12.9: Chain Reactions

A large number of reactions proceed through a series of steps that can collectively be classified as a **chain reaction**. The reactions contain steps that can be classified as

- **initiation step** – a step that creates the intermediates from stable species
- **propagation step** – a step that consumes an intermediate, but creates a new one
- **termination step –** a step that consumes intermediates without creating new ones

These types of reactions are very common when the intermediates involved are radicals. An example, is the reaction

$$H_2 + Br_2 \rightarrow 2HBr$$

The observed rate law for this reaction is

$$\text{rate} = \frac{k[H_2][Br_2]^{3/2}}{[Br_2] + k'[HBr]} \tag{12.9.1}$$

A proposed mechanism is

$$Br_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Br^{\cdot} \tag{12.9.2}$$

$$2Br^{\cdot} + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HBr + H^{\cdot} \tag{12.9.3}$$

$$H^{\cdot} + Br_2 \xrightarrow{k_3} HBr + Br^{\cdot} \tag{12.9.4}$$

Based on this mechanism, the rate of change of concentrations for the intermediates ($H^{\cdot}$ and $Br^{\cdot}$) can be written, and the steady state approximation applied.

$$\frac{d[H^{\cdot}]}{dt} = k_2[Br^{\cdot}][H_2] - k_{-2}[HBr][H^{\cdot}] - k_3[H^{\cdot}][Br_2] = 0$$

$$\frac{d[Br^{\cdot}]}{dt} = 2k_1[Br_2] - 2k_{-1}[Br^{\cdot}]^2 - k_2[Br^{\cdot}][H_2] + k_{-2}[HBr][H^{\cdot}] + k_3[H^{\cdot}][Br_2] = 0$$

Adding these two expressions cancels the terms involving k_2, k_{-2}, and k_3. The result is

$$2k_1[Br_2] - 2k_{-1}[Br^{\cdot}]^2 = 0$$

Solving for $Br^{\cdot}$

$$Br^{\cdot} = \sqrt{\frac{k_1[Br_2]}{k_{-1}}}$$

This can be substituted into an expression for the $H^{\cdot}$ that is generated by solving the steady state expression for $d[H^{\cdot}]/dt$.

$$[H^{\cdot}] = \frac{k_2[Br^{\cdot}][H_2]}{k_{-2}[HBr] + k_3[Br_2]}$$

so

$$[H^{\cdot}] = \frac{k_2\sqrt{\frac{k_1[Br_2]}{k_{-1}}}[H_2]}{k_{-2}[HBr] + k_3[Br_2]}$$

Now, armed with expressions for $H^{\cdot}$ and $Br^{\cdot}$, we can substitute them into an expression for the rate of production of the product HBr:

$$\frac{[HBr]}{dt} = k_2[Br^{\cdot}][H_2] + k_3[H^{\cdot}][Br_2] - k_{-2}[H^{\cdot}][HBr]$$

After substitution and simplification, the result is

$$\frac{[HBr]}{dt} = \frac{2k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[H_2][Br_2]^{1/2}}{1+\frac{k_{-1}}{k_3}\frac{[HBr]}{[Br_2]}}$$

Multiplying the top and bottom expressions on the right by $[Br_2]$ produces

$$\frac{[HBr]}{dt} = \frac{2k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[H_2][Br_2]^{3/2}}{[Br_2]+\frac{k_{-1}}{k_3}[HBr]}$$

which matches the form of the rate law found experimentally (Equation 12.9.1)! In this case,

$$k = 2k_2\sqrt{\frac{k_1}{k_{-1}}}$$

and

$$k' = \frac{k_{-2}}{k_3}$$