12.4: The Rate Determining Step Approximation

The **rate determining step** approximation is one of the simplest approximations one can make to analyze a proposed mechanism to deduce the rate law it predicts. Simply stated, the rate determining step approximation says that a mechanism can proceed no faster than its slowest step. So, for example, if the reaction

$$A + B \rightarrow C$$

is proposed to follow the mechanism

$$\underbrace{A + A \overset{k_1}{\longrightarrow} A_2}_{\text{slow}}$$

$$\underbrace{A_2 \overset{k_2}{\longrightarrow} C + A}_{\text{fast}}$$

the rate determining step approximation suggests that the rate (expressed in terms of the appearance of product C) should be determined by the slow initial step, and so the rate law will be

$$\frac{[C]}{dt} = k_1[A]^2$$

matching the order of the rate law to the molecularity of the slow step. Conversely, if the reaction mechanism is proposed as

$$\underbrace{A \overset{k_1}{\longrightarrow} A^*}_{\text{slow}}$$

$$\underbrace{A^* + B \overset{k_2}{\longrightarrow} C}_{\text{fast}}$$

the rate determining step approximation suggests that the rate of the reaction should be

$$\frac{[C]}{dt} = k_1[A]$$

again, with the order of the rate law matching the molecularity of the rate determining step.