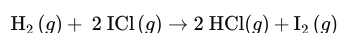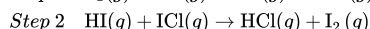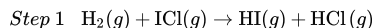# 14.7: Reaction Mechanisms

Most chemical reactions do not occur in a single step, but through several steps. When we write a chemical equation to represent a chemical reaction, *we usually represent the overall reaction, not the series of individual steps by which the reaction occurs*. Consider the reaction in which hydrogen gas reacts with iodine monochloride:

$$H_2(g) + 2\,ICl(g) \rightarrow 2\,HCl(g) + I_2(g)$$

The overall equation shows only the substances present at the beginning of the reaction and the substances formed by the reaction—it does not show the intermediate steps. The **reaction mechanism** ℗ is the series of individual chemical steps by which an overall chemical reaction occurs.
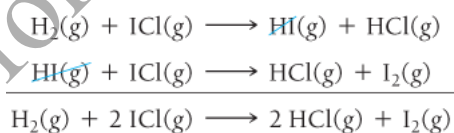
For example, the proposed mechanism for the reaction between hydrogen and iodine monochloride contains two steps:

$$\begin{aligned} Step\ 1 \quad & H_2(g) + ICl(g) \rightarrow HI(g) + HCl(g) \\ Step\ 2 \quad & HI(g) + ICl(g) \rightarrow HCl(g) + I_2(g) \end{aligned}$$

In the first step, an H_2 molecule collides with an ICl molecule and forms an HI molecule and an HCl molecule. In the second step, the HI molecule formed in the first step collides with a second ICl molecule to form another HCl molecule and an I_2 molecule. Each step in a reaction mechanism is an **elementary step** ℗. Elementary steps cannot be broken down into simpler steps—they occur as they are written (they represent the exact species that are colliding in the reaction).

> An elementary step represents an actual interaction between the reactant molecules in the step. An overall reaction equation shows only the starting substances and the ending substances, not the path between them.

In a valid reaction mechanism, the individual steps in the mechanism add to the overall reaction. For example, the mechanism just shown sums to the overall reaction as shown here:
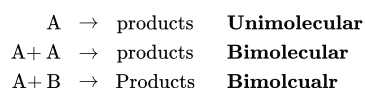
$$\begin{aligned} H_2(g) + ICl(g) &\longrightarrow \cancel{HI(g)} + HCl(g) \\ \cancel{HI(g)} + ICl(g) &\longrightarrow HCl(g) + I_2(g) \\ \hline H_2(g) + 2\,ICl(g) &\longrightarrow 2\,HCl(g) + I_2(g) \end{aligned}$$

Notice that the HI molecule appears in the reaction mechanism but not in the overall reaction equation. We call species such as HI *reaction intermediates*. A **reaction intermediate** ℗ forms in one elementary step and is consumed in another. The reaction mechanism is a complete, detailed description of the reaction at the molecular level—it specifies the individual collisions and reactions that result in the overall reaction. As such, reaction mechanisms are highly sought-after pieces of chemical knowledge.

How do we determine reaction mechanisms? Recall from the opening section of this chapter that chemical kinetics are not only practically important (because they allow us to control the rate of a particular reaction), but also theoretically important because they can help us determine the mechanism of the reaction. We can piece together possible reaction mechanisms by measuring the kinetics of the overall reaction and working backward to write a mechanism consistent with the measured kinetics.

Rate Laws for Elementary Steps

We characterize elementary steps by **molecularity** ℗, the number of reactant particles involved in the step. The

most common molecularities are **unimolecular**[?] and **bimolecular**[?]:

$$
\begin{aligned}
A &\rightarrow \text{products} &&\textbf{Unimolecular}\\
A + A &\rightarrow \text{products} &&\textbf{Bimolecular}\\
A + B &\rightarrow \text{Products} &&\textbf{Bimolcualr}
\end{aligned}
$$

Elementary steps in which three reactant particles collide, called **termolecular**[?] steps, are very rare because the probability of three particles simultaneously colliding is small.

Although we cannot deduce the rate law for an *overall chemical reaction* from the balanced chemical equation, we can deduce the rate law for an *elementary step* from its equation. Since we know that an elementary step occurs through the collision of the reactant particles, the rate is proportional to the product of the concentrations of those particles. For example, the rate for the bimolecular elementary step in which A reacts with B is proportional to the concentration of A multiplied by the concentration of B:

$$A + B \rightarrow \text{products} \quad \text{rate} = k[A][B]$$

Similarly, the rate law for the bimolecular step in which A reacts with A is proportional to the square of the concentration of A:

$$A + A \rightarrow \text{products} \quad \text{rate} = k[A]^2$$

Table 14.3[?] summarizes the rate laws for the common elementary steps, as well as those for the rare termolecular step. Notice that the molecularity of the elementary step is equal to the overall order of the step.

Table 14.3 **Rate Laws for Elementary Steps**

Elementary Step	Molecularity	Rate Law
A $\longrightarrow$ products	1	Rate $= k[A]$
A + A $\longrightarrow$ products	2	Rate $= k[A]^2$
A + B $\longrightarrow$ products	2	Rate $= k[A][B]$
A + A + A $\longrightarrow$ products	3 (rare)	Rate $= k[A]^3$
A + A + B $\longrightarrow$ products	3 (rare)	Rate $= k[A]^2[B]$
A + B + C $\longrightarrow$ products	3 (rare)	Rate $= k[A][B][C]$

# Rate-Determining Steps and Overall Reaction Rate Laws

In most chemical reactions, one of the elementary steps—the **rate-determining step**[?]—is much slower than the others. The rate-determining step (also called the rate-limiting step) in a chemical reaction is analogous to the narrowest section on a freeway. If a section of a freeway narrows from four lanes to two lanes, for even a short distance, the rate at which cars travel along the freeway is limited by the rate at which they can travel through the narrow section (even though the rate might be much faster along the four-lane section). Similarly, the rate-determining step in a reaction mechanism limits the overall rate of the reaction (even though the other steps occur much faster) and therefore determines *the rate law for the overall reaction*.

Rate-limiting section
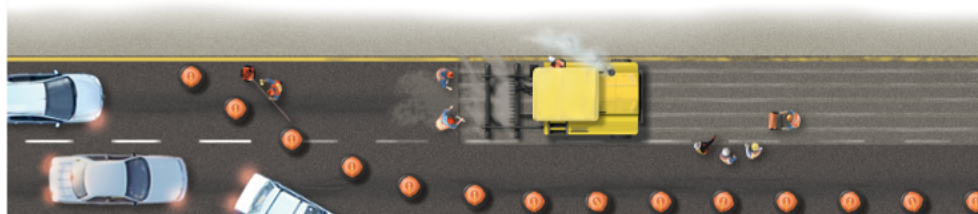
The rate-determining step in a reaction mechanism limits the overall rate of the reaction just as the narrowest section of a highway limits the rate at which traffic can pass.

As an example, consider the reaction between nitrogen dioxide gas and carbon monoxide gas:

$$\mathrm{NO_2\,(g) + CO\,(g) \rightarrow NO\,(g) + CO_2\,(g)}$$
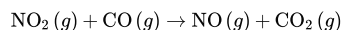
The experimentally determined rate law for this reaction is $\mathrm{rate} = k[\mathrm{NO_2}]^2$. We can see from this rate law that the reaction must not be a single-step reaction—otherwise the rate law would be $\mathrm{rate} = k[\mathrm{NO_2}][\mathrm{CO}]$. A possible mechanism for this reaction involves two steps:

$$\begin{aligned}
\mathrm{NO_2(g) + NO_2\,(g)} &\rightarrow \mathrm{NO_3(g) + NO\,(g)} \quad \text{Slow} \\
\mathrm{NO_3(g) + CO\,(g)} &\rightarrow \mathrm{NO_2\,(g) + CO_2\,(g)} \quad \text{Fast}
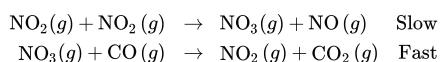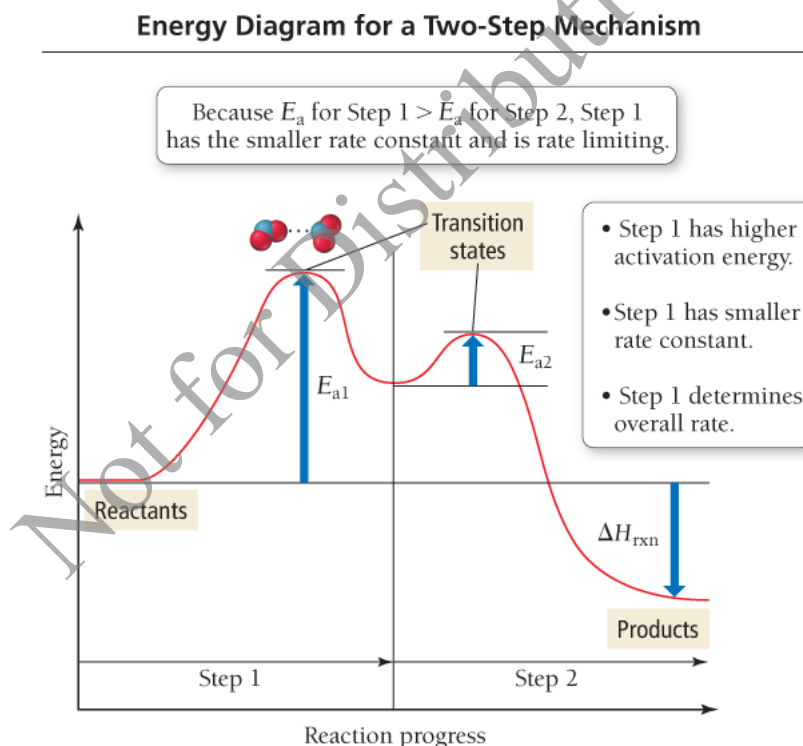\end{aligned}$$

Figure 14.16 ⬜ is the energy diagram for this mechanism. The first step has a much larger activation energy than the second step. This greater activation energy results in a much smaller rate constant for the first step compared to the second step. The first step determines the overall rate of the reaction, and the predicted *overall* rate law is therefore $\mathrm{Rate} = k[\mathrm{NO_2}]^2$, which is consistent with the observed experimental rate law.

Figure 14.16 **Energy Diagram for a Two-Step Mechanism**

Energy Diagram for a Two-Step Mechanism

Because E_a for Step 1 > E_a for Step 2, Step 1 has the smaller rate constant and is rate limiting.

Transition states

E_{a1}

E_{a2}

- Step 1 has higher activation energy.
- Step 1 has smaller rate constant.
- Step 1 determines overall rate.

Energy

Reactants

ΔH_{rxn}

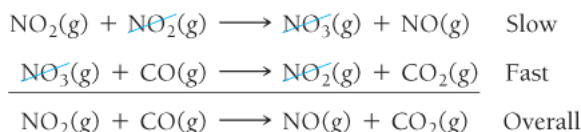Products

Step 1   Step 2

Reaction progress

For a proposed reaction mechanism, such as the one shown in Figure 14.16 ⬜ for NO$_2$ and CO, to be *valid* (mechanisms can only be validated, not proven), two conditions must be met:

1. The elementary steps in the mechanism must sum to the overall reaction.
2. The rate law predicted by the mechanism must be consistent with the experimentally observed rate law.

We have already seen that the rate law predicted by the earlier mechanism is consistent with the experimentally observed rate law. We can check whether the elementary steps sum to the overall reaction by adding them

together:

$$
\begin{aligned}
NO_2(g) + NO_2(g) &\longrightarrow NO_3(g) + NO(g) && \text{Slow} \\
\underline{NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)} && \text{Fast} \\
NO_2(g) + CO(g) &\longrightarrow NO(g) + CO_2(g) && \text{Overall}
\end{aligned}
$$

The mechanism fulfills both of the given requirements and is therefore valid. A valid mechanism is not a *proven* mechanism (because other mechanisms may also fulfill both of the given requirements). We can only say that a given mechanism is consistent with kinetic observations of the reaction and therefore possible. Other types of data—such as the experimental evidence for a proposed intermediate—are necessary to further strengthen the validity of a proposed mechanism.

## Mechanisms with a Fast Initial Step

When the proposed mechanism for a reaction has a slow initial step—like the one shown for the reaction between NO_2 and CO—the rate law predicted by the mechanism normally contains only reactants involved in the overall reaction. However, when a mechanism begins with a fast initial step, some other subsequent step in the mechanism is the rate-limiting step. In these cases, the rate law predicted by the rate-limiting step may contain reaction intermediates. Since reaction intermediates do not appear in the overall reaction equation, a rate law containing intermediates cannot generally correspond to the experimental rate law. Fortunately, however, we can often express the concentration of intermediates in terms of the concentrations of the reactants of the overall reaction.

In a multistep mechanism where the first step is fast, the products of the first step may build up because the rate at which they are consumed is limited by some slower step further down the line. As those products build up, they can begin to react with one another to re-form the reactants. As long as the first step is fast enough compared to the rate-limiting step, the first-step reaction will reach equilibrium. We indicate equilibrium as follows:

$$
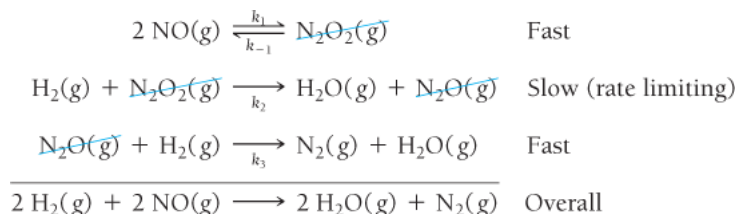\text{reactants} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{products}
$$
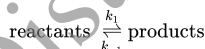
The double arrows indicate that both the forward reaction and the reverse reaction occur. If equilibrium is reached, then the rate of the forward reaction equals the rate of the reverse reaction.

As an example, consider the reaction by which hydrogen reacts with nitrogen monoxide to form water and nitrogen gas:

$$
2\,H_2(g) + 2\,NO(g) \rightarrow 2\,H_2O(g) + N_2(g)
$$
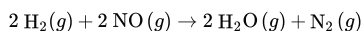
The experimentally observed rate law is rate $= k\left[H_2\right][NO]^2$. The reaction is first order in hydrogen and second order in nitrogen monoxide. The proposed mechanism has a slow second step:

$$
\begin{aligned}
2\,NO(g) &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2(g) && \text{Fast} \\
H_2(g) + N_2O_2(g) &\xrightarrow{k_2} H_2O(g) + N_2O(g) && \text{Slow (rate limiting)} \\
\underline{N_2O(g) + H_2(g) \xrightarrow{k_3} N_2(g) + H_2O(g)} && \text{Fast} \\
2\,H_2(g) + 2\,NO(g) &\longrightarrow 2\,H_2O(g) + N_2(g) && \text{Overall}
\end{aligned}
$$

To determine whether the mechanism is valid, we must determine whether the two conditions described previously are met. As you can see, the steps do indeed sum to the overall reaction, so the first condition is met.

The second condition is that the rate law predicted by the mechanism must be consistent with the experimentally observed rate law. Because the second step is rate limiting, we write the following expression for

the rate law:

[14.28]

$$\text{rate} = k_2[\text{H}_2][\text{N}_2\text{O}_2]$$

This rate law contains an intermediate (N_2O_2) and can therefore not be consistent with the experimentally observed rate law (which does not contain intermediates). Because of the equilibrium in the first step, however, *we can express the concentration of the intermediate in terms of the reactants of the overall equation*. The first step reaches equilibrium, so the rate of the forward reaction in the first step equals the rate of the reverse reaction:

$$\text{rate (forword)} = \text{rate (reverse)}$$

The rate of the forward reaction is given by the rate law:

$$\text{rate} = k_1[\text{NO}]^2$$

The rate of the reverse reaction is given by the rate law:

$$\text{rate} = k_{-1}[\text{N}_2\text{O}_2]$$

Since these two rates are equal at equilibrium, we write the expression:

$$k_1[\text{NO}]^2 = k_{-1}\left[\text{N}_2\text{O}_2\right]$$

Rearranging, we get:

$$[\text{N}_2\text{O}_2] = \frac{k_1}{k_{-1}}[\text{NO}]^2$$

We can now substitute this expression into Equation 14.28, the rate law obtained from the slow step:

$$
\begin{aligned}
\text{rate} \quad &= \quad k_2[\text{H}_2][\text{N}_2\text{O}_2] \\
&= \quad k_2[\text{H}_2]\frac{k_1}{k_{-1}}[\text{NO}]^2 \\
&= \quad \frac{k_2 k_1}{k_{-1}}[\text{H}_2][\text{NO}]^2
\end{aligned}
$$

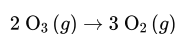If we combine the individual rate constants into one overall rate constant, we get the predicted rate law:

[14.29]

$$\text{rate} = k[\text{H}_2][\text{NO}]^2$$

Since this rate law is consistent with the experimentally observed rate law, the second condition is met and the proposed mechanism is valid.
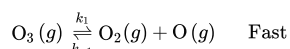
Example 14.9 Reaction Mechanisms

Ozone naturally decomposes to oxygen by this reaction:
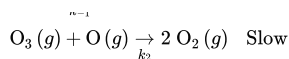
$$2\,\text{O}_3\,(g) \rightarrow 3\,\text{O}_2\,(g)$$
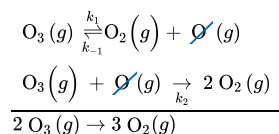
The experimentally observed rate law for this reaction is:

$$\text{rate} = k[\text{O}_3]^2[\text{O}_2]^{-1}$$

Show that this proposed mechanism is consistent with the experimentally observed rate law:

$$\text{O}_3\,(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{O}_2\,(g) + \text{O}\,(g) \qquad \text{Fast}$$

$$O_3(g) + O(g) \xrightarrow[k_2]{} 2\,O_2(g) \quad \text{Slow}$$

SOLUTION

To determine whether the mechanism is valid, you must first determine whether the steps sum to the overall reaction. The steps do indeed sum to the overall reaction, so the first condition is met.

$$O_3(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2\left(g\right) + \cancel{O}(g)$$

$$\frac{O_3\left(g\right) + \cancel{O}(g) \xrightarrow[k_2]{} 2\,O_2(g)}{2\,O_3(g) \rightarrow 3\,O_2(g)}$$

The second condition is that the rate law predicted by the mechanism must be consistent with the experimentally observed rate law. Because the second step is rate limiting, write the rate law based on the second step.

$$\text{rate} = k_2[O_3][O]$$

Because the rate law contains an intermediate (O), you must express the concentration of the intermediate in terms of the concentrations of the reactants of the overall reaction. To do this, set the rates of the forward reaction and the reverse reaction of the first step equal to each other. Solve the expression from the previous step for [O], the concentration of the intermediate.

$$\begin{aligned}
\text{rate (forword)} &= \text{rate (reverse)} \\
k_1[O_3] &= k_{-1}[O_2][O] \\
[O] &= \frac{k_1[O_3]}{k_{-1}[O_2]}
\end{aligned}$$

Finally, substitute [O] into the rate law predicted by the slow step, and combine the rate constants into one overall rate constant, k.

$$\begin{aligned}
\text{rate} &= k_2[O_3][O] \\
&= k_2[O_3]\frac{k_1[O_3]}{k_{-1}[O_2]} \\
&= k_2\frac{k_1[O_3]^2}{k_{-1}[O_2]} \\
&= k[O_3]^2[O_2]^{-1}
\end{aligned}$$

CHECK   Because the two steps in the proposed mechanism sum to the overall reaction, and because the rate law obtained from the proposed mechanism is consistent with the experimentally observed rate law, the proposed mechanism is valid. The −1 reaction order with respect to $[O_2]$ indicates that the rate slows down as the concentration of oxygen increases—oxygen inhibits, or slows down, the reaction.

FOR PRACTICE 14.9   Predict the overall reaction and rate law that results from the following two-step mechanism:

$$\begin{aligned}
2\,A &\rightarrow A_2 & \text{Slow} \\
A_2 + B &\rightarrow A_2B & \text{Fast}
\end{aligned}$$
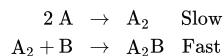
Interactive Worked Example 14.9   Reaction Mechanisms