni] - k_{4,r}[Ni][Z] \tag{8}$$

Bodenstein steady-state approximations can be written for each of the three reactive intermediates, but only two of them are mathematically independent..

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

$$\begin{aligned} 0 &= -r_2 + r_4 \\ &= -k_{2,f}[A][Ni] + k_{2,r}[A{-}Ni] + k_{4,f}[Z{-}Ni] - k_{4,r}[Ni][Z] \end{aligned} \tag{9}$$

$$0 = r_2 - r_3 = k_{2,f}[A][Ni] - k_{2,r}[A{-}Ni] - k_{3,f}[A{-}Ni][H_2] \tag{10}$$

$$0 = r_3 - r_4 = k_{3,f}[A{-}Ni][H_2] - k_{4,f}[Z{-}Ni] + k_{4,r}[Ni][Z] \tag{11}$$

Letting $[Ni]_0$ represent the amount of catalyst initially added to the system, the conservation of catalyst is expressed as shown in equation (10).

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

$$[Ni]_0 = [Ni] + [A{-}Ni] + [Z{-}Ni] \tag{12}$$

Solving equation (10) for the concentration of the Ni-A complex yields equation (13), and solving equation (11) for the concentration of the Ni-Z complex followed by substitution of equation (12) yields equation (14).

$$[A{-}Ni] = \frac{k_{2,f}[A][Ni]}{k_{2,r} + k_{3,f}[H_2]} \tag{13}$$

$$[Z{-}Ni] = \frac{k_{3,f}}{k_{4,f}}[A{-}Ni][H_2] + \frac{k_{4,r}}{k_{4,f}}[Ni][Z]$$

$$[Z{-}Ni] = \frac{k_{3,f}}{k_{4,f}}\frac{k_{2,f}[A][Ni]}{k_{2,r} + k_{3,f}[H_2]}][H_2] + \frac{k_{4,r}}{k_{4,f}}[Ni][Z]$$

$$[Z{-}Ni] = \left(\frac{k_{2,f}k_{3,f}[A][H_2]}{k_{4,f}\left(k_{2,r} + k_{3,f}[H_2]\right)} + \frac{k_{4,r}}{k_{4,f}}[Z] \right)[Ni] \tag{14}$$

Substituting equations (13) and (14) into equation (12) and rearranging yields an expression for the concentration of free Ni, equation (15).

$$[Ni]_0 = [Ni] + \frac{k_{2,f}\left[A\right]\,[Ni]}{k_{2,r} + k_{3,f}\left[H_2\right]} + \left(\frac{k_{2,f}k_{3,f}\left[A\right]\,\left[H_2\right]}{k_{4,f}\left(k_{2,r} + k_{3,f}\left[H_2\right]\right)} + \frac{k_{4,r}}{k_{4,f}}[Z] \right)[Ni]$$

$$\frac{[Ni]_0}{[Ni]} = 1 + \frac{k_{2,f}\left[A\right]}{k_{2,r} + k_{3,f}\left[H_2\right]} + \frac{k_{2,f}k_{3,f}\left[A\right]\left[H_2\right]}{k_{4,f}\left(k_{2,r} + k_{3,f}\left[H_2\right]\right)} + \frac{k_{4,r}}{k_{4,f}}[Z]$$

$$[Ni] = \frac{[Ni]_0}{1 + \frac{k_{2,f}[A]}{k_{2,r} + k_{3,f}[H_2]} + \frac{k_{2,f}k_{3,f}[A]\left[H_2\right]}{k_{4,f}\left(k_{2,r} + k_{3,f}[H_2]\right)} + \frac{k_{4,r}}{k_{4,f}}[Z]} \tag{15}$$

Substitution of equations (14) and (15) in equation (8) yields the desired rate expression, equation (16).

$$r_{Z,1} = \frac{k_{4,f}[Ni]_0\left(\frac{k_{2,f}k_{3,f}[A]\left[H_2\right]}{k_{4,f}\left(k_{2,r} + k_{3,f}[H_2]\right)} + \frac{k_{4,r}}{k_{4,f}}[Z]\right)}{1 + \frac{k_{2,f}[A]}{k_{2,r} + k_{3,f}[H_2]} + \frac{k_{2,f}k_{3,f}[A]\left[H_2\right]}{k_{4,f}\left(k_{2,r} + k_{3,f}[H_2]\right)} + \frac{k_{4,r}}{k_{4,f}}[Z]} - \frac{k_{4,r}[Ni]_0[Z]}{1 + \frac{k_{2,f}[A]}{k_{2,r} + k_{3,f}[H_2]} + \frac{k_{2,f}k_{3,f}[A]\left[H_2\right]}{k_{4,f}\left(k_{2,r} + k_{3,f}[H_2]\right)} + \frac{k_{4,r}}{k_{4,f}}[Z]}$$

$$r_{P,1} = \frac{k_{4,f}[Ni]_0\left(\frac{k_{2,f}k_{3,f}[A]\left[H_2\right]}{k_{4,f}\left(k_{2,r} + k_{3,f}[H_2]\right)} + \frac{k_{4,r}}{k_{4,f}}[Z]\right) - k_{4,r}[Ni]_0[Z]}{1 + \frac{k_{2,f}[A]}{k_{2,r} + k_{3,f}[H_2]} + \frac{k_{2,f}k_{3,f}[A]\left[H_2\right]}{k_{4,f}\left(k_{2,r} + k_{3,f}[H_2]\right)} + \frac{k_{4,r}}{k_{4,f}}[Z]}$$

$$r_{P,1} = \frac{[Ni]_0\frac{k_{2,f}k_{3,f}[A]\left[H_2\right]}{k_{2,r} + k_{3,f}[H_2]}}{1 + \frac{k_{2,f}[A]}{k_{2,r} + k_{3,f}[H_2]} + \frac{k_{2,f}k_{3,f}[A]\left[H_2\right]}{k_{4,f}\left(k_{2,r} + k_{3,f}[H_2]\right)} + \frac{k_{4,r}}{k_{4,f}}[Z]}$$

$$r_{P,1} = \frac{[Ni]_0 \frac{k_{2,f} k_{3,f} k_{4,f} [A] [H_2]}{k_{2,r} + k_{3,f} [H_2]}}{k_{4,f} + \frac{k_{2,f} k_{4,f} [A]}{k_{2,r} + k_{3,f} [H_2]} + \frac{k_{2,f} k_{3,f} [A] [H_2]}{\left(k_{2,r} + k_{3,f} [H_2]\right)} + k_{4,r} [Z]}$$

$$r_{Z,1} = \frac{k_{2,f} k_{3,f} k_{4,f} [Ni]_0 [A] [H_2]}{\left(\begin{array}{c} k_{2,r} k_{4,f} + k_{2,f} k_{4,f} [A] + k_{3,f} k_{4,f} [H_2] \\ + k_{2,f} k_{3,f} [A] [H_2] + k_{3,f} k_{4,r} [H_2] [Z] + k_{2,r} k_{4,r} [Z] \end{array} \right)} \quad (16)$$