Expressing Reaction Rates

Consider this balanced chemical equation:

$$H_2O_2(aq) + 3\,I^-(aq) + 2\,H^+(aq) \longrightarrow I_3^-(aq) + 2\,H_2O(l)$$

In the first 10.0 seconds of the reaction, the concentration of I^- drops from 1.000 M to 0.868 M.

a. Calculate the average rate of this reaction in this time interval.
b. Determine the rate of change in the concentration of H^+ (that is, $\Delta[H^+]/\Delta t$) during this time interval.

Solution

a. Calculate the average rate of the reaction.

$$\begin{aligned}\text{Rate} &= -\frac{1}{3}\frac{\Delta[I^-]}{\Delta t} \\ &= -\frac{1}{3}\frac{(0.868\text{ M} - 1.000\text{ M})}{10.0\text{ s}} \\ &= 4.40 \times 10^{-3}\text{ M/s}\end{aligned}$$

b. Again for the relationship between the rate of the reaction and $\Delta[H^+]/\Delta t$. After solving for $\Delta[H^+]/\Delta t$, substitute the calculated rate from part (a) and calculate $\Delta[H^+]/\Delta t$.

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[H^+]}{\Delta t}$$

$$\begin{aligned}\frac{\Delta[H^+]}{\Delta t} &= -2(\text{rate}) \\ &= -2(4.40 \times 10^{-3}\text{ M/s}) \\ &= -8.80 \times 10^{-3}\text{ M/s}\end{aligned}$$

Determining the Order and Rate Constant of a Reaction

Consider the reaction between nitrogen dioxide and carbon monoxide:

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

The initial rate of the reaction is measured at several different concentrations of the reactants, and the tabulated results are shown here.

$[NO_2]$ (M)	[CO] (M)	Initial Rate (M/s)
0.10	0.10	0.0021
0.20	0.10	0.0082
0.20	0.20	0.0083
0.40	0.10	0.033

From the data, determine:

a. the rate law for the reaction

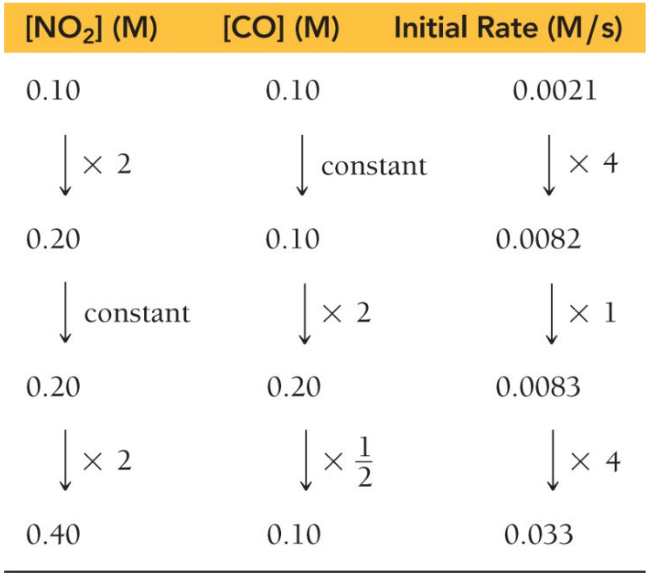
b. the rate constant (k) for the reaction

Solution

a. Begin by examining how the rate changes for each change in concentration. Between the first two experiments, the concentration of NO_2 doubles, the concentration of CO stays constant, and the rate quadruples, suggesting that the reaction is second order in NO_2.

Between the second and third experiments, the concentration of NO_2 stays constant, the concentration of CO doubles, and the rate remains constant (the small change in the least significant figure is simply experimental error), suggesting that the reaction is zero order in CO.

Between the third and fourth experiments, the concentration of NO_2 again, doubles and the concentration of CO halves, yet the rate quadruples again, confirming that the reaction is second order in NO_2 and zero order in CO.



$[NO_2]$ (M)	[CO] (M)	Initial Rate (M/s)
0.10	0.10	0.0021
↓ × 2	↓ constant	↓ × 4
0.20	0.10	0.0082
↓ constant	↓ × 2	↓ × 1
0.20	0.20	0.0083
↓ × 2	↓ × $\frac{1}{2}$	↓ × 4
0.40	0.10	0.033

Determining the Order and Rate Constant of a Reaction

Continued

Write the overall rate expression.

$$\text{Rate} = k[NO_2]^2[CO]^0 = k[NO_2]^2$$

a. Alternative Approach

If the relationship between the changes in concentrations and the changes in initial rates is not immediately obvious, you can determine the reaction order for any reactant by substituting any two initial rates and the corresponding initial concentrations into a ratio of the rate laws to determine the order (n).

$$\frac{\text{rate } 2}{\text{rate } 1} = \frac{k[A]_2^n}{k[A]_1^n}$$

For NO_2 use the first and second concentrations and rates (because $[NO_2]$ changes here, but $[CO]$ is constant). Substitute the rates and concentrations into the expression for the ratio of the rate constants.

$$\text{For } NO_2 \qquad \frac{\text{rate } 2}{\text{rate } 1} = \frac{k[NO_2]_2^n}{k[NO_2]_1^n}$$

$$\frac{0.0082\ \cancel{M/s}}{0.0021\ \cancel{M/s}} = \frac{\cancel{k}(0.20\ \cancel{M})^n}{\cancel{k}(0.10\ \cancel{M})^n}$$

$$3.9 = \left(\frac{0.20}{0.10}\right)^n = 2^n$$

Determining the Order and Rate Constant of a Reaction

Continued

Take the log of both sides of the equation and solve for n.

$$\begin{aligned} \log 3.9 &= \log 2^n \\ &= n \log 2 \\ n &= \frac{\log\ 3.9}{\log\ 2} \\ &= 1.\underline{9}6 = 2 \end{aligned}$$

For CO, use the second and third concentrations and rates (because [CO] changes here, but $[NO_2]$ is constant).

Substitute the rates and concentrations into the expression for the ratio of the rate laws.

$$\text{For CO} \qquad \frac{\text{rate } 3}{\text{rate } 2} = \frac{k[\text{CO}]_3^n}{k[\text{CO}_2]_2^n}$$

$$\frac{0.0083\ \cancel{\text{M/s}}}{0.0082\ \cancel{\text{M/s}}} = \frac{\cancel{k}(0.20\ \cancel{\text{M}})^n}{\cancel{k}(0.10\ \cancel{\text{M}})^n}$$

$$1.01 = \left(\frac{0.20}{0.10}\right)^n = 2^n$$

Determining the Order and Rate Constant of a Reaction

Continued

Take the log of both sides of the equation and solve for *n*.

$$\begin{aligned} \log 1.01 &= \log 2^n \\ &= n \log 2 \\ n &= \frac{\log 1.01}{\log 2} \\ &= 0.01 = 0 \end{aligned}$$

Write the overall rate expression from the order of each reactant.

$$\text{Rate} = k[NO_2]^2[CO]^0 = k[NO_2]^2$$

Determining the Order and Rate Constant of a Reaction

Continued

b. To determine the rate constant for the reaction, solve the rate law for *k* and substitute the concentration and the initial rate from any one of the four measurements. In this case, we use the first measurement.

$$\text{Rate} = k[NO_2]^2$$

$$k = \frac{\text{rate}}{[NO_2]^2} = \frac{0.0021\ M/s}{(0.10\ M)^2} = 0.21\ M^{-1}\cdot s^{-1}$$

For Practice

Consider the equation:

$$CHCl_3(g) + Cl_2(g) \longrightarrow CCl_4(g) + HCl(g)$$

The initial rate of reaction is measured at several different concentrations of the reactants with the tabulated results shown here.

$[CHCl_3]$ (M)	$[Cl_2]$ (M)	Initial Rate (M/s)
0.010	0.010	0.0035
0.020	0.010	0.0069
0.020	0.020	0.0098
0.040	0.040	0.027

From the data, determine:

a. the rate law for the reaction

b. the rate constant (*k*) for the reaction

The First-Order Integrated Rate Law: Using Graphical Analysis of Reaction Data

Consider the equation for the decomposition of SO_2Cl_2:

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

The concentration of SO_2Cl_2 is monitored at a fixed temperature as a function of time during the decomposition reaction, and the following data are tabulated:

Time (s)	$[SO_2Cl_2]$ (M)	Time (s)	$[SO_2Cl_2]$ (M)
0	0.100	800	0.0793
100	0.0971	900	0.0770
200	0.0944	1000	0.0748
300	0.0917	1100	0.0727
400	0.0890	1200	0.0706
500	0.0865	1300	0.0686
600	0.0840	1400	0.0666
700	0.0816	1500	0.0647

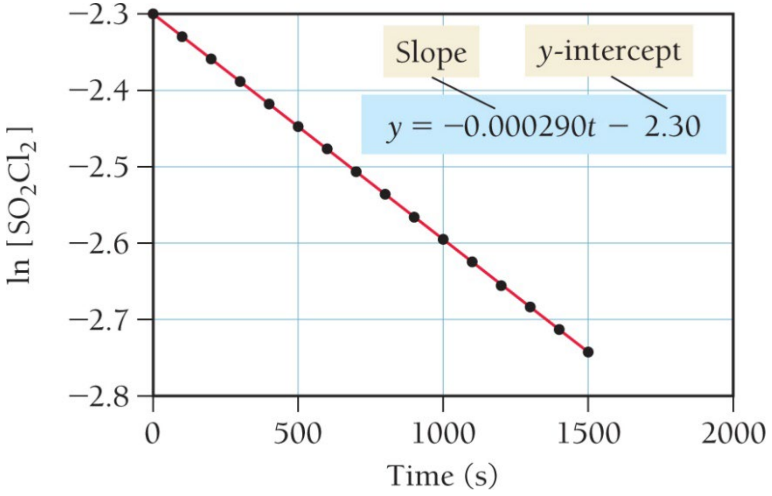
Show that the reaction is first order, and determine the rate constant for the reaction.

The First-Order Integrated Rate Law: Using Graphical Analysis of Reaction Data

Continued

Solution

In order to show that the reaction is first order, prepare a graph of the natural logarithm of $[SO_2Cl_2]$ versus time as shown:



The plot is linear, confirming that the reaction is indeed first order. To obtain the rate constant, fit the data to a line. The slope of the line is equal to –*k*. Since the slope of the best-fitting line (which is most easily determined on a graphing calculator or with spreadsheet software such as Microsoft Excel) is $-2.90 \times 10^{-4}\ s^{-1}$, the rate constant is $+2.90 \times 10^{-4}\ s^{-1}$.

For Practice

Use the graph and the best-fitting line in to predict the concentration of SO_2Cl_2 at 1900 s.

The First-Order Integrated Rate Law: Determining the Concentration of a Reactant at a Given Time

In the previous problem, you determined that the decomposition of SO_2Cl_2 (under the given reaction conditions) is first order and has a rate constant of $+2.90 \times 10^{-4}\ s^{-1}$. If the reaction is carried out at the same temperature and the initial concentration of SO_2Cl_2 is 0.0225 M, what is the SO_2Cl_2 concentration after 865 s?

Sort

You are given the rate constant of a first-order reaction and the initial concentration of the reactant and asked to find the concentration at 865 seconds.

Given: $k = +2.90 \times 10^{-4}\ s^{-1}$
$[SO_2Cl_2]_0 = 0.0225$ M
Find: $[SO_2Cl_2]$ at $t = 865$ s

Strategize

Refer to the first-order integrated rate law to determine the SO_2Cl_2 concentration at $t = 865$ s.

Equation

$$\ln [A]_t = -kt + \ln [A]_0$$

Solve

Substitute the rate constant, the initial concentration, and the time into the integrated rate law. Solve the integrated rate law for the concentration of $[SO_2Cl_2]_t$.

The First-Order Integrated Rate Law: Determining the Concentration of a Reactant at a Given Time

Continued

Solution

$$\begin{aligned}
\ln[SO_2Cl_2]_t &= -kt + \ln[SO_2Cl_2]_0 \\
\ln[SO_2Cl_2]_t &= -(2.90 \times 10^{-4}\,\cancel{s^{-1}})865\,\cancel{s} + \ln(0.0225) \\
\ln[SO_2Cl_2]_t &= -0.251 - 3.79 \\
[SO_2Cl_2]_t &= e^{-4.04} \\
&= 0.0176\ \mathrm{M}
\end{aligned}$$

Check

The concentration is smaller than the original concentration as expected. If the concentration were larger than the initial concentration, this would indicate a mistake in the signs of one of the quantities on the right-hand side of the equation.

For Practice

Cyclopropane rearranges to form propene in the gas phase.

The reaction is first order in cyclopropane and has a measured rate constant of $3.36 \times 10^{-5}\ \mathrm{s}^{-1}$ at 720 K. If the initial cyclopropane concentration is 0.0445 M, what is the cyclopropane concentration after 235.0 minutes?

The Second-Order Integrated Rate Law: Using Graphical Analysis of Reaction Data

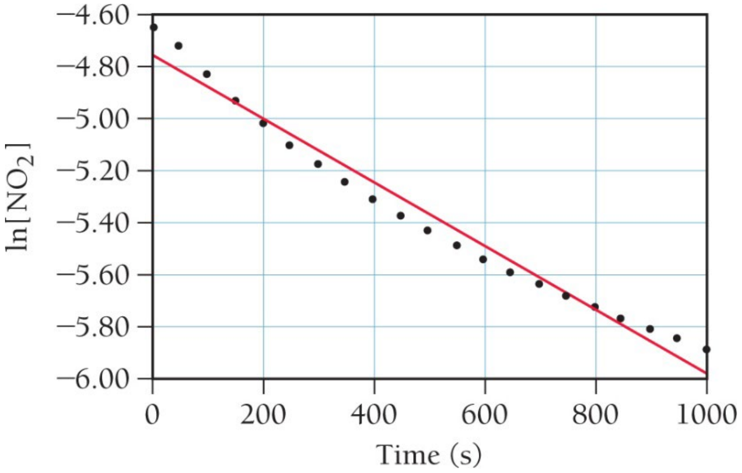
Consider the equation for the decomposition of NO_2:

$$NO_2(g) \longrightarrow NO(g) + O(g)$$

The concentration of NO_2 is monitored at a fixed temperature as a function of time during the decomposition reaction and the data tabulated in the margin at right. Show by graphical analysis that the reaction is not first order and that it is second order. Determine the rate constant for the reaction.

Solution

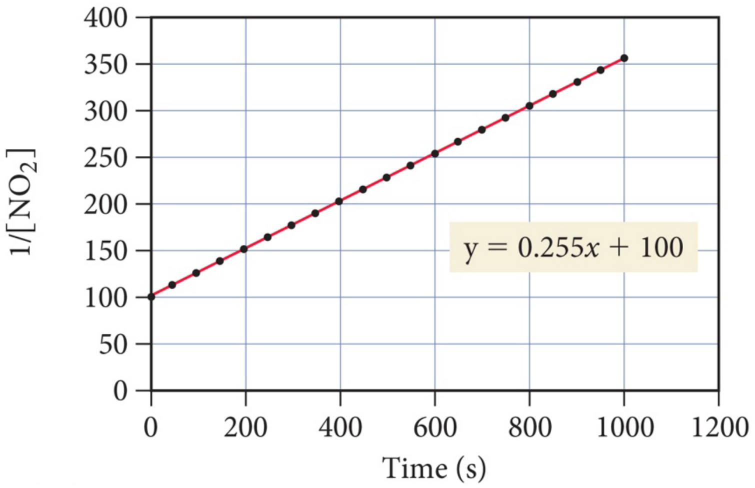
In order to show that the reaction is *not* first order, prepare a graph of $\ln[NO_2]$ versus time as shown:



The plot is *not* linear (the straight line does not fit the data points), confirming that the reaction is not first order. In order to show that the reaction is second order, prepare a graph of $1/[NO_2]$ versus time as shown:

The Second-Order Integrated Rate Law: Using Graphical Analysis of Reaction Data

Continued



This graph is linear (the data points fit well to a straight line), confirming that the reaction is indeed second order. To obtain the rate constant, determine the slope of the best-fitting line. The slope is 0.255 $MM^{-1} \bullet s^{-1}$; therefore, the rate constant is 0.255 $M^{-1} \bullet s^{-1}$.

For Practice

Use the graph and the best-fitting line above to predict the concentration of NO_2 at 2000 s.

Half-Life

Molecular iodine dissociates at 625 K with a first-order rate constant of 0.271 s^{-1}. What is the half-life of this reaction?

Solution

Because the reaction is first order, the half-life is given by below. Substitute the value of *k* into the expression and calculate $t_{1/2}$.

$$t_{1/2} = \frac{0.693}{k}$$

$$= \frac{0.693}{0.271\ \mathrm{s}^{-1}} = 2.56\ \mathrm{s}$$

For Practice

A first-order reaction has a half-life of 26.4 seconds. How long does it take for the concentration of the reactant in the reaction to fall to one-eighth of its initial value?

Using an Arrhenius Plot to Determine Kinetic Parameters

The decomposition of ozone shown here is important to many atmospheric reactions:

$$O_3(g) \longrightarrow O_2(g) + O(g)$$

A study of the kinetics of the reaction results in the following data:

Temperature (K)	Rate Constant ($M^{-1} \cdot s^{-1}$)	Temperature (K)	Rate Constant ($M^{-1} \cdot s^{-1}$)
600	3.37×10^3	1300	7.83×10^7
700	4.85×10^4	1400	1.45×10^8
800	3.58×10^5	1500	2.46×10^8
900	1.70×10^6	1600	3.93×10^8
1000	5.90×10^6	1700	5.93×10^8
1100	1.63×10^7	1800	8.55×10^8
1200	3.81×10^7	1900	1.19×10^9

Determine the value of the frequency factor and activation energy for the reaction.

Using an Arrhenius Plot to Determine Kinetic Parameters

Continued

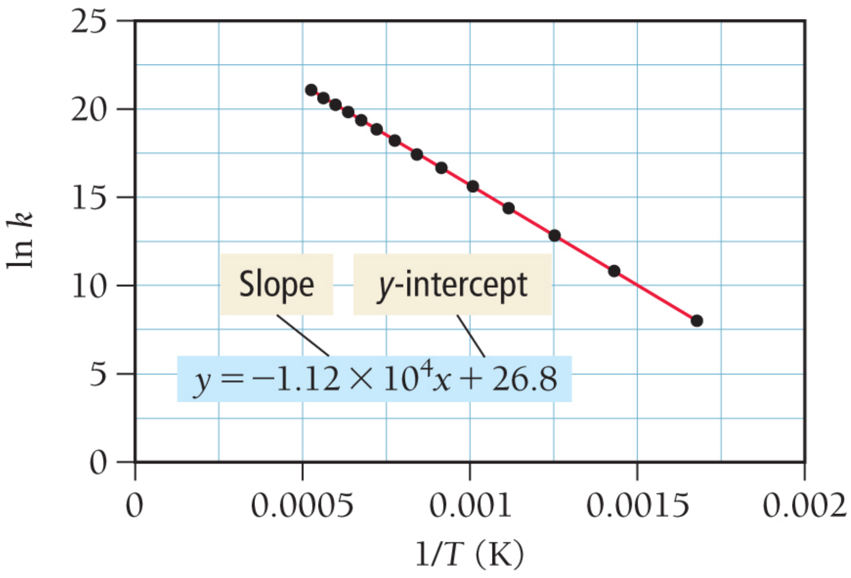
Solution

To determine the frequency factor and activation energy, prepare a graph of the natural log of the rate constant (ln k) versus the inverse of the temperature ($1/T$).

The plot is linear, as expected for Arrhenius behavior. The line that fits best has a slope of -1.12×10^4 K and a y-intercept of 26.8. Calculate the activation energy from the slope by setting the slope equal to $-E_a/R$ and solving for E_a:

$$-1.12 \times 10^4\,\text{K} = \frac{-E_a}{R}$$

$$\begin{aligned} E_a &= 1.12 \times 10^4\,\cancel{\text{K}}\left(8.314\,\frac{\text{J}}{\text{mol}\cdot\cancel{\text{K}}}\right) \\ &= 9.31 \times 10^4\,\text{J/mol} \\ &= 93.1\,\text{kJ/mol} \end{aligned}$$



The Second-Order Integrated Rate Law: Using Graphical Analysis of Reaction Data

Continued

Calculate the frequency factor (*A*) by setting the intercept equal to ln *A*.

$$26.8 = \ln A$$
$$A = e^{26.8}$$
$$= 4.36 \times 10^{11}$$

Since the rate constants are measured in units of $M^{-1} \bullet s^{-1}$, the frequency factor is in the same units. Consequently, you can conclude that the reaction has an activation energy of 93.1 kJ/mol and a frequency factor of 4.36×10^{11} $M^{-1} \bullet s^{-1}$.

For Practice

For the decomposition of ozone reaction, use the results of the Arrhenius analysis to predict the rate constant at 298 K.

Using the Two-Point Form of the Arrhenius Equation

Consider the reaction between nitrogen dioxide and carbon monoxide:

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

The rate constant at 701 K is measured as 2.57 $M^{-1} \bullet s^{-1}$ and that at 895 K is measured as 567 $M^{-1} \bullet s^{-1}$. Find the activation energy for the reaction in kJ/mol.

Sort

You are given the rate constant of a reaction at two different temperatures and asked to find the activation energy.

Given: $T_1 = 701$ K, $k_1 = 2.57\ M^{-1} \bullet s^{-1}$

$T_2 = 895$ K, $k_2 = 567\ M^{-1} \bullet s^{-1}$

Find: E_a

Strategize

Use the two-point form of the Arrhenius equation, which relates the activation energy to the given information and R (a constant).

Equation

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Solve

Substitute the two rate constants and the two temperatures into the equation.

Solve the equation for E_a, the activation energy, and convert to kJ/mol.

Using the Two-Point Form of the Arrhenius Equation

Continued

Solution

$$\ln \frac{567\,\cancel{\text{M}^{-1}\cdot\text{s}^{-1}}}{2.57\,\cancel{\text{M}^{-1}\cdot\text{s}^{-1}}} = \frac{E_\text{a}}{R}\left(\frac{1}{701\text{ K}} - \frac{1}{895\text{ K}}\right)$$

$$5.40 = \frac{E_\text{a}}{R}\left(\frac{3.\underline{0}9 \times 10^{-4}}{\text{K}}\right)$$

$$\begin{aligned}
E_\text{a} &= 5.40\left(\frac{\text{K}}{3.\underline{0}9 \times 10^{-4}}\right)R \\
&= 5.40\left(\frac{\cancel{\text{K}}}{3.\underline{0}9 \times 10^{-4}}\right)8.314\,\frac{\text{J}}{\text{mol}\cdot\cancel{\text{K}}} \\
&= 1.\underline{4}5 \times 10^{5}\text{ J/mol} \\
&= 1.5 \times 10^{2}\text{ kJ/mol}
\end{aligned}$$

Check

The magnitude of the answer is reasonable. Activation energies for most reactions range from tens to hundreds of kilojoules per mole.

For Practice

Use the results from previous and the given rate constant of the reaction at either of the two temperatures to predict the rate constant for this reaction at 525 K.

Reaction Mechanisms

Ozone naturally decomposes to oxygen by this reaction:

$$2\,O_3(g) \longrightarrow 3\,O_2(g)$$

The experimentally observed rate law for this reaction is:

$$\text{Rate} = k[O_3]^2[O_2]^{-1}$$

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

$$O_3(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2(g) + O(g) \qquad \text{Fast} \qquad O_3(g) + O(g) \xrightarrow[k_2]{} 2\,O_2(g) \qquad \text{Slow}$$

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.

$$\begin{array}{l} O_3(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2(g) + \cancel{O}(g) \\ O_3(g) + \cancel{O}(g) \xrightarrow[k_2]{} 2\,O_2(g) \\ \hline 2\,O_3(g) \longrightarrow 3\,O_2(g) \end{array}$$

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

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

Reaction Mechanisms

Continued

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.

$$\begin{aligned} \text{Rate (forward)} &= \text{Rate (backward)} \\ k_1[\mathrm{O_3}] &= k_{-1}[\mathrm{O_2}][\mathrm{O}] \\ [\mathrm{O}] &= \frac{k_1[\mathrm{O_3}]}{k_{-1}[\mathrm{O_2}]} \end{aligned}$$

Finally, substitute [O] into the rate law predicted by the slow step.

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

Reaction Mechanisms

Continued

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

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

$$\begin{array}{rcll} 2\,A & \longrightarrow & A_2 & \text{Slow} \\ A_2 + B & \longrightarrow & A_2B & \text{Fast} \end{array}$$