## Application of Steady State Approximation

The mechanism of the reaction of $H_2$ with $Br_2$:

$$H_2 + Br_2 \rightarrow 2HBr$$

is not a concerted, 4-center transition state. The kinetics are, therefore, not first order in $H_2$ and first order in $Br_2$. Instead, there are five elementary reactions involved in the radical chain reaction:

| | | |
|---|---|---|
| $Br_2 \rightarrow 2\ Br$ | $k_1$ | (Initiation) |
| $Br + H_2 \rightarrow HBr + H$ | $k_2$ | (Propagation) |
| $H + Br_2 \rightarrow HBr + Br$ | $k_3$ | (Propagation) |
| $H + HBr \rightarrow H_2 + Br$ | $k_4$ | (Termination) |
| $Br + Br \rightarrow Br_2$ | $k_5$ | (Termination) |

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:

$$d[Br]/dt = 2k_1[Br_2] - k_2[Br][H_2] + k_3[H][Br_2] + k_4[H][HBr] - 2k_5[Br]^2$$

$$d[H]/dt = + k_2[Br][H_2] - k_3[H][Br_2] - k_4[H][HBr]$$

$$d[Br]/dt = 2k_1[Br_2] \quad -d[H]/dt \quad - 2k_5[Br]^2 \quad \text{by subtraction}$$

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

$$d[Br]/dt = 0 = 2k_1[Br_2] - 0 - 2k_5[Br]^2$$

$$[Br]_{ss}^2 = 2k_1[Br_2]/2k_5 = k_1[Br_2]/k_5 = (k_1/k_5)[Br_2]$$

$$[Br]_{ss} = (k_1/k_5)^{1/2}\ [Br_2]^{1/2}$$

$$d[H]/dt = k_2[Br][H_2] - k_3[H][Br_2] - k_4[H][HBr] = 0$$

$$k_2[Br][H_2] = k_3[H][Br_2] + k_4[H][HBr] = [H]\ (k_3[Br_2] + k_4[HBr])$$

$$[H]_{ss} = k_2[Br][H_2]/\ (k_3[Br_2] + k_4[HBr])$$ next, substitute in $[Br]_{ss} = (k_1/k_5)^{1/2}\ [Br_2]^{1/2}$

$$[H]_{ss} = k_2\ (k_1/k_5)^{1/2}\ [Br_2]^{1/2}[H_2]/\ (k_3[Br_2] + k_4[HBr])$$

$$d[HBr]/dt = k_2[Br][H_2] + k_3[H][Br_2] - k_4[H][HBr]$$

$$= k_2\ (k_1/k_5)^{1/2}\ [Br_2]^{1/2}\ [H_2]$$ substituting for $[Br]_{ss}$ in 1st term

$$+ k_3\ \{k_2\ (k_1/k_5)^{1/2}\ [Br_2]^{1/2}[H_2]/(k_3[Br_2] + k_4[HBr])\}[Br_2]$$ substituting for $[H]_{ss}$ in 2nd term

$$- k_4\ \{k_2\ (k_1/k_5)^{1/2}\ [Br_2]^{1/2}[H_2]/\ (k_3[Br_2] + k_4[HBr])\}[HBr]$$ substituting for $[H]_{ss}$ in 3rd term

$$= k_2\ (k_1/k_5)^{1/2}\ [Br_2]^{1/2}\ [H_2] * \{\ 1+ (k_3\ [Br_2] - k_4[HBr])\ /\ (k_3[Br_2] + k_4[HBr])\ \}$$

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

$\{ 1+ (k_3 [Br_2] - k_4[HBr]) / (k_3[Br_2] + k_4[HBr]) \}$ (next, get to common denominator)

$= \{ k_3[Br_2] + k_4[HBr] + (k_3 [Br_2] - k_4[HBr])\} / (k_3[Br_2] + k_4[HBr])$

$= \{2 (k_3[Br_2] / (k_3[Br_2] + k_4[HBr]) \}$

$= \{2 [Br_2] / ([Br_2] + (k_4/ k_3)[HBr]) \}$ after dividing top and bottom by $k_3$

Now, let's put this back into our expression for d[HBr]/dt

$d[HBr]/dt = k_2 (k_1 /k_5)^{1/2} [Br_2]^{1/2} [H_2] *\{2 [Br_2] / ([Br_2] + (k_4/ k_3)[HBr]) \}$

$= 2 k_2 (k_1 /k_5)^{1/2} [Br_2]^{1/2} [H_2] [Br_2] /([Br_2] + (k_4/ k_3)[HBr])$

$= 2 k_2 (k_1 /k_5)^{1/2} [Br_2]^{3/2} [H_2] /([Br_2] + (k_4/ k_3)[HBr])$

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)

$d[HBr]/dt = k[Br_2]^{3/2} [H_2] /([Br_2] + k'[HBr])$ just as in equation 25.4 on page 868.

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