Rate Laws and Reaction Pathway

The form of the rate law depends on the reaction mechanism. For a reaction that occurs in a *single step,* the reaction rate of that step is proportional to the product of the reactant concentrations, each of which is raised to its stoichiometric coefficient. For example, suppose one molecule of gas A collides with one molecule of gas B to form two molecules of substance C, according to the following equation.

$$A + B \longrightarrow 2C$$

One particle of each reactant is involved in each collision. Thus, doubling the concentration of either reactant will double the collision frequency. It will also double the reaction rate *for this step.* Therefore, the rate for this step is directly proportional to the concentration of A and B. The rate law for this one-step forward reaction follows.

$$R_{forward} = k_{forward}[A][B]$$

Now suppose the reaction is reversible. In the reverse step, two molecules of C must decompose to form one molecule of A and one of B or $2C \longrightarrow A + B$.

Thus, the reaction rate for this reverse step is directly proportional to $[C] \times [C]$. The rate law for the reverse step is $R_{reverse} = k_{reverse}[C]^2$.

The power to which the molar concentration of each reactant is raised in the rate laws above corresponds to the coefficient for the reactant in the balanced chemical equation. Such a relationship holds *only* if the reaction follows a simple one-step path, that is, if the reaction occurs at the molecular level exactly as written in the chemical equation.

If a chemical reaction proceeds in a sequence of steps, the rate law is determined from the slowest step because it has the lowest rate. *This slowest-rate step is called the* **rate-determining step** *for the chemical reaction.*

Consider the reaction of nitrogen dioxide and carbon monoxide.

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

The reaction is believed to be a two-step process represented by the following mechanism.

Step 1: $NO_2 + NO_2 \longrightarrow NO_3 + NO$ slow
Step 2: $NO_3 + CO \longrightarrow NO_2 + CO_2$ fast

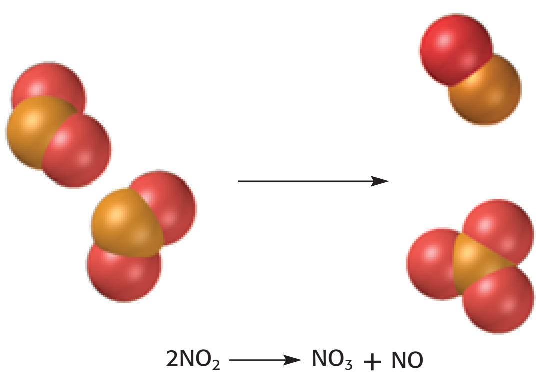

FIGURE 11 This diagram is a representation of Step 1 in the reaction of nitrogen dioxide and carbon monoxide. Notice the formation of the intermediate species NO_3 after two molecules of NO_2 collide.

In the first step, shown in **Figure 11,** two molecules of NO_2 collide, forming the intermediate species NO_3. This molecule then collides with one molecule of CO and reacts quickly to produce one molecule each of NO_2 and CO_2. The first step is the slower of the two and is therefore the rate-determining step. We can write the rate law from this rate-determining step, which has two molecules of NO_2 as the reactants.

$$R = k[NO_2]^2$$

The rate law does not include [CO] because CO reacts after the rate-determining step and does not affect the rate.