14.1 In any sequence of steps, the slowest one will be rate-determining. (a) Pouring the coffee from the urn into the cup; (b) Entering the items on the cash register (if the market has a good laser scanner, paying and receiving change may be rate-determining); (c) Preparing for the jump and passing through the door.

14.2 In any sequence of steps, the slowest one will be rate-determining. (a) Paying at the cash register; (b) Going through the turnstile and having tickets collected; (c) Paying the bill.

14.3 Every elementary reaction must depict actual molecular processes.
(a) $I_2 \rightarrow I + I$;
(b) $H_2 + I_2 \rightarrow H_2I_2$;
(c) $H_2 + I_2 \rightarrow H + HI_2$.

14.4 Every elementary reaction must depict actual molecular processes.
(a) $Cl_2 \rightarrow Cl + Cl$;
(b) $NO + Cl_2 \rightarrow NOCl + Cl$;
(c) $2 NO + Cl_2 \rightarrow 2 NOCl$.

14.5 A molecular picture of an elementary reaction shows the reactants, the products, and (if necessary) the intermediate collision complex.

14.6 A molecular picture of an elementary reaction shows the reactants, the products, and (if necessary) the intermediate collision complex.
14.7 A satisfactory mechanism must consist entirely of reasonable elementary steps that sum to give the correct overall stoichiometry of the reaction.
(a) \( I_2 \rightarrow I + I \)
\( I + H_2 \rightarrow HI + H \)
\( H + I \rightarrow HI \)

(b) \( H_2 + I_2 \rightarrow H_2I_2 \)
\( H_2I_2 \rightarrow HI + HI \)

(c) \( H_2 + I_2 \rightarrow H + HI_2 \)
\( H + HI_2 \rightarrow HI + HI \)

14.8 A satisfactory mechanism must consist entirely of reasonable elementary steps that sum to give the correct overall stoichiometry of the reaction.
(a) \( Cl_2 \rightarrow Cl + Cl \)
\( NO + Cl \rightarrow NOCl \)
\( NO + Cl \rightarrow NOCl \)

(b) \( NO + Cl_2 \rightarrow NOCl + Cl \)
\( NO + Cl \rightarrow NOCl \)

(c) \( 2 NO + Cl_2 \rightarrow 2 NOCl. \)

14.9 The rate of a reaction can be expressed using the general expression, \( \text{Rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} \). 
(a) \( \text{Rate} = - \frac{\Delta[Cl_2]}{\Delta t} \)

(b) \( -\frac{\Delta[Cl_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[NOCl]}{\Delta t} \)

(c) Use the result of (b) to calculate that NOCl appears at a rate of 94 M s\(^{-1}\)

14.10 The rate of a reaction can be expressed using the general expression, \( \text{Rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} \). 
The reaction is \( 2 O_3 \rightarrow 3 O_2. \)
(a) \( \text{Rate} = \frac{1}{3} \frac{\Delta[O_2]}{\Delta t} \)

(b) \( \frac{1}{3} \frac{\Delta[O_2]}{\Delta t} = -\frac{1}{2} \frac{\Delta[O_3]}{\Delta t} \)

(c) Use the result of (b) to calculate that ozone disappears at a rate of \( 1.8 \times 10^{-6} \) M s\(^{-1}\).
14.11 In the reaction of NO and Cl\(_2\), two NO molecules react for every Cl\(_2\) that reacts, producing two NOCl molecules.

14.12 In the reaction of NO and O\(_3\), one NO molecule reacts for every O\(_3\) that reacts, producing one O\(_2\) and one NO\(_2\) molecule.
14.13 (a) To calculate the average rate of production, determine how many moles form during the time interval and divide by the time:

\[
\frac{PV}{RT} = \frac{273.15 + 550 \times 0.08206 \times 5.0}{1.11 \times 10^{-2}} = 1.11 \times 10^{-2} \text{ mol;}
\]

\[
\frac{\Delta [\text{CO}_2]}{\Delta t} = \frac{1.11 \times 10^{-2} \text{ mol}}{5.0 \text{ min}} = 2.2 \times 10^{-3} \text{ mol/min}
\]

(b) The reaction is \( \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \), so the amount of \( \text{CaCO}_3 \) decomposing is the same as the amount of \( \text{CO}_2 \) produced, \( 1.1 \times 10^{-2} \text{ mol} \).

14.14 (a) To calculate the average rate of reaction, determine how many moles are consumed during the time interval and divide by the time:

\[
\Delta n = (0.25 \text{ mol/L}) - (0.50 \text{ mol/L}) = -0.25 \text{ mol/L};
\]

\[
\text{Rate} = -\frac{1}{3} \frac{\Delta [H_2]}{\Delta t} = -\frac{1}{3} \left( \frac{-0.25 \text{ M}}{30 \text{ s}} \right) = 2.77 \times 10^{-3} \text{ M/s};
\]

Round to two significant figures: \( \text{Rate} = 2.8 \times 10^{-3} \text{ M/s} \)

(b) The rate for any particular reagent is the coefficient for that reagent times the rate of reaction: \( \text{Rate}(\text{NH}_3) = 2(2.8 \times 10^{-3} \text{ M/s}) = 5.6 \times 10^{-3} \text{ M/s} \)

(c) The concentration of any particular reagent is its initial concentration minus the change during the time interval:

\[
\text{Change} = (\text{Coeff})(\text{Rate})(\text{time}) = -1(2.8 \times 10^{-3} \text{ M/s})(30 \text{ s}) = -8.4 \times 10^{-2} \text{ M}
\]

\[
\text{Concentration} = (1.25 \text{ M}) - (0.084 \text{ M}) = 1.17 \text{ M}
\]

14.15 (a) Before the reaction begins

(b) After 20 minutes, the amount reacted is \( (20 \text{ min})(0.25 \text{ molecules/min}) = 5 \text{ molecules} \)

14.16 (a) Before the reaction begins
(b) After 2.0 s, the amount reacted is \( (2.0 \text{ s})(1.5 \text{ molecules/min}) = 3 \text{ molecules} \)

14.17 (a) The number of decays is independent of the starting amount of the isotope in first-order kinetics, therefore there would be 60 decays in the 5.00 mol case.
(b) The fraction decaying is the same in both cases: 12 isotopes decay per 1 mole, or 12 decays/mol = 12 decays/6.022 \( \times 10^{23} \) nuclei.
(c) In first-order kinetics the fraction reacting is independent of concentrations.

14.18 Rates of elementary "unimolecular" reactions depend on how many reacting items are present. When an amount changes by some factor, the rate changes by the same factor.
(a) After 50 kernels have popped, 100 remain, so the number popping is \( 6(100/150) = 4 \).
(b) The fraction of kernels popping per second is \( \frac{6}{(150)(5 \text{ s})} = 8 \times 10^{-3} / \text{s} \) initially, and it is \( \frac{4}{(100)(5 \text{ s})} = 8 \times 10^{-3} / \text{s} \) after 50 have popped. The fraction remains constant.
(c) After 50 kernels have popped, there are fewer unpopped kernels remaining in the popcorn popper, so the overall rate of popping is lower even though the fraction popping is a constant.

14.19 (a) The rate law for an elementary step contains the product of the reactant concentrations: Rate = \( k[C][AB] \);
(b) The units of a rate constant have time in the denominator along with concentrations one power less than the number of reactants: units = \( \text{(conc.)}^{-1} \text{ (time)}^{-1} \);
(c) The steps of the mechanism must sum to give the observed stoichiometry for the reaction. Intermediate A can react with AB, then B and C can react:
\[
\begin{align*}
\text{C + AB} & \rightarrow \text{BC + A} \\
\text{A + AB} & \rightarrow \text{B + A}_2 \\
\text{B + C} & \rightarrow \text{BC} \\
\text{Net: 2 C + 2 AB} & \rightarrow \text{2 BC + A}_2
\end{align*}
\]

14.20 (a) The rate law for an elementary step contains the product of the reactant concentrations: Rate = \( k[AB][AB] = k[AB]^2 \);
(b) The units of a rate constant have time in the denominator along with concentrations one power less than the number of reactants: units = \( \text{(conc.)}^{-1} \text{ (time)}^{-1} \);
(c) The steps of the mechanism must sum to give the observed stoichiometry for the reaction. A bimolecular reaction between the intermediate (B) and C is the simplest possibility:
2 AB → A_2 + 2 B
B + C → BC. This reaction occurs twice for each time the first step occurs.
Net: 2 C + 2 AB → 2 BC + A_2

14.21 (a) The rate law for an elementary step contains the product of the reactant concentrations:
Rate = k[C][C][AB] = k[C]^2[AB];
(b) The units of a rate constant have time in the denominator along with concentrations one power less than the number of reactants: units = (conc.)^{-2} (time)^{-1};
(c) The steps of the mechanism must sum to give the observed stoichiometry for the reaction. A bimolecular reaction between the intermediate (AC) and AB is the simplest possibility:
2 C + AB → BC + AC
AC + AB → BC + A_2
Net: 2 C + 2 AB → 2 BC + A_2

14.22 (a) The rate law for an elementary step contains the product of the reactant concentrations:
Rate = k[AB];
(b) The units of a rate constant have time in the denominator along with concentrations one power less than the number of reactants: units = (time)^{-1};
(c) The steps of the mechanism must sum to give the observed stoichiometry for the reaction. Intermediate A can react with AB, then B and C can react:
AB → A + B
A + AB → B + A_2
B + C → BC. This reaction occurs twice for each time the first step occurs.
Net: 2 C + 2 AB → 2 BC + A_2

14.23 According to the stated rate law, the rate of reaction is proportional to each concentration. A contains 6 molecules of each type, while B contains 10 NO and 2 O_3:
A: Rate = k(6)(6) = 36 k;
B: Rate = k(10)(2) = 20 k;
B will react slower by a factor of 20/36 = 0.56.

14.24 According to the stated rate law, the rate of reaction is proportional to each concentration. A contains 6 molecules of each type, while B contains 3 NO_2 and 12 O_2:
A: Rate = k(6)(6) = 36 k;
B: Rate = k(3)(12) = 36 k;
B will react at the same rate as A.

14.25 (a) One way to treat experimental data is by plotting: For first-order behavior, ln \( \frac{c_o}{c} \) vs. \( t \) is a straight line, and for second-order behavior, \( \frac{1}{c} - \frac{1}{c_o} \) vs. \( t \) is a straight line. Here, the plot of ln \( c \) vs. \( t \) gives a straight line, so this reaction is first-order.
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(b) For a first-order reaction, $k = \text{slope of the graph}$

$$ k = \text{slope} = \frac{\Delta y}{\Delta x} = \frac{0.491 - 0}{800 \text{ s} - 0 \text{ s}} = 6.14 \times 10^{-4} \text{ s}^{-1} $$

(c) To find concentration at any particular time, use $\ln[A] = \ln[A]_0 - kt$

$$ \ln[A] = \ln[2.50] - (6.14 \times 10^{-4} \text{ s}^{-1})(1600 \text{ s}) = -0.0661 $$

$$ [A] = e^{0.0661} = 0.936 \text{ atm} $$

(d) To find the time at which concentration reaches a particular value, use

$$ kt = \ln\left(\frac{[A]_0}{[A]}\right) $$

$$ t = \frac{\ln\left(\frac{2.50 \text{ atm}}{0.500 \text{ atm}}\right)}{6.14 \times 10^{-4} \text{ s}^{-1}} = 2.62 \times 10^3 \text{ s} $$

14.26 (a) One way to treat experimental data is by plotting: For first-order behavior, $\ln c$ vs. $t$ is a straight line, and for second-order behavior, $1/c$ vs. $t$ is a straight line. Here, however, there is a quicker way, because the data show half-lives (the time required for the concentration to fall by a factor of two). It takes 8.0 days for mass to fall from 12.0 $\mu$g to 6.0 $\mu$g and 8.0 days for the mass to fall from 6.0 to 3.0 $\mu$g. Thus, the half-life is independent of concentration, a characteristic of first-order reactions.

(b) The half-life of a first-order reaction provides a convenient way to calculate a rate constant. Use Equation 14-4: $t_{1/2} = \frac{\ln 2}{k}$, rearranged to give $k = \frac{\ln 2}{t_{1/2}}$;

$$ k = \frac{0.693}{8.0 \text{ days}} = 8.7 \times 10^{-2} \text{ days}^{-1} $$

(c) To find concentration at any particular time, use $\ln[A] = \ln[A]_0 - kt$

$$ \ln[A] = \ln[12.0] - (8.7 \times 10^{-2} \text{ days}^{-1})(32 \text{ days}) = -0.299 $$
[A] = e^{-0.299} = 0.74 \mu g (a simple half-life analysis can also be used to give 0.75 \mu g)

(d) To find the time at which concentration reaches a particular value, use

$$kt = \ln \left( \frac{[A]_o}{[A]} \right)$$

$$t = \frac{\ln \left( \frac{[A]_o}{[A]} \right)}{k} = \frac{\ln \left( \frac{12.0 \mu g}{1.2 \mu g} \right)}{8.7 \times 10^{-2} \text{ days}^{-1}} = 27 \text{ days}.$$

14.27 This is stated to be a second-order reaction, so Rate = $k[\text{NOBr}]^2$ and Equation 14-5 applies:

$$\frac{1}{[A]} - \frac{1}{[A]_o} = kt ;$$

The problem states that $k = 25 \text{ M}^{-1} \text{ min}^{-1}$.

(a) $kt = \frac{1}{0.010 \text{ M}} - \frac{1}{0.025 \text{ M}} = (100 - 40) \text{ M}^{-1} = 60 \text{ M}^{-1};$

$$t = \frac{60 \text{ M}^{-1}}{25 \text{ M}^{-1} \text{ min}^{-1}} = 2.4 \text{ min};$$

(b) $\frac{1}{[A]} = \frac{1}{0.025 \text{ M}} + (25 \text{ M}^{-1} \text{ min}^{-1})(125 \text{ min}) = (40 + 3125) \text{ M}^{-1} = 3165 \text{ M}^{-1}$

$$[A] = 3.2 \times 10^{-4} \text{ M}.$$

14.28 (a) This is stated to be a second-order reaction, so Rate = $k[C_4H_6]^2$ and Equation 14-5 applies:

$$\frac{1}{[A]} - \frac{1}{[A]_o} = kt ;$$

The problem states that $k = 0.93 \text{ M}^{-1} \text{ min}^{-1}$.

(a) $kt = \frac{1}{0.100 \text{ M}} - \frac{1}{0.240 \text{ M}} = (10.0 - 4.17) \text{ M}^{-1} = 5.83 \text{ M}^{-1};$

$$t = \frac{5.83 \text{ M}^{-1}}{0.93 \text{ M}^{-1} \text{ min}^{-1}} = 6.3 \text{ min};$$

(b) $\frac{1}{[A]} = \frac{1}{0.240 \text{ M}} + (0.93 \text{ M}^{-1} \text{ min}^{-1})(25 \text{ min}) = (4.17 + 23.25) \text{ M}^{-1}$

$$[A] = 3.6 \times 10^{-2} \text{ M}.$$

14.29 This is stated to be a first-order reaction, so Rate = $k[C_5H_{11}Br]$ and Equation 14.3 applies:

$$kt = \ln \left( \frac{[A]_o}{[A]} \right)$$
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(a) \( k_t = \ln \left( \frac{0.125}{1.25 \times 10^{-3}} \right) = 4.61 \)

\[ t = \frac{4.61}{0.385 \text{ hr}^{-1}} = 12.0 \text{ hr} \]

(b) \( \ln[A] = \ln[0.125] - 3.5 \text{ hr}(0.385 \text{ hr}^{-1}) = -2.08 - 1.35 = -3.43 \)

\[ [A] = e^{-3.43} = 0.0324 \text{ M or } 3.24 \times 10^{-2} \text{ M} \]

14.30 This is stated to be a first-order reaction, so Rate = \( k[Hg^*] \) and Equation 14-3 applies:

\( kt = \ln \left( \frac{[A]_o}{[A]} \right) \); The problem states that \( k = 1.65 \times 10^6 \text{ s}^{-1} \).

(a) \( kt = \ln \left( \frac{4.5 \times 10^{-6}}{4.5 \times 10^{-7}} \right) = 2.303; \)

\[ t = \frac{2.303}{1.65 \times 10^6 \text{ s}^{-1}} = 1.4 \times 10^{-6} \text{ s}; \]

(b) \( \ln[A] = \ln(4.5 \times 10^{-6}) - (1.65 \times 10^6 \text{ s}^{-1})(2.5 \times 10^{-6} \text{ s}) \)

\[ \ln[A] = (-12.311) - (4.125) = -16.436; \]

\[ [A] = e^{-16.436} = 7.3 \times 10^{-8} \text{ M}. \]

14.31 To determine the order of a reaction from a set of experimental data, prepare plots of

\( \ln \frac{c_o}{c} \text{ vs. } t \) and \( \frac{1}{c} - \frac{1}{c_o} \text{ vs. } t: \)

1st order plot

2nd order plot

The first-order plot is linear, while the second-order plot is not. This reaction is first-order. Determine the rate constant from

\[ k = \text{Slope} = \frac{\Delta y}{\Delta x} = \frac{0.766 - 0}{300 \text{ s} - 0 \text{ s}} = 2.55 \times 10^{-3} \text{ s}^{-1}. \]
14.32 To determine the order of a reaction from a set of experimental data, prepare plots of
\[ \ln \frac{c}{c_0} \text{ vs. } t \] and \[ \frac{1}{c} - \frac{1}{c_0} \text{ vs. } t: \]
1st order plot

The first-order plot is linear, while the second-order plot is not. This reaction is first-order.
Determine the rate constant from
\[ k = \text{Slope} = \frac{\Delta y}{\Delta x} = \frac{0.491 - 0}{800 \text{ s} - 0 \text{ s}} = 6.14 \times 10^{-4} \text{ s}^{-1}. \]

14.33 The rate law should relate the rate of reaction to the concentration of the reactants.
Reactive intermediates should not be shown in the rate law.
2C + AB \rightarrow BC + AC, followed by
AC + AB \rightarrow BC + A_2 \text{ (slow)}
Net: 2 C + 2 AB \rightarrow 2 BC + A_2
The rate law is determined by the rate-determining step: Rate = \( k_2[AC][AB] \). This is not satisfactory, however, because it contains the concentration of an intermediate (AC). Set the rates equal for the forward and reverse first step:
\[ k_1[C]^2[AB] = k_{-1}[BC][AC]; \]
Solve this equality for [AC]:
\[ [AC] = \frac{\left( \frac{k_1}{k_{-1}} \right) [C]^2[AB]}{[BC]}; \]
Substitute into the rate expression:
\[ \text{Rate} = k_2 \left( \frac{k_1}{k_{-1}} \right) \frac{[C]^2[AB]^2}{[BC]}; \]

14.34 The rate law should relate the rate of reaction to the concentration of the reactants.
Reactive intermediates should not be shown in the rate law.
(a) Cl_2 \rightarrow Cl + Cl, followed by
NO + Cl \rightarrow NOCl
The rate law is determined by the rate-determining step: Rate = \( k_2[NO][Cl] \). This is not satisfactory, however, because it contains the concentration of an intermediate. Set the rates equal for the forward and reverse first step:
\[ k_1[Cl_2] = k_{-1}[Cl]^2; \]
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Solve this equality for \( [Cl] \): 
\[
[Cl] = \left( \frac{k_1}{k_-} \right)^{1/2} [Cl_2]^{1/2};
\]

Substitute into the rate expression: 
\[
Rate = k_2 \left( \frac{k_1}{k_-} \right)^{1/2} [NO][Cl_2]^{1/2}
\]

(b) \( NO + Cl_2 \leftrightarrow NOCl + Cl \), followed by \( NO + Cl \rightarrow NOCl \)

The rate law is determined by the rate-determining step: 
\[
Rate = k_2[NO][Cl].
\]

This is not satisfactory, however, because it contains the concentration of an intermediate. Set the rates equal for the forward and reverse first step:
\[
k_1[NO][Cl_2] = k_-1[NOCl][Cl];
\]

Solve this equality for \( [Cl] \): 
\[
[Cl] = \left( \frac{k_1}{k_-1} \right) \frac{[NO] [Cl_2]}{[NOCl]};
\]

Substitute into the rate expression: 
\[
Rate = k_2 \left( \frac{k_1}{k_-1} \right) \frac{[NO]^2 [Cl_2]}{[NOCl]}
\]

14.35 (a) The steps of a mechanism must sum to give the observed overall stoichiometry of the reaction. For ozone decomposition, this is \( 2 O_3 \rightarrow 3 O_2 \). The two steps proposed by the student consume \( 1 O_3 \), produce \( 1 O_2 \), and generate an O atom which must be consumed:
\[
O_3 + O \rightarrow 2 O_2
\]

(b) The rate law is determined by the rate-determining step: 
\[
Rate = k_2[O_5].
\]

This is not satisfactory, however, because it contains the concentration of an intermediate. Set the rates equal for the forward and reverse first step:
\[
k_1[O_3][O_2] = k_-1[O_5];
\]

Solve this equality for \( [O_5] \): 
\[
[O_5] = \frac{k_1}{k_-1} [O_3][O_2];
\]

Substitute into the rate expression:
\[
Rate = k_2 \frac{k_1}{k_-1} [O_3][O_2]
\]

(c) Atmospheric chemists would consider this mechanism to be molecularly unreasonable because fragmentation of \( O_5 \) in the second step (the breaking of two bonds simultaneously) is highly unlikely.

14.36 (a) The steps of a mechanism must sum to give the observed overall stoichiometry of the reaction. For phosgene formation, this is \( CO + Cl_2 \rightarrow COCl_2 \). The first step of the mechanism proceeds rapidly in both directions, leading to no net change. In the second and third steps, Cl is consumed and then produced, for no net change; and COCl is produced and consumed, for no net change:
(b) The rate law is determined by the rate-determining step: Rate = $k_2[\text{CO}][\text{Cl}]$. This is not satisfactory, however, because it contains the concentration of an intermediate. Set the rates equal for the forward and reverse first step: $k_1[\text{Cl}_2] = k_{-1}[\text{Cl}]^2$;

Solve this equality for [Cl]: $[\text{Cl}] = \left( \frac{k_1}{k_{-1}} \right)^{1/2} [\text{Cl}_2]^{1/2}$;

Substitute into the rate expression: Rate = $k_2 \left( \frac{k_1}{k_{-1}} \right)^{1/2} [\text{CO}][\text{Cl}_2]^{1/2}$

(c) Reactive intermediates are those species that are produced and consumed in the mechanism but do not appear in the overall stoichiometry of the reaction: Cl and COCl.

14.37 (a) The rate law is determined by the rate-determining step: Rate = $k_2[\text{N}_2\text{O}_2][\text{O}_2]$. This is not satisfactory, however, because it contains the concentration of an intermediate. Set the rates equal for the forward and reverse first step: $k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2]$;

Solve this equality for [\text{N}_2\text{O}_2]: [\text{N}_2\text{O}_2] = \left( \frac{k_1}{k_{-1}} \right)[\text{NO}]^2$;

Substitute into the rate expression:

Rate = $k_2 \left( \frac{k_1}{k_{-1}} \right)[\text{NO}]^2[\text{O}_2]$

(b) This rate expression has an overall order of $(2 + 1) = 3$, so the mechanism is consistent with third-order behavior.
(c) The intermediate species is $\text{N}_2\text{O}_2$. Two NO molecules could bind together in several ways:

In the second step, $\text{O}_2$ collides with the intermediate and reacts to form two NO$_2$ molecules. The ONNO arrangement is the only one for which this rearrangement of bonds can easily occur:
14.38 (a) Steps 2 and 3 of the mechanism consume one NO\textsubscript{3} each, so step 1 occurs twice to produce two molecules of this intermediate. Now the intermediates, NO\textsubscript{3} and NO, both cancel:

\[
\begin{align*}
2 \text{N}_2\text{O}_5 & \rightleftharpoons 2 \text{NO}_2 + 2 \text{NO}_3 \\
\text{NO}_2 + \text{NO}_3 & \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2 \\
\text{NO} + \text{NO}_3 & \rightarrow 2 \text{NO}_2 \\
\text{Net: } 2 \text{N}_2\text{O}_5 & \rightarrow 4 \text{NO}_2 + \text{O}_2
\end{align*}
\]

(b) The rate law is determined by the rate-determining step: \( \text{Rate} = k_2[\text{NO}_2][\text{NO}_3] \). This is not satisfactory, however, because it contains the concentration of an intermediate. Set the rates equal for the forward and reverse first step:

\[
k_1[\text{N}_2\text{O}_5] = k_{-1}[\text{NO}_2][\text{NO}_3];
\]

Solve this equality for \([\text{NO}_3]: [\text{NO}_3] = \left( \frac{k_1}{k_{-1}} \right) \frac{[\text{N}_2\text{O}_5]}{[\text{NO}_2]} \);

Substitute into the rate expression: \( \text{Rate} = k_2 \left( \frac{k_1}{k_{-1}} \right) [\text{N}_2\text{O}_5] \)

(c) The mechanism with step 2 as the rate-determining step predicts first-order behavior with respect to \( \text{N}_2\text{O}_5 \). If the first step is rate-determining, the rate law is \( \text{Rate} = k_1[\text{N}_2\text{O}_5] \). Thus, although it is consistent with the mechanism, the information does not prove that step 2 is rate-determining.

14.39 The rate constant for a reaction depends on temperature according to the Arrhenius equation (Equation 14-6): \( k = Ae^{-E_a/RT} \). When \( E_a = 0 \), the exponent is \( e^0 = 1 \) and \( k \) is independent of temperature. A zero activation energy exists when a reaction can occur without first breaking any chemical bonds. The most common example is the combination of two free radicals, such as \( \text{H}_3\text{C}^\bullet + \bullet\text{CH}_3 \rightarrow \text{H}_3\text{C}^\text{CH}_3 \).

14.40 When \( E_a = 0 \), there is no energy "hump" to overcome before products form, so the activation energy for the reverse reaction is the negative of the energy change for the forward reaction:

14.41 An exothermic reaction has products lower in energy than reactants. In the activated complex A will be bonded to both B and C:
14.42 An endothermic reaction is "uphill" from reactants to products. In the activated complex, A will be bonded to both B and C:

\[ \text{Activated complex:} \]

\[ \begin{align*}
E_a & \quad \text{E} \\
\Delta E_{\text{reaction}} & \quad \text{CAB} \\
E_{\text{reactants}} & \quad \text{AC} + \text{B} \\
E_{\text{products}} & \quad \text{AB} + \text{C}
\end{align*} \]

14.43 An exothermic reaction is "downhill" from reactants to products, and the activation energy plot should show this:

\[ \text{Reaction coordinate} \]

14.44 The activation energy for the forward reaction can be found from the exothermicity of the reaction and the activation energy for the reverse reaction:

\[ E_{a, \text{forward}} = 70 - 57 = 13 \text{ kJ/mol} \]
14.45 Assume that the ratio of the rate constants is proportional to the ratio of the number of flashes, then use the equation:

\[ E_a = R \ln \left( \frac{k_2}{k_1} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \right)^{-1} = (8.314 \text{ J/molK}) \ln \left( \frac{2.7}{3.3} \right) \left( \frac{1}{(29 + 273)K} - \frac{1}{(23 + 273)K} \right) \]

\[ E_a = \left( \frac{-1.67 \text{ J mol}^{-1} \text{ K}^{-1}}{\ln \left( \frac{10^{-3} \text{ kJ}}{1 \text{ J}} \right) = 25 \text{ kJ/mol} \right) \]

14.46 Activation energies are calculated from the Arrhenius equation using Equation 14-8:

\[ E_a = R \ln \left( \frac{k_2}{k_1} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \right)^{-1}. \]

\[ k_1 = 1.9 \times 10^2/\text{min}, \]
\[ T_1 = 28 + 273 = 301 \text{ K}; \]
\[ k_2 = 39.6/\text{min}, \]
\[ T_2 = 5 + 273 = 278 \text{ K}; \]
\[ \left( \frac{1}{T_1} - \frac{1}{T_2} \right)^{-1} = (3.322 \times 10^{-3} - 3.597 \times 10^{-3})^{-1} = -3636 \text{ K}; \]
\[ \frac{k_2}{k_1} = \frac{39.6 \text{ min}^{-1}}{1.9 \times 10^2 \text{ min}^{-1}} = 0.208; \]
\[ \ln \left( \frac{k_2}{k_1} \right) = -1.568 \]
\[ E_a = \left( \frac{8.314 \text{ J}}{1 \text{ molK}} \right) \left( \frac{10^{-3} \text{ kJ}}{1 \text{ J}} \right) \left( -1.568 \right) \left( -3636 \text{ K} \right) = 47 \text{ kJ/mol.} \]

14.47 A catalyst, such as Pd metal from problem 14.49, would cause hydrogen gas to adsorb on the catalyst’s surface as H atoms which will then react with the CO molecules much more easily (and quickly) than having the CO molecules break apart an H\(_2\) molecule to get the hydrogens it needs. Bonds that must be broken for this reaction to occur (depicted by the squiggly lines) are two H-H single bonds and both the \(\pi\) bonds in the CO molecule. Bonds that are formed (dashed lines) are three C-H bonds and one O-H bond.
14.48 The C-O bond in methanol and one of the π bonds in CO need to be broken. The bonds to be formed are a C-C bond and a C-O bond. A catalyst would make it easier for this reaction to occur by helping break the C-O bonds.

14.49 (a) The effect of a catalyst on a reaction is to reduce the activation energy, it has nothing to do with the energy of the reactants or the products. In an activation energy diagram the starting (energy of reactants) and ending (energy of the products) lines will be the same for both curves. Only the “bump” in the activation energy diagram will change, being smaller when Pd (the catalyst) is used than when Pd is not used.
(b) A catalyst is anything that will speed up the rate of a reaction and is also never used up (it’s a reactant as well as a product). The only thing that fits these criteria is the Pd metal. An intermediate is anything that is produced in one step of the mechanism and then used up in another step. The intermediates for this reaction are the H atoms that are formed when the H$_2$ gas is absorbed onto the Pd metal surface and then added to the ethylene (hence, the valley present between the 2 peaks).

(c) 

![Diagram showing reaction mechanisms](image)

H$_2$ adding to Pd metal and dissociating  
C taking one H  
2nd C taking other H  
Ethane molecule

14.50 (a) The overall reaction, addition of O atoms to O$_3$, is exothermic. The first step is slow, indicating a high activation energy barrier; the second is fast, indicating a low barrier:

![Reaction coordinate diagram](image)

(b) NO is present at the beginning and end, so it is a catalyst; NO$_2$ is produced and then consumed, so it is an intermediate.
(c) Because the Cl-catalyzed reaction has a very low activation energy barrier, this reaction can proceed effectively even at the low temperature of the upper stratosphere, so Cl is a more serious threat than NO.

14.51 When the concentration of a reactant increases by a factor of three (triples), the rate of reaction changes by $3^n$, where $n$ is the order with respect to that concentration.

(a) nine-fold increase; (b) no change; (c) rate increases by 5.2 times.
14.52 When the concentration of a reactant increases by a factor of two (doubles), the rate of reaction changes by \(2^n\), where \(n\) is the order with respect to that concentration.
(a) rate doubles; (b) rate increases by 1.4 times; (c) rate is cut in half.

14.53 (a) The second step must use up the extra product, O, to form one of the reactants. Therefore one possible step would be, \(O + O \rightarrow O_2\).

(b) \[\text{The first step occurs twice for a net reaction of } 2\text{NO} + O_2 \rightarrow 2\text{NO}_2\]

14.54 (a) Before determining the steps in a mechanism, it is necessary to know the balanced overall reaction: \(O_2 + 2\text{CO} \rightarrow 2\text{CO}_2\)
The first step consumes one molecule each of \(O_2\) and \(\text{CO}\) and produces one molecule of product and an O atom. The easiest way to complete the mechanism is by combining the O atom with another \(\text{CO}\) molecule: \(\text{CO} + O \rightarrow \text{CO}_2\).
(b) A molecular picture of a reaction shows reactants, reactive intermediate, and products:

14.55 (a) A rate expression relates rate to \(\Delta c\): \[\text{Rate} = \frac{\Delta [\text{C}_6\text{H}_6]}{\Delta t} = -\frac{1}{3} \left(\frac{\Delta [\text{C}_2\text{H}_2]}{\Delta t}\right)\]
(b) Rate laws must always be determined experimentally. Thus, there is insufficient information to write the rate law. Experiments would have to be carried out measuring the rate as a function of [\(\text{C}_2\text{H}_2\)] and the data analyzed using techniques described in your textbook.

14.56 Rates of reaction of various reagents are related to one another through the stoichiometric coefficients of the net chemical equation.
\[
\begin{align*}
\text{Rate (NH}_3\text{)} &= \left(-\frac{4}{4}\right) \text{Rate (NO)} = -1.5 \times 10^{-3} \text{ M s}^{-1}; \\
\text{Rate (O}_2\text{)} &= \left(-\frac{5}{4}\right) \text{Rate (NO)} = \left(-\frac{5}{4}\right) (1.5 \times 10^{-3} \text{ M s}^{-1}) = -1.9 \times 10^{-3} \text{ M s}^{-1}; \\
\text{Rate (H}_2\text{O)} &= \left(\frac{6}{4}\right) \text{Rate (NO)} = \left(\frac{6}{4}\right) (1.5 \times 10^{-3} \text{ M s}^{-1}) = 2.3 \times 10^{-3} \text{ M s}^{-1}.
\end{align*}
\]
14.57 The essential units of information needed to construct an activation energy diagram are the energy change and activation energy. Here, the reaction is a formation reaction and the change in moles of gas is zero during the reaction, so $\Delta E = \Delta H_f^o$:

![Energy Diagram 1](image1)

14.58 The essential units of information needed to construct an activation energy diagram are the energy change and activation energy. Two curves must be shown, one for the uncatalyzed and one for the catalyzed reaction:

![Energy Diagram 2](image2)

14.59 The mechanism has the rate law, $\text{Rate} = k[X_2]$, first-order in $X_2$ and independent of $Y$. $A$ contains 5 $X_2$ and 8 $Y$, while $B$ contains 10 $X_2$ and 8 $Y$. The rate for $B$ will be twice that for $A$, because the concentration of $X_2$ is twice as great.

14.60 The mechanism has the rate law, $\text{Rate} = k[X_2]$, first-order in $X_2$ and independent of $Y$. $A$ contains 5 $X_2$ and 8 $Y$, while $B$ contains 5 $X_2$ and 16 $Y$. The rate for $B$ will be the same as that for $A$, because the concentration of $X_2$ is unchanged.

14.61 Reaction times for first-order reactions can be calculated using Equation 14-3, suitably rearranged: $t = \frac{\ln \left( \frac{[A]_o}{[A]} \right)}{k}$:

for 10.0%. $[A] = 0.900[A]_o$ and $\ln \left( \frac{[A]_o}{[A]} \right) = \ln \left( \frac{1.000}{0.900} \right) = 0.105$;
\[ t = \frac{0.105}{5.5 \times 10^{-4} \text{ s}^{-1}} = 1.9 \times 10^2 \text{ s}; \]

for 50.0\%, \([A] = 0.500[A]_0\) and \(\ln \left( \frac{[A]_0}{[A]} \right) = \ln \left( \frac{1.000}{0.500} \right) = 0.693;\)

\[ t = \frac{0.693}{5.5 \times 10^{-4} \text{ s}^{-1}} = 1.3 \times 10^3 \text{ s}; \]

for 99.9\%, \([A] = 0.001[A]_0\) and \(\ln \left( \frac{[A]_0}{[A]} \right) = \ln \left( \frac{1.000}{0.001} \right) = 6.91; \)

\[ t = \frac{6.91}{5.5 \times 10^{-4} \text{ s}^{-1}} = 1.3 \times 10^4 \text{ s}. \]

14.62 The reaction is first-order in each reactant, but the initial concentrations are such that \(\text{H}_2\text{S}\) is isolated, so the kinetics are described by \(\text{Rate} = k_{\text{obs}}[\text{H}_2\text{S}], \) with \(k_{\text{obs}} = k[\text{Cl}_2]_0.\)

\(k_{\text{obs}} = (3.5 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1})(0.035 \text{ M}) = 1.2 \times 10^{-3} \text{ s}^{-1};\)

(a) \(\ln[A] = \ln[A]_0 - kt = \ln(5.0 \times 10^{-5}) - (1.2 \times 10^{-3} \text{ s}^{-1})(225 \text{ s}) = -9.903 - 0.27\)

\(\ln[A] = -10.173; \)

\([A] = e^{-10.173} = 3.8 \times 10^{-5} \text{ M}; \)

(b) \(t = \frac{\ln \left( \frac{[A]_0}{[A]} \right)}{k} = \frac{\ln \left( \frac{5.0 \times 10^{-5} \text{ M}}{1.0 \times 10^{-5} \text{ M}} \right)}{1.2 \times 10^{-3} \text{ s}^{-1}} = 1.3 \times 10^3 \text{ s}. \)

14.63 (a) False (overall reaction would give fourth-order kinetics); (b) False (rate constants must be measured for at least two different temperatures to calculate \(E_a;\)) (c) True (rates of reaction increase with increasing temperature); (d) True (a unimolecular step has first-order kinetics).

14.64 (a) True (\(\text{N}_2\) is a reactant with coefficient of 1); (b) False (reaction order must always be determined by experiments); (c) True (3 molecules of \(\text{H}_2\) react for every 1 molecule of \(\text{N}_2\)); (d) False (3 \(\text{H}_2\) disappear for every \(\text{N}_2\)); (e) False (reactants always have negative concentration changes as time increases); (f) True (simultaneous four-molecule collisions do not occur); (g) True (bonds must break for this reaction to proceed).

14.65 Reaction orders are given by the exponents on the concentrations appearing in the rate law. Overall order is the sum of those exponents.

(a) first-order in \(\text{N}_2\text{O}_5\) and first-order overall;
(b) second-order in \(\text{NO},\) first-order in \(\text{H}_2,\) and third-order overall;
(c) first-order in enzyme and first-order overall.
14.66 Reaction orders are given by the exponents on the concentrations appearing in the rate law. Overall order is the sum of those exponents.
(a) zero-order overall (no concentration dependence);
(b) first-order in sucrose, $H_2O$, and $H_3O^+$, and third-order overall;
(c) first-order in CHCl$_3$, one-half order in Cl$_2$, and three-halves order overall.

14.67 (a) Obtain the overall stoichiometry by adding the three steps, ignoring the reverse reaction of step one which leads to no net change: $2 \text{NO} + 2 \text{H}_2 \rightarrow \text{N}_2 + 2 \text{H}_2\text{O};$

(b) The rate law is determined by the rate-determining step: $\text{Rate} = k_2[\text{N}_2\text{O}_2][\text{H}_2]$. This is not satisfactory, however, because it contains the concentration of an intermediate. Set the rates equal for the forward and reverse first step:

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

Solve this equality for $[\text{N}_2\text{O}_2]$:

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

Substitute into the rate expression: $\text{Rate} = k_2\frac{k_1}{k_{-1}}[\text{NO}]^2[\text{H}_2]$

14.68 (a) Obtain the overall stoichiometry by adding the three steps, ignoring the reverse reaction of step one which leads to no net change: $2 \text{B} + \text{D} \rightarrow 2 \text{F};$

(b) The rate law is determined by the rate-determining step: $\text{Rate} = k_2[\text{C}][\text{D}]$. This is not satisfactory, however, because it contains the concentration of an intermediate. Set the rates equal for the forward and reverse first step:

$$k_1[\text{A}][\text{B}] = k_{-1}[\text{C}];$$

Solve this equality for $[\text{C}]$:

$$[\text{C}] = \frac{k_1}{k_{-1}}[\text{A}][\text{B}];$$

Substitute into the rate expression: $\text{Rate} = k_2\frac{k_1}{k_{-1}}[\text{A}][\text{B}][\text{D}]$

(c) A is a catalyst (consumed in an early step and regenerated in a later step), while C and E are intermediates (produced in early steps and consumed in later steps).

14.69 Ultraviolet light causes chlorofluorocarbons to fragment, producing Cl atoms which catalyze the destruction of ozone:

$$\text{CF}_2\text{Cl}_2 \xrightarrow{\text{hv}} \text{CF}_2\text{Cl} + \text{Cl}$$

$$\text{O}_3 \xrightarrow{\text{hv}} \text{O}_2 + \text{O}$$

$$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$$

$$\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$$
Because the fourth reaction regenerates a Cl atom, the 2nd-4th reactions occur many hundreds of times for every CF$_2$Cl$_2$ molecule that fragments.

14.70 In the unpolluted stratosphere, ozone is generated by the action of ultraviolet light on O$_2$ and is destroyed by the action of ultraviolet light on O$_3$:

\[
\begin{align*}
O_2 \xrightarrow{hv} & \quad O + O \\
O + O_2 & \rightarrow O_3 \\
O_3 \xrightarrow{hv} & \quad O_2 + O \\
O_3 + O & \rightarrow 2 O_2
\end{align*}
\]

14.71 The speed of a chemical reaction refers to how fast it proceeds. The spontaneity of a chemical reaction refers to whether or not the reaction can go in the direction written without outside intervention. A spontaneous reaction may nevertheless have a very slow speed.

14.72 In any reacting system, concentrations of reactants and products are changing with time, even though these changes may be slow for some species. A changing concentration requires a non-zero net rate for each process involved in the mechanism of the reaction. Thus, for a reacting system, forward and reverse rates can never be exactly equal. (As discussed in Chapter 15, when forward and reverse rates are exactly equal the system is at equilibrium.)

14.73 (a) At the molecular level, a catalyst binds to one or more of the reactants in a way that weakens chemical bonds and makes it easier for bonds to rearrange to form the products. (b) When temperature increases, the average kinetic energies of the molecules increase, with the result that enough energy is present for reaction to occur in a larger fraction of molecular collisions. (c) When concentration increases, the molecular density increases. There are more molecules to react, leading to a higher rate of molecular collisions. Both factors contribute to a greater rate of reaction.

14.74 Elementary reactions must be processes that can actually occur at the molecular level. The Haber reaction involves one molecule of N$_2$ and three molecules of H$_2$, which would have to collide in a simultaneous four-molecule process. In addition, four bonds must break and six new bonds form. It is not molecularly reasonable for all this to occur in a single step.

14.75 Flask 1 contains 5 molecules, and Flask 2 contains 10 molecules, so the concentration is doubled. The problem states that Flask 2 reacts four times as fast. This is $2^2$, so the rate law is $\text{Rate} = k[A]^2$. At the molecular level, the rate-determining step could be a reaction between two A molecules. For this process, the rate increases because the higher concentration provides for a higher rate of collisions.
Chapter 14

14.76 Each flask contains the same number of radioactive phosphorus atoms (six). The question asks about the half-lives (how long it takes for the initial amount, six atoms, to fall to half that amount, three atoms). For first-order decay, the half-life is independent of concentration, so the times will be identical for the two flasks.

14.77 The hint for this problem suggests using the Arrhenius equation, \( k = Ae^{-Ea/RT} \). Evaluate \( \frac{Ea}{RT} \) for the catalyzed and uncatalyzed situations; \( T = 21 + 273 = 294 \text{ K} \):

\[
\left( \frac{Ea}{RT} \right)_{\text{uncat}} = \frac{125 \text{ kJ mol}^{-1}}{(8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})(294 \text{ K})} = 51.1;
\]

\[
\left( \frac{Ea}{RT} \right)_{\text{cat}} = \frac{46 \text{ kJ mol}^{-1}}{(8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})(294 \text{ K})} = 18.8;
\]

\( k_{\text{uncat}} = Ae^{-51.1} \) and \( k_{\text{cat}} = Ae^{-18.8} \);

Divide one of these by the other to eliminate \( A \) and find the ratio of rate constants:

\[
\frac{k_{\text{cat}}}{k_{\text{uncat}}} = e^{(51.1 - 18.8)} = e^{32.3} = 1.1 \times 10^{14}.
\]

14.78 Here, there are two concentration variables, \([O_2]\) and \([NO]\). In the first experiment, \([NO]\) >> \([O_2]\), so \(O_2\) is isolated and the data can be analyzed to determine the order with respect to \(O_2\). The data could be plotted, but half-lives can be recognized. It takes 3.0 s for the concentration to fall from 4.1 to 2.05 \(\times\) \(10^{-4}\) M, 3.0 s to fall from 2.05 to 1.02 \(\times\) \(10^{-4}\) M, and 3.0 s to fall from 0.51 to 0.25 \(\times\) \(10^{-4}\) M. Thus the half-life is a constant value, 3.0 s, and the reaction is first-order in \(O_2\). In the second experiment, \([O_2]\) >> \([NO]\), so \(NO\) is isolated and the data can be analyzed to determine the order with respect to \(NO\). The half-life is not constant, so try a second-order plot:

\[2\text{nd order plot}\]

This plot is a straight line, so the reaction is second-order with respect to \(NO\).
The rate law is Rate = \( k[O_2][NO]^2 \);

(b) The half-life of a first-order reaction provides a convenient way to calculate a rate constant. Apply Equation 14-4 to the first experiment:

\[
t_{1/2} = \frac{\ln 2}{k}, \text{ rearranged to give } k = \frac{\ln 2}{t_{1/2}};
\]

\[ k = \frac{0.693}{3.0 \text{ s}} = 2.3 \times 10^{-1} \text{ s}^{-1} \]

This is not the true rate constant, because it describes the conditions under which \( O_2 \) was isolated: \( k = k_{\text{true}}[NO]_0^2 \) and \( k_{\text{true}} = \frac{k}{[NO]_0^2} = \frac{0.23 \text{ s}^{-1}}{(9.63 \times 10^{-3} \text{ M})^2} \);

\[ k_{\text{true}} = 2.5 \times 10^3 \text{ M}^{-2} \text{ s}^{-1}. \]

14.79 Activation energies are calculated from the Arrhenius equation using Equation 14-8:

\[
E_a = R \ln \left( \frac{k_2}{k_1} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \right)^{-1}.
\]

Development time is inversely proportional to rate constant, so \( \frac{k_2}{k_1} = \frac{t_1}{t_2} \).

(a) \( \frac{t_1}{t_2} = 2; \)

\( T_1 = 20 + 273 = 293 \text{ K}; \)

\( T_2 = 293 + 10 = 303 \text{ K}; \)

\[
\left( \frac{1}{T_1} - \frac{1}{T_2} \right)^{-1} = (3.413 \times 10^{-3} \text{ K}^{-1} - 3.300 \times 10^{-3} \text{ K}^{-1})^{-1} = 8880. \text{ K};
\]

\[
E_a = \left( \frac{8.314 \text{ J}}{1 \text{ mol K}} \left( \frac{10^{-3} \text{ kJ}}{1 \text{ J}} \right) \right) (\ln 2)(8880. \text{ K}) = 51 \text{ kJ/mol}. \]

(b) To determine the time it takes at 25\(^o\)C use \( \ln \left( \frac{t_1}{t_2} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \).

\( E_a = 51 \text{ kJ/mol}; \)

\( T_1 = 20 + 273 = 293 \text{ K}; \)

\( t_1 = 10 \text{ min}; \)

\( T_2 = 25 + 273 = 298 \text{ K}; \)

\[
\left( \frac{1}{T_1} - \frac{1}{T_2} \right) = (3.413 \times 10^{-3} - 3.356 \times 10^{-3}) = 5.726 \times 10^{-5} \text{ K}^{-1};
\]
\[
\ln\left(\frac{10 \text{ min}}{t_2}\right) = 5.726 \times 10^{-3} \text{K}^{-1}\left(\frac{1 \text{ mol K}}{8.314 \times 10^{-3} \text{ kJ}}\right) \left(\frac{51 \text{ kJ}}{1 \text{ mol}}\right) = 0.351;
\]

\[
\frac{10 \text{ min}}{t_2} = 1.42;
\]

\[
t_2 = \frac{10 \text{ min}}{1.42} = 7.0 \text{ min}.
\]

14.80 Figure 14-21 shows that while the activation energy for the uncatalyzed forward reaction, \(\text{O}_3 + \text{O}\), is about 19 kJ/mol, the activation energy for the uncatalyzed reverse reaction, \(\text{O}_2 + \text{O}_2\), is about 410 kJ/mol. Adding the catalyst reduces both values by about 15 kJ/mol, so the forward reaction has an activation energy of only about 4 kJ/mol, but the reverse reaction still has an immense activation energy, about 395 kJ/mol. The rate of the forward reaction is increased immensely by the catalyst, while the reverse reaction has essentially zero rate whether catalyzed or uncatalyzed.

14.81 The only true statements are (d) and (f). Statement (a) is false because \(\Delta E_{\text{reaction}} = C - A\).

Here is an energy diagram showing the quantities involved:

```
\[
\begin{align*}
\text{Energy} & \quad \text{Forward} \ E_a \quad \text{Reverse} \ E_a \\
\Delta E & \quad A \quad \quad B \quad \quad C
\end{align*}
\]
```

14.82 Plots of \(\ln c\) vs. \(t\) and \(1/c\) vs. \(t\) are not linear, showing that the reaction is neither first-order or second-order. Further examination of the data shows that the concentration change per unit time is independent of the concentration:

\[
\begin{align*}
0 - 10 \text{ s}, \quad \frac{\Delta c}{\Delta t} & = \frac{0.12 \text{ M}}{10 \text{ s}} = 0.012 \text{ M/s}; \\
10 - 20 \text{ s}, \quad \frac{\Delta c}{\Delta t} & = \frac{0.12 \text{ M}}{10 \text{ s}} = 0.012 \text{ M/s}; \\
20 - 30 \text{ s}, \quad \frac{\Delta c}{\Delta t} & = \frac{0.12 \text{ M}}{10 \text{ s}} = 0.012 \text{ M/s};
\end{align*}
\]

A rate that is totally independent of concentration indicates zero-order behavior: \(\text{Rate} = k\).
14.83  (a) The rate law is that for an elementary bimolecular reaction: \( \text{Rate} = k[H_2][X_2] \);  
(b) When a first step is rate-determining, it determines the rate law: \( \text{Rate} = k[X_2] \);  
(c) The rate law is determined by the rate-determining step: \( \text{Rate} = k_2[X][H_2] \). This is not satisfactory, however, because it contains the concentration of an intermediate. Set the rates equal for the forward and reverse first step: \( k_1[X_2] = k_{-1}[X]^2 \).

Solve this equality for \([X]\): \( [X] = \left( \frac{k_1}{k_{-1}} \right)^{1/2} [X_2]^{1/2} \);

Substitute into the rate expression: \( \text{Rate} = k_2 \left( \frac{k_1}{k_{-1}} \right)^{1/2} [H_2][X_2]^{1/2} \).

14.84  This reaction is 1/2 order in one reactant and first-order in the other reactant. There is more than one way to increase the concentrations so that the rate doubles. The simplest is to double the concentration of the reactant for which there is first-order behavior. The illustration shows three diatomic molecules and six atoms, so the new view should show three diatomic molecules and twelve atoms:

14.85  (a) The net reaction can be obtained by summing the three steps, because when the reverse step occurs there is no net change: \( \text{Cl}_2 + \text{CHCl}_3 \rightarrow \text{HCl} + \text{CCl}_4 \);
(b) Intermediates are produced in early steps and consumed in later steps: \( \text{Cl} \) and \( \text{CCl}_3 \);
(c) The rate law is determined by the rate-determining step: \( \text{Rate} = k_2[\text{CHCl}_3][\text{Cl}] \). This is not satisfactory, however, because it contains the concentration of an intermediate. Set the rates equal for the forward and reverse first step: \( k_1[\text{Cl}_2] = k_{-1}[\text{Cl}]^2 \).

Solve this equality for \([\text{Cl}]\): \( [\text{Cl}] = \left( \frac{k_1}{k_{-1}} \right)^{1/2} [\text{Cl}_2]^{1/2} \);

Substitute into the rate expression: \( \text{Rate} = k_2 \left( \frac{k_1}{k_{-1}} \right)^{1/2} [\text{CHCl}_3][\text{Cl}_2]^{1/2} \).

14.86  (a) The half-life is not constant, so test for second-order behavior by plotting \( 1/c \) vs. \( t \):
The second-order plot is a straight line, so Rate = $k[NH_4NCO]^2$;

(b) $k = \text{(Slope)} = \frac{6.00 \text{ M}^{-1} - 0.00 \text{ M}^{-1}}{9.0 \text{ hr} - 0.0 \text{ hr}} = 0.67 \text{ M}^{-1} \text{ hr}^{-1}$;

(c) At 50 °C, it takes 2.0 hr for concentration to fall from 0.500 to 0.300 M, while at 25 °C, it takes 6.0 hr for the same change in concentration to occur. The reaction is three times as fast at 50 °C as at 25 °C, so $k_2/k_1 = 3.0$; Use Equation 14-8 to calculate $E_a$:

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

$$= (298^{-1} \text{K}^{-1} - 323^{-1} \text{K}^{-1})^{-1} = 3850. \text{ K}$$

$$E_a = \left( \frac{8.314 \text{ J}}{1 \text{ mol K}} \right) \left( \frac{10^{-3} \text{ kJ}}{1 \text{ J}} \right) (\ln 3.0)(3850. \text{ K}) = 35 \text{ kJ/mol}.$$ 

14.87 Neither intermediates nor catalysts appear in the overall stoichiometry of the reaction, so any species that appears in the mechanism but not in the overall stoichiometry is either an intermediate or a catalyst. Catalysts are consumed in early steps and regenerated in later steps, while intermediates are produced in early steps and consumed in later steps.

14.88 To determine which set of concentrations leads to the fastest rate, determine the product of concentrations for each set:

(a) $$\left( \frac{0.5 \text{ mol}}{2.0 \text{ L}} \right) \left( \frac{0.5 \text{ mol}}{2.0 \text{ L}} \right) = 0.06 \text{ mol}^2/\text{L}^2;$$
(b) \( \left( \frac{0.5 \text{ mol}}{1.0 \text{ L}} \right) \left( \frac{0.5 \text{ mol}}{1.0 \text{ L}} \right) = 0.25 \text{ mol}^2/\text{L}^2; \)

(c) \( \left( \frac{0.1 \text{ mol}}{1.0 \text{ L}} \right) \left( \frac{2.0 \text{ mol}}{1.0 \text{ L}} \right) = 0.20 \text{ mol}^2/\text{L}^2; \)

thus (b), with the highest product, has the fastest rate.

14.89 (a) Prepare first-order and second-order plots and look for linear behavior:

<table>
<thead>
<tr>
<th>( t ) (s)</th>
<th>0</th>
<th>1000</th>
<th>2000</th>
<th>3000</th>
<th>4000</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c ) (M)</td>
<td>0.250</td>
<td>0.118</td>
<td>0.0770</td>
<td>0.0572</td>
<td>0.0455</td>
</tr>
<tr>
<td>( \ln \left( \frac{c_o}{c} \right) )</td>
<td>0.000</td>
<td>0.751</td>
<td>1.18</td>
<td>1.47</td>
<td>1.70</td>
</tr>
<tr>
<td>( 1/c - 1/c_o ) (M(^{-1}))</td>
<td>0.00</td>
<td>4.47</td>
<td>8.99</td>
<td>13.5</td>
<td>18.0</td>
</tr>
</tbody>
</table>

1st order plot

The second-order plot is linear, so \( \text{Rate} = k[\text{CH}_3\text{CHO}]^2; \)

(b) Determine the rate constant from the slope of the second-order plot:

\[ k = \text{Slope} = \frac{18.0 \text{ M}^{-1} - 0.00 \text{ M}^{-1}}{4000 \text{ s} - 0 \text{ s}} = 4.5 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}; \]

(c) Use Equation 14-5, suitably rearranged:

\[ kt = \frac{1}{[A]} - \frac{1}{[A]_o}; \]

\( [A]_o = 0.250 \text{ M}; \) \( [A] = 0.250 \text{ M} \left( \frac{100\% - 75\%}{100\%} \right) = 0.0625 \text{ M}; \)

\( t = \frac{16.0 \text{ M}^{-1} - 4.00 \text{ M}^{-1}}{4.5 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}} = 2.7 \times 10^3 \text{ s}. \)

14.90 Here, there are two concentration variables, \([A]\) and \([B]\). In the first experiment, \([B] >> [A]\), so \(A\) is isolated and the data can be analyzed to determine the order with respect to \(A\). The data could be plotted, but half-lives can be recognized. It takes 30 s for the concentration to fall from 0.050 M to 0.025 M, 30 s to fall from 0.040 to 0.020 M, and 30 s to fall from 0.032 to 0.016 M. Thus, the half-life is a constant value, 30 s, and the reaction is first-order in \(A\). In the second experiment, the rate of disappearance of \(A\)
Chapter 14

does not change even though the initial concentration of B is increased. Consequently, the rate law does not depend on [B].
(a) Rate = \( k[A] \);
(b) The half-life of a first-order reaction provides a convenient way to calculate a rate constant. Use Equation 14-4: \( t_{1/2} = \frac{\ln 2}{k} \), rearranged to give \( k = \frac{\ln 2}{t_{1/2}} \);
\[
k = \frac{0.693}{30 \text{ s}} = 2.3 \times 10^{-2} \text{ s}^{-1}
\]

14.91 When an enzyme binds a reactant, bonds between enzyme and reactant result in a reduction in the strength of the bonds that need to be broken in order for the catalyzed reaction to occur. This reduction in strength in turn reduces the amount of energy that must be supplied for the reaction to occur, accounting for the decrease in the activation energy for the enzyme-catalyzed reaction.

14.92 (a) The first step in the proposed mechanism generates an intermediate which must be consumed in the second step. To give the correct overall stoichiometry, the second step also must consume a Cl\(^-\) ion: \([\text{Co(NH}_3\text{)}_5\text{H}_2\text{O}]^{3+} + \text{Cl}^- \rightarrow [\text{Co(NH}_3\text{)}\text{Cl}]^{2+}\);
(b) The rate law is determined by the rate-determining step: Rate = \( k_2[I][\text{Cl}^-] \), where \( I = [\text{Co(NH}_3\text{)}_5]^{3+} \). This is not satisfactory, however, because it contains the concentration of an intermediate. Set the rates equal for the forward and reverse first step:
\[
k_1[[\text{Co(NH}_3\text{)}_5\text{H}_2\text{O}]^{3+}] = k_{-1}[I][\text{H}_2\text{O}]\]
Solve this equality for [I]:
\[
[I] = \frac{k_1}{k_{-1}} \frac{[[\text{Co(NH}_3\text{)}_5\text{H}_2\text{O}]^{3+}]}{[\text{H}_2\text{O}]};
\]
Substitute into the rate expression:
\[
\text{Rate} = k_2 \frac{k_1}{k_{-1}} \frac{[[\text{Co(NH}_3\text{)}_5\text{H}_2\text{O}]^{3+}][\text{Cl}^-]}{[\text{H}_2\text{O}]}\]
(c) The observed rate is consistent with the predicted rate law. Although H\(_2\)O appears in the rate expression, its concentration in aqueous solution is so great that [H\(_2\)O] = constant. Also,
in 1 M HCl solution, \([\text{Cl}^-] = 1 \text{ M}\), so the complex is isolated when it is present at 1 mM concentration. The observed rate constant under these conditions is 
\[
\text{k}_{\text{obs}} = \frac{k_2}{k_{-1}} \frac{[\text{Cl}^-]}{[\text{H}_2\text{O}]}.
\]

14.93 Your explanation should include the main features of the induced-fit model: a cavity into which the molecule fits, that adjusts its shape to the target molecule (square), then distorts to catalyze decomposition of the square:

14.94 Rates of elementary two-body reactions depend on concentration of each type of body: When a concentration is increased by some factor, the rate increases by the same factor.
(a) There are half as many red balls, so half as many pairs will form: 2;
(b) There are 1.5 times as many white balls, so 1.5 times as many pairs will form: 6;
(c) There are half as many red but twice as many white balls: Pairs = \((1/2)(2)(4) = 4\);
(d) There are twice as many of each type of balls: Pairs = \((2)(2)(4) = 16\);
(e) When the concentration of either type of ball changes, the frequency of collisions with other balls changes in the same proportion, so the rate of formation of pairs, which depends on collision rate, also changes proportionally.

14.95 (a) The catalyst, \(\text{Br}^-\), is consumed in the first step, so it must be regenerated in a later step. Thus, \(A = \text{Br}^-\). For the stoichiometry to be correct, \(B = \text{O}_2\);
(b) For the overall reaction,
\[
\Delta E = \Delta H = [2 \text{ mol}(–285.83 \text{ kJ/mol}) + 1 \text{ mol}(0 \text{ kJ/mol})]
- 2 \text{ mol}(–187.8 \text{ kJ/mol}) = – 196.1 \text{ kJ};
\]
For the first step (\(\Delta n_g = 0\)),
\[
\Delta E = \Delta H = [1 \text{ mol}(–285.83 \text{ kJ/mol}) + 1 \text{ mol}(–94.1 \text{ kJ/mol})]
- [1 \text{ mol}(–187.8 \text{ kJ/mol}) + 1 \text{ mol}(–121.4 \text{ kJ/mol})] = – 70.73 \text{ kJ};
\]
14.96  (a) The information provided suggests that transfer of an O atom between NO$_2$ and O$_3$, giving NO$_3$, is a reasonable first step. Then NO$_3$ could react with NO$_2$, giving the correct overall stoichiometry: If the first reaction is rate-determining, the observed rate law results:

\[
\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad \text{(slow, rate determining)}
\]
\[
\text{NO}_3 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_5 \quad \text{(rapid)}
\]

(b) A molecular picture of a reaction shows reactants, reactive intermediate, and products:

(c) The activation energy diagram should indicate the exothermicity and activation energy of the overall process: