A First Course on Kinetics and Reaction Engineering

Activity 7.2

The algebra associated with Activity 7.2 is presented below.

Concentrations of the Reactive Intermediates (all three cases)

$$P_{Br\bullet} = \sqrt{\frac{k_{2,f} P_{Br_2}}{k_{2,r}}}$$

$$P_{H\bullet} = \frac{k_{3,f} P_{H_2} \sqrt{\dfrac{k_{2,f} P_{Br_2}}{k_{2,r}}}}{k_{3,r} P_{HBr} + k_{4,f} P_{Br_2}}$$

Rate with Respect to H₂

$$r_{H_2,1} = -\left(k_{3,f} P_{Br\bullet} P_{H_2} - k_{3,r} P_{HBr} P_{H\bullet} \right)$$

$$r_{H_2,1} = -\left(k_{3,f} \sqrt{\frac{k_{2,f} P_{Br_2}}{k_{2,r}}} P_{H_2} - k_{3,r} P_{HBr} \frac{k_{3,f} P_{H_2} \sqrt{\dfrac{k_{2,f} P_{Br_2}}{k_{2,r}}}}{k_{3,r} P_{HBr} + k_{4,f} P_{Br_2}} \right)$$

$$r_{H_2,1} = k_{3,f} \sqrt{\frac{k_{2,f} P_{Br_2}}{k_{2,r}}} P_{H_2} \left(\frac{k_{3,r} P_{HBr}}{k_{3,r} P_{HBr} + k_{4,f} P_{Br_2}} - 1 \right)$$

$$r_{H_2,1} = k_{3,f} \sqrt{\frac{k_{2,f} P_{Br_2}}{k_{2,r}}} P_{H_2} \left(\frac{-k_{4,f} P_{Br_2}}{k_{3,r} P_{HBr} + k_{4,f} P_{Br_2}} \right)$$

$$r_{H_2,1} = -\frac{k_{3,f} k_{4,f} \sqrt{\dfrac{k_{2,f}}{k_{2,r}}} P_{H_2} P_{Br_2}^{3/2}}{k_{3,r} P_{HBr} + k_{4,f} P_{Br_2}}$$

Rate with Respect to Br₂

$$r_{Br_2,1} = -\left(k_{2,f} P_{Br_2} - k_{2,r} P_{Br\bullet}^2 \right) - \left(k_{4,f} P_{H\bullet} P_{Br_2} \right)$$

$$r_{Br_2,1} = -\left(k_{2,f}P_{Br_2} - k_{2,r}\left(\sqrt{\frac{k_{2,f}P_{Br_2}}{k_{2,r}}}\right)^2\right) - \left(k_{4,f}\left(\frac{k_{3,f}P_{H_2}\sqrt{\frac{k_{2,f}P_{Br_2}}{k_{2,r}}}}{k_{3,r}P_{HBr}+k_{4,f}P_{Br_2}}\right)P_{Br_2}\right)$$

$$r_{Br_2,1} = -\left(k_{2,f}P_{Br_2} - k_{2,r}\left(\frac{k_{2,f}P_{Br_2}}{k_{2,r}}\right)\right) - \left(\frac{k_{3,f}k_{4,f}P_{H_2}P_{Br_2}\sqrt{\frac{k_{2,f}P_{Br_2}}{k_{2,r}}}}{k_{3,r}P_{HBr}+k_{4,f}P_{Br_2}}\right)$$

$$r_{Br_2,1} = -\left(k_{2,f}P_{Br_2} - k_{2,f}P_{Br_2}\right) - \left(\frac{k_{3,f}k_{4,f}P_{H_2}P_{Br_2}^{3/2}\sqrt{\frac{k_{2,f}}{k_{2,r}}}}{k_{3,r}P_{HBr}+k_{4,f}P_{Br_2}}\right)$$

$$r_{Br_2,1} = -\frac{k_{3,f}k_{4,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}}P_{H_2}P_{Br_2}^{3/2}}{k_{3,r}P_{HBr}+k_{4,f}P_{Br_2}}$$

Rate with Respect to HBr

$$r_{HBr,1} = \left(k_{3,f}P_{Br\bullet}P_{H_2} - k_{3,r}P_{HBr}P_{H\bullet}\right) + \left(k_{4,f}P_{H\bullet}P_{Br_2}\right)$$

$$r_{HBr,1} = \left(k_{3,f}\left(\sqrt{\frac{k_{2,f}P_{Br_2}}{k_{2,r}}}\right)P_{H_2} - k_{3,r}P_{HBr}\left(\frac{k_{3,f}P_{H_2}\sqrt{\frac{k_{2,f}P_{Br_2}}{k_{2,r}}}}{k_{3,r}P_{HBr}+k_{4,f}P_{Br_2}}\right)\right) + \left(k_{4,f}\left(\frac{k_{3,f}P_{H_2}\sqrt{\frac{k_{2,f}P_{Br_2}}{k_{2,r}}}}{k_{3,r}P_{HBr}+k_{4,f}P_{Br_2}}\right)P_{Br_2}\right)$$

$$r_{HBr,1} = \left(k_{3,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}}P_{H_2}P_{Br_2}^{1/2} - \frac{k_{3,f}k_{3,r}\sqrt{\frac{k_{2,f}}{k_{2,r}}}P_{H_2}P_{Br_2}^{1/2}P_{HBr}}{k_{3,r}P_{HBr}+k_{4,f}P_{Br_2}}\right) + \left(\frac{k_{3,f}k_{4,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}}P_{H_2}P_{Br_2}^{3/2}}{k_{3,r}P_{HBr}+k_{4,f}P_{Br_2}}\right)$$

$$r_{HBr,1} = k_{3,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}}P_{H_2}P_{Br_2}^{1/2} - \frac{k_{3,f}k_{3,r}\sqrt{\frac{k_{2,f}}{k_{2,r}}}P_{H_2}P_{Br_2}^{1/2}P_{HBr}}{k_{3,r}P_{HBr}+k_{4,f}P_{Br_2}} + \frac{k_{3,f}k_{4,f}\sqrt{\frac{k_{2,f}}{k_{2,r}}}P_{H_2}P_{Br_2}^{3/2}}{k_{3,r}P_{HBr}+k_{4,f}P_{Br_2}}$$

$$r_{HBr,1} = k_{3,f} \sqrt{\frac{k_{2,f}}{k_{2,r}}} P_{H_2} P_{Br_2}^{\frac{1}{2}} \left(1 - \frac{k_{3,r} P_{HBr}}{k_{3,r} P_{HBr} + k_{4,f} P_{Br_2}} + \frac{k_{4,f} P_{Br_2}}{k_{3,r} P_{HBr} + k_{4,f} P_{Br_2}} \right)$$

$$r_{HBr,1} = k_{3,f} \sqrt{\frac{k_{2,f}}{k_{2,r}}} P_{H_2} P_{Br_2}^{\frac{1}{2}} \left(\frac{k_{3,r} P_{HBr} + k_{4,f} P_{Br_2} - k_{3,r} P_{HBr} + k_{4,f} P_{Br_2}}{k_{3,r} P_{HBr} + k_{4,f} P_{Br_2}} \right)$$

$$r_{HBr,1} = k_{3,f} \sqrt{\frac{k_{2,f}}{k_{2,r}}} P_{H_2} P_{Br_2}^{\frac{1}{2}} \left(\frac{2 k_{4,f} P_{Br_2}}{k_{3,r} P_{HBr} + k_{4,f} P_{Br_2}} \right)$$

$$r_{HBr,1} = 2 \frac{k_{3,f} k_{4,f} \sqrt{\frac{k_{2,f}}{k_{2,r}}} P_{H_2} P_{Br_2}^{\frac{3}{2}}}{k_{3,r} P_{HBr} + k_{4,f} P_{Br_2}}$$