A First Course on Kinetics and Reaction Engineering
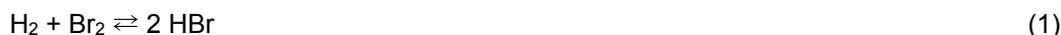
Example 7.1

Problem Purpose

This problem illustrates the simplification of mechanistic rate expressions when there are irreversible and kinetically insignificant reactions in the mechanism, and it also illustrates the elimination of reactive intermediate concentrations (or partial pressures) from mechanistic rate expressions by use of the Bodenstein steady state approximation.

Problem Statement

In the mechanism for synthesis of HBr given below, assume step (4) is irreversible and step (5) is kinetically insignificant. Use the Bodenstein steady-state approximation to derive a rate expression for the overall reaction rate in terms of the partial pressures of stable species.

Overall reaction:

$$H_2 + Br_2 \rightleftarrows 2\ HBr \tag{1}$$

Proposed mechanism:

$$Br_2 \rightleftarrows 2\ Br\bullet \tag{2}$$

$$Br\bullet + H_2 \rightleftarrows HBr + H\bullet \tag{3}$$

$$H\bullet + Br_2 \rightleftarrows HBr + Br\bullet \tag{4}$$

$$2\ H\bullet \rightleftarrows H_2 \tag{5}$$

Problem Analysis

An expression for the rate of reaction (1) with respect to H_2, Br_2 or HBr can be generated as described in Unit 6. Any place that the rate of step (5) appears, it can be deleted since the problem states that step is kinetically insignificant. In addition, any place that the rate of step (4) appears, the term for its reverse reaction can be deleted since the problem states that step is irreversible. The Bodenstein steady state approximation can then be used to eliminate the partial pressures of the reactive intermediates.

Problem Solution

The stable species in this problem are H_2, Br_2 and HBr; $Br\bullet$ and $H\bullet$ are reactive intermediates. We can choose to write an expression for the rate of reaction (1) with respect to H_2, Br_2 or HBr; here I will write the expression for the rate of reaction (1) with respect to H_2. The rate with respect to H_2 is simply the sum of the rates of each step in the mechanism with respect to H_2. Noting that H_2 only appears in reaction (3), with a stoichiometric coefficient of -1, and in reaction (5), with a stoichiometric coefficient of +1, this leads to the rate expression given in equation (7), where partial pressures have been used as the composition variables.

$$r_{H_2,1} = \sum_{\substack{s=\text{ all} \\ \text{steps}}} \nu_{H_2,s} \left(k_{s,f} \prod_{\substack{m=\text{all} \\ \text{reactants}}} \left[m \right]^{-\nu_{m,s}} - k_{s,r} \prod_{\substack{n=\text{all} \\ \text{products}}} \left[n \right]^{\nu_{n,s}} \right) \tag{6}$$

$$r_{H_2,1} = -\left(k_{3,f} P_{Br\cdot} P_{H_2} - k_{3,r} P_{HBr} P_{H\cdot} \right) + \left(k_{5,f} P_{H\cdot}^2 - k_{5,r} P_{H_2} \right) \tag{7}$$

The problem statement says that reaction (5) is kinetically insignificant. As a consequence, the term corresponding to its rate can be deleted from equation (7), leading to equation (8).

$$r_{H_2,1} = -\left(k_{3,f} P_{Br\cdot} P_{H_2} - k_{3,r} P_{HBr} P_{H\cdot} \right) \tag{8}$$

The partial pressures of the reactive intermediates, Br• and H•, appear in equation (8), limiting its utility. They can be eliminated through the use of the Bodenstein steady state approximation. The application of the Bodenstein steady state approximation involves writing expressions for the net rate of formation of each reactive intermediate and setting it equal to zero. The results of doing so for Br• and H• is shown in equations (10) and (12), respectively.

$$0 = \sum_{\substack{s=\text{ all} \\ \text{steps}}} \nu_{Br\cdot,s} \left(k_{s,f} \prod_{\substack{m=\text{all} \\ \text{reactants}}} \left[m \right]^{-\nu_{m,s}} - k_{s,r} \prod_{\substack{n=\text{all} \\ \text{products}}} \left[n \right]^{\nu_{n,s}} \right) \tag{9}$$

$$0 = 2\left(k_{2,f} P_{Br_2} - k_{2,r} P_{Br\cdot}^2 \right) - \left(k_{3,f} P_{Br\cdot} P_{H_2} - k_{3,r} P_{HBr} P_{H\cdot} \right) + \left(k_{4,f} P_{H\cdot} P_{Br_2} - k_{4,r} P_{HBr} P_{Br\cdot} \right) \tag{10}$$

$$0 = \sum_{\substack{s=\text{ all} \\ \text{steps}}} \nu_{H\cdot,s} \left(k_{s,f} \prod_{\substack{m=\text{all} \\ \text{reactants}}} \left[m \right]^{-\nu_{m,s}} - k_{s,r} \prod_{\substack{n=\text{all} \\ \text{products}}} \left[n \right]^{\nu_{n,s}} \right) \tag{11}$$

$$0 = \left(k_{3,f} P_{Br\cdot} P_{H_2} - k_{3,r} P_{HBr} P_{H\cdot} \right) - \left(k_{4,f} P_{H\cdot} P_{Br_2} - k_{4,r} P_{HBr} P_{Br\cdot} \right) - 2\left(k_{5,f} P_{H\cdot}^2 - k_{5,r} P_{H_2} \right) \tag{12}$$

Again, the problem statement says that step 5 is kinetically insignificant, so the last term in equation (12) can be deleted. It also says that step (4) is irreversible, so the term corresponding to the reverse rate of that step can be deleted in both equation (10) and equation (12), leading to equations (13) and (14).

$$0 = 2\left(k_{2,f} P_{Br_2} - k_{2,r} P_{Br\cdot}^2 \right) - \left(k_{3,f} P_{Br\cdot} P_{H_2} - k_{3,r} P_{HBr} P_{H\cdot} \right) + \left(k_{4,f} P_{H\cdot} P_{Br_2} \right) \tag{13}$$

$$0 = \left(k_{3,f} P_{Br\cdot} P_{H_2} - k_{3,r} P_{HBr} P_{H\cdot} \right) - \left(k_{4,f} P_{H\cdot} P_{Br_2} \right) \tag{14}$$

Equations (13) and (14) can be solved to obtain expressions for the partial pressures of Br• and H•. This can be done manually, or one can use software that performs symbolic algebra. In either case, the results are given in equations (15) and (16).

$$P_{Br\bullet} = \sqrt{\frac{k_{2,f}P_{Br_2}}{k_{2,r}}} \tag{15}$$

$$P_{H\bullet} = \frac{k_{3,f}P_{H_2}\sqrt{\dfrac{k_{2,f}P_{Br_2}}{k_{2,r}}}}{k_{3,r}P_{HBr}+k_{4,f}P_{Br_2}} \tag{16}$$

Finally, substitution of equations (15) and (16) into equation (8) leads to the desired rate expression, equation (20).

$$r_{H_2,1} = -\left(k_{3,f}\sqrt{\frac{k_{2,f}P_{Br_2}}{k_{2,r}}}P_{H_2} - k_{3,r}P_{HBr}\frac{k_{3,f}P_{H_2}\sqrt{\dfrac{k_{2,f}P_{Br_2}}{k_{2,r}}}}{k_{3,r}P_{HBr}+k_{4,f}P_{Br_2}}\right) \tag{17}$$

$$r_{H_2,1} = k_{3,f}\sqrt{\frac{k_{2,f}P_{Br_2}}{k_{2,r}}}P_{H_2}\left(\frac{k_{3,r}P_{HBr}}{k_{3,r}P_{HBr}+k_{4,f}P_{Br_2}}-1\right) \tag{18}$$

$$r_{H_2,1} = k_{3,f}\sqrt{\frac{k_{2,f}P_{Br_2}}{k_{2,r}}}P_{H_2}\left(\frac{-k_{4,f}P_{Br_2}}{k_{3,r}P_{HBr}+k_{4,f}P_{Br_2}}\right) \tag{19}$$

$$r_{H_2,1} = -\frac{k_{3,f}k_{4,f}\sqrt{\dfrac{k_{2,f}}{k_{2,r}}}P_{H_2}P_{Br_2}^{3/2}}{k_{3,r}P_{HBr}+k_{4,f}P_{Br_2}} \tag{20}$$