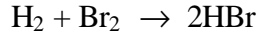
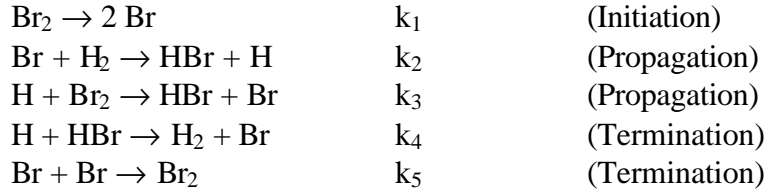


Application of Steady State Approximation

The mechanism of the reaction of H₂ with Br₂:



is not a concerted, 4-center transition state. The kinetics are, therefore, not first order in H₂ and first order in Br₂. Instead, there are five elementary reactions involved in the radical chain reaction:



Let's write the expressions for the time rate of change of concentration of the radical species that do not appear in the balanced chemical reaction, as a preliminary step to applying the steady state approximation:

$$d[\text{Br}]/dt = 2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2$$

$$d[\text{H}]/dt = \quad \quad + k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$$

$$d[\text{Br}]/dt = 2k_1[\text{Br}_2] \quad \quad -d[\text{H}]/dt \quad \quad - 2k_5[\text{Br}]^2 \quad \text{by subtraction}$$

Now, apply the steady state approximation: $d[\text{H}]/dt = 0 = d[\text{Br}]/dt$

$$\begin{aligned} d[\text{Br}]/dt = 0 &= 2k_1[\text{Br}_2] - 0 - 2k_5[\text{Br}]^2 \\ [\text{Br}]_{\text{ss}}^2 &= 2k_1[\text{Br}_2] / 2k_5 = k_1[\text{Br}_2] / k_5 = (k_1/k_5)[\text{Br}_2] \\ [\text{Br}]_{\text{ss}} &= (k_1/k_5)^{1/2} [\text{Br}_2]^{1/2} \end{aligned}$$

$$\begin{aligned} d[\text{H}]/dt &= k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] = 0 \\ k_2[\text{Br}][\text{H}_2] &= k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] = [\text{H}] (k_3[\text{Br}_2] + k_4[\text{HBr}]) \\ [\text{H}]_{\text{ss}} &= k_2[\text{Br}][\text{H}_2] / (k_3[\text{Br}_2] + k_4[\text{HBr}]) \quad \text{next, substitute in } [\text{Br}]_{\text{ss}} = (k_1/k_5)^{1/2} [\text{Br}_2]^{1/2} \\ [\text{H}]_{\text{ss}} &= k_2 (k_1/k_5)^{1/2} [\text{Br}_2]^{1/2} [\text{H}_2] / (k_3[\text{Br}_2] + k_4[\text{HBr}]) \end{aligned}$$

$$d[\text{HBr}]/dt = k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$$

$$\begin{aligned} &= k_2 (k_1/k_5)^{1/2} [\text{Br}_2]^{1/2} [\text{H}_2] && \text{substituting for } [\text{Br}]_{\text{ss}} \text{ in 1}^{\text{st}} \text{ term} \\ &+ k_3 \{ k_2 (k_1/k_5)^{1/2} [\text{Br}_2]^{1/2} [\text{H}_2] / (k_3[\text{Br}_2] + k_4[\text{HBr}]) \} [\text{Br}_2] && \text{substituting for } [\text{H}]_{\text{ss}} \text{ in 2}^{\text{nd}} \text{ term} \\ &- k_4 \{ k_2 (k_1/k_5)^{1/2} [\text{Br}_2]^{1/2} [\text{H}_2] / (k_3[\text{Br}_2] + k_4[\text{HBr}]) \} [\text{HBr}] && \text{substituting for } [\text{H}]_{\text{ss}} \text{ in 3}^{\text{rd}} \text{ term} \\ &= k_2 (k_1/k_5)^{1/2} [\text{Br}_2]^{1/2} [\text{H}_2] * \{ 1 + (k_3 [\text{Br}_2] - k_4[\text{HBr}]) / (k_3[\text{Br}_2] + k_4[\text{HBr}]) \} \end{aligned}$$

Let's just focus on the terms between the braces for moment:

$$\begin{aligned}
 & \{ 1 + (k_3 [\text{Br}_2] - k_4[\text{HBr}]) / (k_3[\text{Br}_2] + k_4[\text{HBr}]) \} \quad (\text{next, get to common denominator}) \\
 & = \{ k_3[\text{Br}_2] + k_4[\text{HBr}] + (k_3 [\text{Br}_2] - k_4[\text{HBr}]) \} / (k_3[\text{Br}_2] + k_4[\text{HBr}]) \\
 & = \{ 2 (k_3[\text{Br}_2]) / (k_3[\text{Br}_2] + k_4[\text{HBr}]) \} \\
 & = \{ 2 [\text{Br}_2] / ([\text{Br}_2] + (k_4/k_3)[\text{HBr}]) \} \quad \text{after dividing top and bottom by } k_3
 \end{aligned}$$

Now, let's put this back into our expression for $d[\text{HBr}]/dt$

$$\begin{aligned}
 d[\text{HBr}]/dt & = k_2 (k_1/k_5)^{1/2} [\text{Br}_2]^{1/2} [\text{H}_2] * \{ 2 [\text{Br}_2] / ([\text{Br}_2] + (k_4/k_3)[\text{HBr}]) \} \\
 & = 2 k_2 (k_1/k_5)^{1/2} [\text{Br}_2]^{1/2} [\text{H}_2] [\text{Br}_2] / ([\text{Br}_2] + (k_4/k_3)[\text{HBr}]) \\
 & = 2 k_2 (k_1/k_5)^{1/2} [\text{Br}_2]^{3/2} [\text{H}_2] / ([\text{Br}_2] + (k_4/k_3)[\text{HBr}])
 \end{aligned}$$

define $k = 2 k_2 (k_1/k_5)^{1/2}$ and $k' = (k_4/k_3)$ (k' is not a pseudo-1st order rate constant here)

$$d[\text{HBr}]/dt = k[\text{Br}_2]^{3/2} [\text{H}_2] / ([\text{Br}_2] + k' [\text{HBr}]) \text{ just as in equation 25.4 on page 868.}$$

P.S. I do not guarantee that all brackets, parentheses, and braces are properly placed!