

14 Chemical Kinetics

Visualizing Concepts

- 14.1 *Analyze/Plan.* Given three sets of initial conditions for the same chemical reaction, decide which set will react fastest. Consider the four factors that affect reaction rate.
- Solve.* All vessels are at the same temperature and no catalyst is present, so these two factors are not pertinent. The initial conditions do differ in physical state and concentration. Vessel 2 has the greatest concentration of reactants A and B, and they are in solution; vessel 2 has the fastest reaction. Vessel 1 has fewer reactants and they are in the solid state. The number of reactant collisions is much less than for mobile reactants in solution. Vessel 3 has reactants in solution, but the concentrations are four times less than in Vessel 2.
- 14.2 *Analyze/Plan.* Given the plot of [X] vs time, answer questions about reaction speed and rate. Consider the definitions of average reaction rate and instantaneous rate. *Solve.*
- X is a product, because its concentration increases with time.
 - The speed of a reaction is its rate, or how quickly the concentration of a reactant or product changes over time. This graph shows how [X] increases over time. The rate at any particular time, the instantaneous rate, is the slope of the tangent to the curve at that time. Visualizing the tangents at points 0, 1, 2 and 3, we see that the slopes of these lines are decreasing with time. That is, the rate of reaction is decreasing; the reaction is slowing down as time progresses.
 - The average rate of reaction between any two points on the graph is the slope of the line connecting the two points. Points 1 and 2 are earlier in the reaction when more reactants are available, so the average rate of formation of products is greater. As reactants are used up, the rate of X production decreases, and the average rate between points 2 and 3 is smaller.
- 14.3 Chemical equation (d), $B \rightarrow 2A$, is consistent with the data. The concentration of A increases with time, and concentration B decreases with time, so B must be a reactant and A must be a product. The ending concentration of A is approximately twice as large as the starting concentration of B, so mole ratio of A:B is 2:1. The reaction is $B \rightarrow 2A$.
- 14.4 *Analyze/Plan.* Given a plot of increase in [M] over time, answer questions about reaction rate and progress. Consider the definition of reaction rate. *Solve.*
- Well, the reaction occurs at a constant rate from $t = 0$ to $t = \sim 12$ min. The plot of [M] vs time from $t = 0$ to $t = 12$ is a straight line, so [M] increases at a constant rate and the reaction occurs at a constant rate. The rate is zero after $t = 12$ min.

- (b) Yes, the reaction is definitely complete at $t = 15$ min. (It is actually complete near $t = 12$ min.) $[M]$ does not change after ~ 12 min. This means that no more M is being produced and the reaction is no longer occurring.

14.5 *Analyze/Plan.* Using the relationship $\text{rate} = k[A]^x$, determine the value of x that produces a rate law to match the described situation. *Solve.*

- (a) $x = 0$. The rate of reaction does not depend on $[A]_0$, so the reaction is zero-order in A .
- (b) $x = 2$. When $[A]_0$ increases by a factor of 3, rate increases by a factor of $(3)^2 = 9$.
- (c) $x = 3$. When $[A]_0$ increases by a factor of 2, rate increases by a factor of $(2)^3 = 8$.

14.6 *Analyze.* Given three mixtures and the order of reaction in each reactant, determine which mixture will have the fastest initial rate.

Plan. Write the rate law. Count the number of reactant molecules in each container. The three containers have equal volumes and total numbers of molecules. Use the molecule count as a measure of concentration of NO and O_2 . Calculate the initial rate for each container and compare.

Solve. $\text{Rate} = k[\text{NO}]^2[\text{O}_2]$; rate is proportional to $[\text{NO}]^2[\text{O}_2]$

Container	$[\text{NO}]$	$[\text{O}_2]$	$[\text{NO}]^2[\text{O}_2] \propto \text{rate}$
(1)	5	4	100
(2)	7	2	98
(3)	3	6	54

The relative rates in containers (1) and (2) are very similar, with (1) having the slightly faster initial rate.

14.7 *Plan.* For a first-order reaction, a plot of $\ln[A]$ vs. time is linear, as shown in the diagram. The slope is $-k$, and the intercept is $[A]_0$. According to the Arrhenius equation [14.19], k increases with increasing temperature. *Solve.*

- (a) Graphs 1 and 2 have the same slope, and thus the same rate constant, k . These experiments are done at the same temperature. The y -intercepts of the two graphs are different; the experiments had different initial concentrations of A .
- (b) Graphs 2 and 3 have the same y -intercept and thus the same starting concentration of A . The slopes of the two graphs are different, so their rate constants are different and they occur at different temperatures. Graph 3, with the smaller slope and k value will occur at the lower temperature.

14.8 *Analyze.* Given concentrations of reactants and products at two times, as represented in the diagram, find $t_{1/2}$ for this first-order reaction.

Plan. For a first order reaction, $t_{1/2} = 0.693/k$; $t_{1/2}$ depends only on k . Use Equation [14.12] to solve for k . *Solve.*

- (a) Since reactants and products are in the same container, use number of particles as a measure of concentration. The red dots are reactant A , and the blue are product B . $[A]_0 = 8$, $[A]_{30} = 2$, $t = 30$ min.

$$\ln \frac{[A]_t}{[A]_0} = -kt. \quad \ln(2/8) = -k(30 \text{ min}); \quad \frac{-1.3863}{-30 \text{ min}} = k;$$

$$k = 0.046210 = 0.0462 \text{ min}^{-1}$$

$$t_{1/2} = 0.693/k = 0.693/0.046210 = 15 \text{ min}$$

By examination, $[A]_0 = 8$, $[A]_{30} = 2$. After 1 half-life, $[A] = 4$; after a second half-life, $[A] = 2$. Thirty minutes represents exactly 2 half-lives, so $t_{1/2} = 15 \text{ min}$. [This is more straightforward than the calculation, but a less general method.]

- (b) After 4 half-lives, $[A]_t = [A]_0 \times 1/2 \times 1/2 \times 1/2 \times 1/2 = [A]_0/16$. In general, after n half-lives, $[A] = [A]_0/2^n$.

14.9

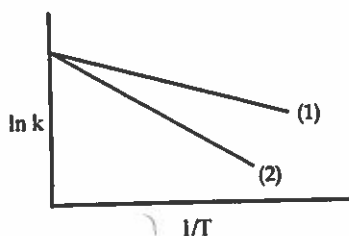
The reaction profile has a single high point (peak), so the reaction occurs in a single step. This step is necessarily the rate-determining step.

- (1) Total potential energy of the reactants
- (2) E_a , activation energy of the reaction. This is the difference in energy between the potential energy of the activated complex (transition state) and the potential energy of the reactants.
- (3) ΔE , net energy change for the reaction. This is the difference in energy between the products and reactants. (Under appropriate conditions, this could also be ΔH .) For this reaction, the energy of products is lower than the energy of reactants, and the reaction releases energy to the surroundings.
- (4) Total potential energy of the products.

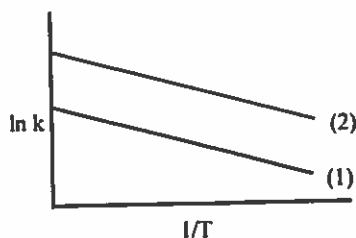
14.10

On a plot of $\ln k$ vs. $1/T$, the slope is $-E_a$ and the y-intercept is $\ln A$, where E_a is activation energy and A is the frequency factor.

- (a) If $E_a(2) > E_a(1)$ and $A_1 = A_2$, the lines will have the same y-intercept, negative slope direction, and the slope of line 2 will be steeper than the slope of line 1.



- (b) If $A_2 > A_1$ and $E_a(1) = E_a(2)$, the lines will be parallel with the same negative slopes and different y-intercepts.



- 14.11 (a) The red pathway is slower, because it has the greater activation energy, E_a .
 (b) The reaction could occur by both catalyzed and uncatalyzed mechanisms. The initial reactants and final products would be the same, but the transition state and activation energy would be different.
- 14.12 (a) $\text{NO}_2 + \text{F}_2 \rightarrow \text{NO}_2\text{F} + \text{F}$
 $\text{NO}_2 + \text{F} \rightarrow \text{NO}_2\text{F}$
 (b) $2\text{NO}_2 + \text{F}_2 \rightarrow 2\text{NO}_2\text{F}$
 (c) F is the intermediate, because it is produced and then consumed during the reaction.
 (d) $\text{rate} = k[\text{NO}_2][\text{F}_2]$

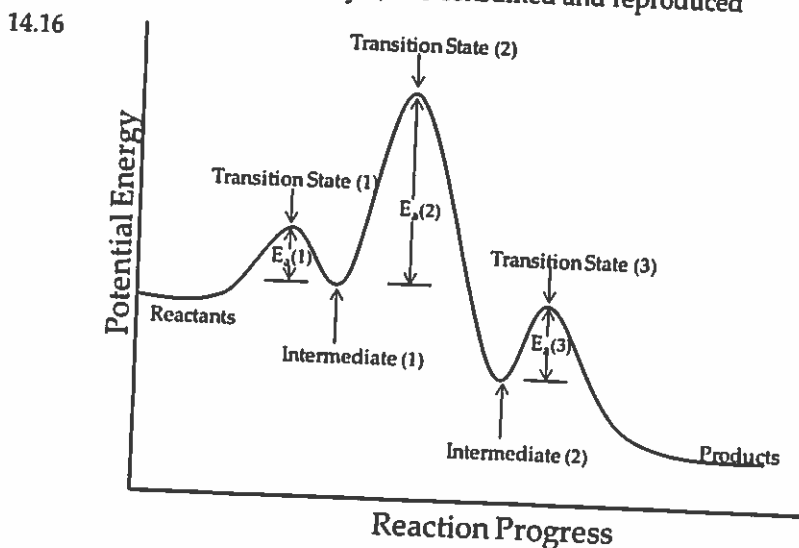
14.13 This is the profile of a two-step mechanism, $\text{A} \rightarrow \text{B}$ and $\text{B} \rightarrow \text{C}$. There is one intermediate, B. Because there are two energy maxima, there are two transition states. The $\text{B} \rightarrow \text{C}$ step is faster, because its activation energy is smaller. The reaction is exothermic because the energy of the products is lower than the energy of the reactants.

14.14 The most likely transition state shows the relative geometry of both reactants and products. It is reasonable to assume that multiple bonds, with greater total bond energy, remain intact at the expense of single bonds. In the black-and-white diagram below, open circles represent the red balls and closed circles represent the blue.



- 14.15 (a) $\text{A}_2 + \text{AB} + \text{AC} \rightarrow \text{BA}_2 + \text{A} + \text{AC}$
 $\text{BA}_2 + \text{A} + \text{AC} \rightarrow \text{A}_2 + \text{BA}_2 + \text{C}$

 net: $\text{AB} + \text{AC} \rightarrow \text{BA}_2 + \text{C}$
- (b) A is the intermediate; it is produced and consumed.
 (c) A_2 is the catalyst; it is consumed and reproduced



The reaction is exothermic because the energy of products is lower than the energy of reactants. The two intermediates are formed at different rates because $E_a(1) \neq E_a(2)$. In order to have two intermediates, the mechanism must have at least three steps.

Reaction Rates (sections 14.1 and 14.2)

- 14.17 (a) Reaction rate is the change in the amount of products or reactants in a given amount of time; it is the speed of a chemical reaction.
- (b) Rates depend on concentration of reactants, physical state (or surface area) of reactants, temperature and presence of catalyst.
- (c) No, the rate of disappearance of reactants is not necessarily the same as the rate of appearance of products. The stoichiometry of the reaction (mole ratios of reactants and products) must be known in order to relate rate of disappearance of reactants to rate of appearance of products.
- 14.18 (a) M/s
- (b) The hotter the oven, the faster the cake bakes. Milk sours faster in hot weather than cool weather.
- (c) The *average rate* is the rate over a period of time, while the *instantaneous rate* is the rate at a particular time.
- 14.19 *Analyze/Plan.* Given mol A at a series of times in minutes, calculate mol B produced, molarity of A at each time, change in M of A at each 10 min interval, and ΔM A/s. For this reaction, mol B produced equals mol A consumed. M of A or [A] = mol A/0.100 L. The average rate of disappearance of A for each 10 minute interval is

$$-\frac{\Delta[A]}{s} = -\frac{[A]_1 - [A]_0}{10 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}}$$

Solve.

Time (min)	Mol A	(a) Mol B	[A]	$\Delta[A]$	(b) Rate $-(\Delta[A]/s)$
0	0.065	0.000	0.65		
10	0.051	0.014	0.51	-0.14	2.3×10^{-4}
20	0.042	0.023	0.42	-0.09	2×10^{-4}
30	0.036	0.029	0.36	-0.06	1×10^{-4}
40	0.031	0.034	0.31	-0.05	0.8×10^{-4}

(c) $\frac{\Delta M_B}{\Delta t} = \frac{(0.029 - 0.014) \text{ mol}/0.100 \text{ L}}{(30 - 10) \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} = 1.25 \times 10^{-4} = 1.3 \times 10^{-4} \text{ M/s}$

14.20

Time(s)	Mol A	(a) Mol B	Δ Mol A	(b) Rate $-(\Delta \text{ mol A/s})$
0	0.100	0.000		
40	0.067	0.033	-0.033	8.3×10^{-4}
80	0.045	0.055	-0.022	5.5×10^{-4}
120	0.030	0.070	-0.015	3.8×10^{-4}
160	0.020	0.080	-0.010	2.5×10^{-4}

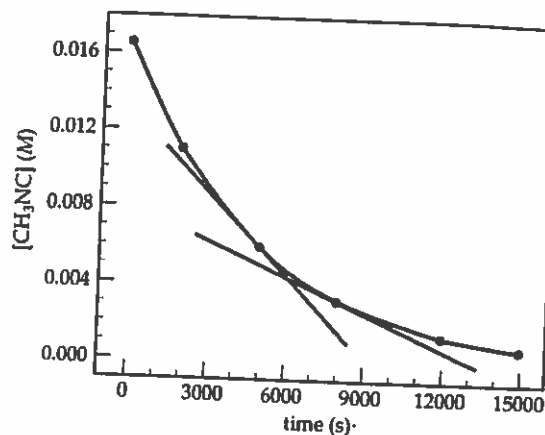
- (c) The volume of the container must be known to report the rate in units of concentration (mol/L) per time.

14.21 (a) Analyze/Plan. Follow the logic in Sample Exercises 14.1 and 14.2. Solve.

Time (sec)	Time Interval (sec)	Concentration (M)	ΔM	Rate (M/s)
0		0.0165		
2,000	2,000	0.0110	-0.0055	28×10^{-7}
5,000	3,000	0.00591	-0.0051	17×10^{-7}
8,000	3,000	0.00314	-0.00277	9.23×10^{-7}
12,000	4,000	0.00137	-0.00177	4.43×10^{-7}
15,000	3,000	0.00074	-0.00063	2.1×10^{-7}

$$(b) \frac{\Delta M_B}{\Delta t} = \frac{(0.0165 - 0.00074) \text{ M}}{(15,000 - 0) \text{ s}} = 1.0507 \times 10^{-6} = 1.05 \times 10^{-6} \text{ M/s}$$

(c) From the slopes of the lines in the figure at right, the rates are:
 at 5000 s,
 $12 \times 10^{-7} \text{ M/s}$;
 at 8000 s,
 $5.8 \times 10^{-7} \text{ M/s}$

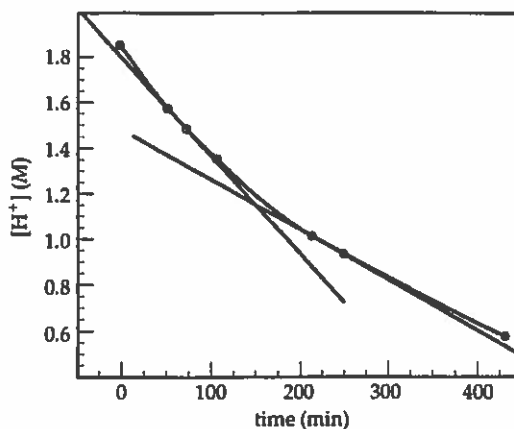


14.22 (a)

Time (min)	Time Interval (min)	Concentration (M)	ΔM	Rate (M/s)
0.0		1.85		
54.0	54.0	1.58	-0.27	8.3×10^{-5}
107.0	53.0	1.36	-0.22	6.9×10^{-5}
215.0	108	1.02	-0.34	5.2×10^{-5}
430.0	215	0.580	-0.44	3.4×10^{-5}

$$(b) \frac{\Delta M_B}{\Delta t} = \frac{(1.85 - 0.580) \text{ M}}{(430 - 0) \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} = 4.9225 \times 10^{-5} = 4.92 \times 10^{-5} \text{ M/s}$$

- (c) From the slopes of the lines in the figure at the right, the rates are: at 75.0 min, $4.2 \times 10^{-3} M/\text{min}$, or $7.0 \times 10^{-5} M/\text{s}$; at 250 min, $2.1 \times 10^{-3} M/\text{min}$ or $3.5 \times 10^{-5} M/\text{s}$



- 14.23 *Analyze/Plan.* Follow the logic in Sample Exercise 14.3. *Solve.*

- (a) $-\Delta[\text{H}_2\text{O}_2]/\Delta t = \Delta[\text{H}_2]/\Delta t = \Delta[\text{O}_2]/\Delta t$
 (b) $-\Delta[\text{N}_2\text{O}]/2\Delta t = \Delta[\text{N}_2]/2\Delta t = \Delta[\text{O}_2]/\Delta t$
 $-\Delta[\text{N}_2\text{O}]/\Delta t = \Delta[\text{N}_2]/\Delta t = 2\Delta[\text{O}_2]/\Delta t$
 (c) $-\Delta[\text{N}_2]/\Delta t = \Delta[\text{NH}_3]/2\Delta t$; $-\Delta[\text{H}_2]/3\Delta t = \Delta[\text{NH}_3]/2\Delta t$
 $-2\Delta[\text{N}_2]/\Delta t = \Delta[\text{NH}_3]/\Delta t$; $-\Delta[\text{H}_2]/\Delta t = 3\Delta[\text{NH}_3]/2\Delta t$
 (d) $-\Delta[\text{C}_2\text{H}_5\text{NH}_2]/\Delta t = \Delta[\text{C}_2\text{H}_4]/\Delta t = \Delta[\text{NH}_3]/\Delta t$

- 14.24 (a) $\text{rate} = -\Delta[\text{H}_2\text{O}]/2\Delta t = \Delta[\text{H}_2]/2\Delta t = \Delta[\text{O}_2]/\Delta t$
 (b) $\text{rate} = -\Delta[\text{SO}_2]/2\Delta t = -\Delta[\text{O}_2]/\Delta t = \Delta[\text{SO}_3]/2\Delta t$
 (c) $\text{rate} = -\Delta[\text{NO}]/2\Delta t = -\Delta[\text{H}_2]/2\Delta t = \Delta[\text{N}_2]/\Delta t = \Delta[\text{H}_2\text{O}]/2\Delta t$
 (d) $\text{rate} = -\Delta[\text{N}_2]/\Delta t = -\Delta[\text{H}_2]/2\Delta t = \Delta[\text{N}_2\text{H}_4]/\Delta t$

- 14.25 *Analyze/Plan.* Use Equation [14.4] to relate the rate of disappearance of reactants to the rate of appearance of products. Use this relationship to calculate desired quantities. *Solve.*

- (a) $\Delta[\text{H}_2\text{O}]/2\Delta t = -\Delta[\text{H}_2]/2\Delta t = -\Delta[\text{O}_2]/\Delta t$
 H_2 is burning, $-\Delta[\text{H}_2]/\Delta t = 0.48 \text{ mol/s}$
 O_2 is consumed, $-\Delta[\text{O}_2]/\Delta t = -\Delta[\text{H}_2]/2\Delta t = 0.48 \text{ mol/s}/2 = 0.24 \text{ mol/s}$
 H_2O is produced, $+\Delta[\text{H}_2\text{O}]/\Delta t = -\Delta[\text{H}_2]/\Delta t = 0.48 \text{ mol/s}$
- (b) The change in total pressure is the sum of the changes of each partial pressure. NO and Cl_2 are disappearing and NOCl is appearing.
 $-\Delta P_{\text{NO}}/\Delta t = -56 \text{ torr/min}$
 $-\Delta P_{\text{Cl}_2}/\Delta t = \Delta P_{\text{NO}}/2\Delta t = -28 \text{ torr/min}$
 $+\Delta P_{\text{NOCl}}/\Delta t = -\Delta P_{\text{NO}}/\Delta t = +56 \text{ torr/min}$
 $\Delta P_{\text{T}}/\Delta t = -56 \text{ torr/min} - 28 \text{ torr/min} + 56 \text{ torr/min} = -28 \text{ torr/min}$

- 14.26 (a) $-\Delta[\text{C}_2\text{H}_4]/\Delta t = \Delta[\text{CO}_2]/2\Delta t = \Delta[\text{H}_2\text{O}]/2\Delta t$
 $-2\Delta[\text{C}_2\text{H}_4]/\Delta t = \Delta[\text{CO}_2]/\Delta t = \Delta[\text{H}_2\text{O}]/\Delta t$
 C_2H_4 is burning, $-\Delta[\text{C}_2\text{H}_4]/\Delta t = 0.036 \text{ M/s}$
 CO_2 and H_2O are produced, at twice the rate that C_2H_4 is consumed.
 $\Delta[\text{CO}_2]/\Delta t = \Delta[\text{H}_2\text{O}]/\Delta t = 2(0.036) \text{ M/s} = 0.072 \text{ M/s}$
- (b) In this reaction, pressure is a measure of concentration.
 $-\Delta[\text{N}_2\text{H}_4]/\Delta t = -\Delta[\text{H}_2]/\Delta t = \Delta[\text{NH}_3]/2\Delta t$
 N_2H_4 is consumed, $-\Delta[\text{N}_2\text{H}_4]/\Delta t = 74 \text{ torr/hr}$
 H_2 is consumed, $-\Delta[\text{H}_2]/\Delta t = 74 \text{ torr/hr}$
 NH_3 is produced at twice the rate that N_2H_4 and H_2 are consumed,
 $\Delta[\text{NH}_3]/\Delta t = -2\Delta[\text{N}_2\text{H}_4]/\Delta t = 2(74) \text{ torr/hr} = 148 \text{ torr/hr}$
 $\Delta P_T/\Delta t = (+148 \text{ torr/hr} - 74 \text{ torr/hr} - 74 \text{ torr/hr}) = 0 \text{ torr/hr}$

Rate Laws (section 14.3 and 14.2)

- 14.27 *Analyze/Plan.* Follow the logic in Sample Exercises 14.4 and 14.5. *Solve.*
- (a) If $[\text{A}]$ is doubled, there will be no change in the rate or the rate constant. The overall rate is unchanged because $[\text{A}]$ does not appear in the rate law; the rate constant changes only with a change in temperature.
- (b) The reaction is zero order in A, second order in B and second order overall.
- (c) Units of $k = \frac{\text{M/s}}{\text{M}^2} = \text{M}^{-1} \text{ s}^{-1}$
- 14.28 (a) $\text{rate} = k[\text{A}][\text{C}]^2$
 (b) rate is proportional to $[\text{A}]$, rate doubles
 (c) rate is not affected by $[\text{B}]$, no change
 (d) rate changes as $[\text{C}]^2$, rate increases by a factor of 3^2 or 9
 (e) rate increases by a factor of $(3)(3)^2 = 27$
 (f) rate decreases by a factor of $(1/2)(1/2)^2 = 1/8$
- 14.29 *Analyze/Plan.* Follow the logic in Sample Exercise 14.4. *Solve.*
- (a) $\text{rate} = k[\text{N}_2\text{O}_5] = 4.82 \times 10^{-3} \text{ s}^{-1} [\text{N}_2\text{O}_5]$
 (b) $\text{rate} = 4.82 \times 10^{-3} \text{ s}^{-1} (0.0240 \text{ M}) = 1.16 \times 10^{-4} \text{ M/s}$
 (c) $\text{rate} = 4.82 \times 10^{-3} \text{ s}^{-1} (0.0480 \text{ M}) = 2.31 \times 10^{-4} \text{ M/s}$
 When the concentration of N_2O_5 doubles, the rate of the reaction doubles.
 (d) $\text{rate} = 4.82 \times 10^{-3} \text{ s}^{-1} (0.0120 \text{ M}) = 5.78 \times 10^{-5} \text{ M/s}$
 When the concentration of N_2O_5 is halved, the rate of the reaction is halved.

- 14.30 (a) $\text{rate} = k[\text{H}_2][\text{NO}]^2$
 (b) $\text{rate} = (6.0 \times 10^4 \text{ M}^{-2} \text{ s}^{-1})(0.035 \text{ M})^2(0.015 \text{ M}) = 1.1 \text{ M/s}$
 (c) $\text{rate} = (6.0 \times 10^4 \text{ M}^{-2} \text{ s}^{-1})(0.10 \text{ M})^2(0.010 \text{ M}) = 6.0 \text{ M/s}$
 (d) $\text{rate} = (6.0 \times 10^4 \text{ M}^{-2} \text{ s}^{-1})(0.010 \text{ M})^2(0.030 \text{ M}) = 0.18 \text{ M/s}$
- 14.31 *Analyze/Plan.* Write the rate law and rearrange to solve for k . Use the given data to calculate k , including units. *Solve.*
 (a, b) $\text{rate} = k[\text{CH}_3\text{Br}][\text{OH}^-]; k = \frac{\text{rate}}{[\text{CH}_3\text{Br}][\text{OH}^-]}$
 at 298 K, $k = \frac{0.0432 \text{ M/s}}{(5.0 \times 10^{-3} \text{ M})(0.050 \text{ M})} = 1.7 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$
 (c) Since the rate law is first order in $[\text{OH}^-]$, if $[\text{OH}^-]$ is tripled, the rate triples.
 (d) If $[\text{OH}^-]$ and $[\text{CH}_3\text{Br}]$ both triple, the rate increases by a factor of $(3)(3) = 9$.
- 14.32 (a, b) $\text{rate} = k[\text{C}_2\text{H}_5\text{Br}][\text{OH}^-]; k = \frac{\text{rate}}{[\text{C}_2\text{H}_5\text{Br}][\text{OH}^-]}$
 at 298 K, $k = \frac{1.7 \times 10^{-7} \text{ M/s}}{[0.0477 \text{ M}][0.100 \text{ M}]} = 3.6 \times 10^{-5} \text{ M}^{-1}\text{s}^{-1}$
 (c) Adding an equal volume of ethyl alcohol reduces both $[\text{C}_2\text{H}_5\text{Br}]$ and $[\text{OH}^-]$ by a factor of two. new rate = $(1/2)(1/2) = 1/4$ of old rate
- 14.33 *Analyze/Plan.* Follow the logic in Sample Exercise 14.6. *Solve.*
 (a) From the data given, when $[\text{OCl}^-]$ doubles, rate doubles. When $[\text{I}^-]$ doubles, rate doubles. The reaction is first order in both $[\text{OCl}^-]$ and $[\text{I}^-]$. $\text{rate} = k[\text{OCl}^-][\text{I}^-]$
 (b) Using the first set of data:

$$k = \frac{\text{rate}}{[\text{OCl}^-][\text{I}^-]} = \frac{1.36 \times 10^{-4} \text{ M/s}}{(1.5 \times 10^{-3} \text{ M})(1.5 \times 10^{-3} \text{ M})} = 60.444 = 60 \text{ M}^{-1} \text{ s}^{-1}$$

 (c) $\text{rate} = \frac{60.444}{\text{M}\cdot\text{s}}(2.0 \times 10^{-3} \text{ M})(5.0 \times 10^{-4} \text{ M}) = 6.0444 \times 10^{-5} = 6.0 \times 10^{-5} \text{ M/s}$
- 14.34 (a) From the data given, when $[\text{ClO}_2]$ increases by a factor of 3 (experiment 2 to experiment 1), the rate increases by a factor of 9. When $[\text{OH}^-]$ increases by a factor of 3 (experiment 2 to experiment 3), the rate increases by a factor of 3. The reaction is second order in $[\text{ClO}_2]$ and first order in $[\text{OH}^-]$. $\text{rate} = k[\text{ClO}_2]^2[\text{OH}^-]$.
 (b) Using data from Expt 2:

$$k = \frac{\text{rate}}{[\text{ClO}_2]^2[\text{OH}^-]} = \frac{0.00276 \text{ M/s}}{(0.020 \text{ M})^2(0.030 \text{ M})} = 2.3 \times 10^2 \text{ M}^{-2}\text{s}^{-1}$$

 (c) $\text{rate} = 2.3 \times 10^2 \text{ M}^{-2} \text{ s}^{-1}(0.100 \text{ M})^2(0.050 \text{ M}) = 0.115 = 0.12 \text{ M/s}$
- 14.35 *Analyze/Plan.* Follow the logic in Sample Exercise 14.6 to deduce the rate law. Rearrange the rate law to solve for k and deduce units. Calculate a k value for each set of concentrations and then average the three values. *Solve.*

- (a) Doubling $[\text{NH}_3]$ while holding $[\text{BF}_3]$ constant doubles the rate (experiments 1 and 2). Doubling $[\text{BF}_3]$ while holding $[\text{NH}_3]$ constant doubles the rate (experiments 4 and 5).

Thus, the reaction is first order in both BF_3 and NH_3 ; rate = $k[\text{BF}_3][\text{NH}_3]$.

- (b) The reaction is second order overall.

(c) From experiment 1: $k = \frac{0.2130 \text{ M/s}}{(0.250 \text{ M})(0.250 \text{ M})} = 3.41 \text{ M}^{-1} \text{ s}^{-1}$

(Any of the five sets of initial concentrations and rates could be used to calculate the rate constant k . The average of these 5 values is $k_{\text{avg}} = 3.408 = 3.41 \text{ M}^{-1} \text{ s}^{-1}$)

(d) rate = $3.408 \text{ M}^{-1} \text{ s}^{-1} (0.100 \text{ M})(0.500 \text{ M}) = 0.1704 = 0.170 \text{ M/s}$

14.36

Analyze/Plan. Follow the logic in Sample Exercise 14.6 to deduce the rate law. Rearrange the rate law to solve for k and deduce units. Calculate a k value for each set of concentrations and then average the three values. *Solve.*

- (a) Doubling $[\text{NO}]$ while holding $[\text{O}_2]$ constant increases the rate by a factor of 4 (experiments 1 and 2). Doubling $[\text{O}_2]$ while holding $[\text{NO}]$ constant doubles the rate (experiments 2 and 3). The reaction is second order in $[\text{NO}]$ and first order in $[\text{O}_2]$. rate = $k[\text{NO}]^2[\text{O}_2]$

(b, c) From experiment 1: $k_1 = \frac{1.41 \times 10^{-2} \text{ M/s}}{(0.0126 \text{ M})^2 (0.0125 \text{ M})} = 7105 = 7.11 \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$

$$k_2 = 0.113 / (0.0252)^2 (0.0250) = 7118 = 7.12 \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$$

$$k_3 = 5.64 \times 10^{-2} / (0.0252)^2 (0.125) = 7105 = 7.11 \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$$

$$k_{\text{avg}} = (7105 + 7118 + 7105) / 3 = 7109 = 7.11 \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$$

(d) rate = $7.109 \times 10^3 \text{ M}^{-2} \text{ s}^{-1} (0.0750 \text{ M})^2 (0.0100 \text{ M}) = 0.3999 = 0.400 \text{ M/s}$

- (e) The data are given in terms of the disappearance of NO . Use Equation [14.4] to relate the disappearance of NO to the disappearance of O_2 .

$$-\Delta[\text{NO}] / 2\Delta t = -[\text{O}_2] / \Delta t$$

For the concentrations given in part (d), $\Delta[\text{NO}] / \Delta t = 0.400 \text{ M/s}$.

$$\Delta[\text{O}_2] / \Delta t = \Delta[\text{NO}] / 2\Delta t = 0.400 \text{ M/s} / 2 = 0.200 \text{ M/s}$$

14.37

Analyze/Plan. Follow the logic in Sample Exercise 4.6 to deduce the rate law. Rearrange the rate law to solve for k and deduce units. Calculate a k value for each set of concentrations and then average the three values. *Solve.*

- (a) Increasing $[\text{NO}]$ by a factor of 2.5 while holding $[\text{Br}_2]$ constant (experiments 1 and 2) increases the rate by a factor 6.25 or $(2.5)^2$. Increasing $[\text{Br}_2]$ by a factor of 2.5 while holding $[\text{NO}]$ constant increases the rate by a factor of 2.5. The rate law for the appearance of NOBr is: rate = $\Delta[\text{NOBr}] / \Delta t = k[\text{NO}]^2[\text{Br}_2]$.

(b) From experiment 1: $k_1 = \frac{24 \text{ M/s}}{(0.10 \text{ M})^2 (0.20 \text{ M})} = 1.20 \times 10^4 = 1.2 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$

$$k_2 = 150 / (0.25)^2(0.20) = 1.20 \times 10^4 = 1.2 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$$

$$k_3 = 60 / (0.10)^2(0.50) = 1.20 \times 10^4 = 1.2 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$$

$$k_4 = 735 / (0.35)^2(0.50) = 1.2 \times 10^4 = 1.2 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$$

$$k_{\text{avg}} = (1.2 \times 10^4 + 1.2 \times 10^4 + 1.2 \times 10^4 + 1.2 \times 10^4) / 4 = 1.2 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$$

(c) Use the reaction stoichiometry and Equation [14.4] to relate the designated rates. $\Delta[\text{NOBr}] / 2\Delta t = -\Delta[\text{Br}_2] / \Delta t$; the rate of disappearance of Br_2 is half the rate of appearance of NOBr .

(d) Note that the data are given in terms of appearance of NOBr .

$$\frac{-\Delta[\text{Br}_2]}{\Delta t} = \frac{k[\text{NO}]^2[\text{Br}_2]}{2} = \frac{1.2 \times 10^4}{2 \text{ M}^2 \text{ s}} \times (0.075 \text{ M})^2 \times (0.250 \text{ M}) = 8.4 \text{ M/s}$$

14.38

(a) Increasing $[\text{S}_2\text{O}_8^{2-}]$ by a factor of 1.5 while holding $[\text{I}^-]$ constant increases the rate by a factor of 1.5 (Experiments 1 and 2). Doubling $[\text{S}_2\text{O}_8^{2-}]$ and increasing $[\text{I}^-]$ by a factor of 1.5 triples the rate ($2 \times 1.5 = 3$, experiments 1 and 3). Thus the reaction is first order in both $[\text{S}_2\text{O}_8^{2-}]$ and $[\text{I}^-]$; rate = $k [\text{S}_2\text{O}_8^{2-}] [\text{I}^-]$.

(b) $k = \text{rate} / [\text{S}_2\text{O}_8^{2-}] [\text{I}^-]$

$$k_1 = 2.6 \times 10^{-6} \text{ M/s} / (0.018 \text{ M})(0.036 \text{ M}) = 4.01 \times 10^{-3} = 4.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

$$k_2 = 3.9 \times 10^{-6} / (0.027)(0.036) = 4.01 \times 10^{-3} = 4.01 \times 10^{-3} = 4.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

$$k_3 = 7.8 \times 10^{-6} / (0.036)(0.054) = 4.01 \times 10^{-3} = 4.01 \times 10^{-3} = 4.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

$$k_4 = 1.4 \times 10^{-5} / (0.050)(0.072) = 3.89 \times 10^{-3} = 3.9 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

$$k_{\text{avg}} = 3.98 \times 10^{-3} = 4.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

(c) $-\Delta[\text{S}_2\text{O}_8^{2-}] / \Delta t = -\Delta[\text{I}^-] / 3\Delta t$; the rate of disappearance of $\text{S}_2\text{O}_8^{2-}$ is one-third the rate of disappearance of I^- .

(d) Note that the data are given in terms of disappearance of $\text{S}_2\text{O}_8^{2-}$.

$$\frac{-\Delta[\text{I}^-]}{\Delta t} = \frac{-3\Delta[\text{S}_2\text{O}_8^{2-}]}{\Delta t} = 3(3.98 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1})(0.025 \text{ M})(0.050 \text{ M}) = 1.5 \times 10^{-5} \text{ M/s}$$

Change of Concentration with Time (section 14.4)

14.39 (a) $[\text{A}]_0$ is the molar concentration of reactant A at time zero, the initial concentration of A. $[\text{A}]_t$ is the molar concentration of reactant A at time t. $t_{1/2}$ is the time required to reduce $[\text{A}]_0$ by a factor of 2, the time when $[\text{A}]_t = [\text{A}]_0/2$. k is the rate constant for a particular reaction. k is independent of reactant concentration but varies with reaction temperature.

(b) A graph of $\ln[\text{A}]$ vs time yields a straight line for a first-order reaction.

(c) On graph of $\ln[\text{A}]$ vs time, the rate constant, k , is the (-slope) of the straight line.

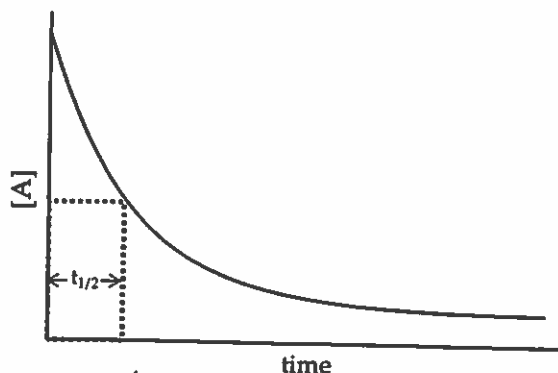
14.40 (a) A graph of $1/[\text{A}]$ vs time yields a straight line for a second-order reaction.

(b) On a graph of $1/[\text{A}]$ vs time, the slope of the straight line is the rate constant, k .

- (c) The half-life of a first-order reaction is independent of $[A]_0$, $t_{1/2} = 0.693/k$. Whereas, the half-life of a second-order reaction does depend on $[A]_0$, $t_{1/2} = 1/k[A]_0$.

14.41 For a reaction $A \rightarrow B$ that is zero-order in A, rate = k. A plot of [A] vs time will be linear, with a slope of -k. (A plot of [B] vs time will also be linear, with a slope of +k.)

14.42



- (a) The graph is not linear. For a reaction first-order in [A], rate changes as [A] changes and the plot of [A] vs time is not linear. If a graph of [A] vs time is linear, the reaction is zero-order in [A]; rate does not depend on [A]. (Or, a plot of $\ln[A]$ vs t would also be linear.)
- (b) The time at which $[A] = [A]_0/2$ is the half-life, $t_{1/2}$.
- 14.43 *Analyze/Plan.* The half-life of a first-order reaction depends only on the rate constant, $t_{1/2} = 0.693/k$. Use this relationship to calculate k for a given $t_{1/2}$, and, at a different temperature, $t_{1/2}$ given k. *Solve.*
- (a) $t_{1/2} = 2.3 \times 10^5 \text{ s}$; $t_{1/2} = 0.693/k$, $k = 0.693/t_{1/2}$
 $k = 0.693/2.3 \times 10^5 \text{ s} = 3.0 \times 10^{-6} \text{ s}^{-1}$
- (b) $k = 2.2 \times 10^{-5} \text{ s}^{-1}$. $t_{1/2} = 0.693/2.2 \times 10^{-5} \text{ s}^{-1} = 3.15 \times 10^4 = 3.2 \times 10^4 \text{ s}$
- 14.44 (a) For a first order reaction, $t_{1/2} = 0.693/k$.
 $t_{1/2} = 0.693/0.271 \text{ s}^{-1} = 2.5572 = 2.56 \text{ s}$
- (b) For a first order reaction, $\ln[A]_t - \ln[A]_0 = -kt$. $\ln[A]_t = -kt + \ln[A]_0$
 $[A]_0 = 0.050 \text{ M I}_2$, $t = 5.12 \text{ s}$, $k = 0.271 \text{ s}^{-1}$
 $\ln[I_2] = -0.271 \text{ s}^{-1} (5.12 \text{ s}) + \ln(0.050)$
 $\ln[I_2] = -4.3833$, $[I_2] = 0.0125 \text{ M}$
- Check.* 5.12 s is 2 half-lives. $[I_2]$ should be reduced by a factor of 4, and it is.
- 14.45 *Analyze/Plan.* Follow the logic in Sample Exercise 14.7. In this reaction, pressure is a measure of concentration. In (a) we are given k, $[A]_0$, t and asked to find $[A]_t$, using Equation [14.13], the integrated form of the first-order rate law. In (b), $[A]_t = 0.1[A]_0$, find t. *Solve.*

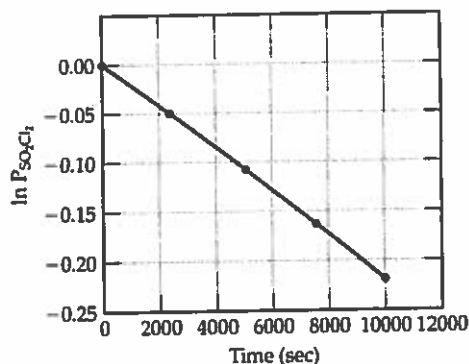
- (a) $\ln P_t = -kt + \ln P_0$; $P_0 = 450$ torr; $t = 60$ s
 $\ln P_{60} = -4.5 \times 10^{-2} \text{ s}^{-1}(60) + \ln(450) = -2.70 + 6.109 = 3.409$
 $P_{60} = 30.24 = 30$ torr
- (b) $P_t = 0.10 P_0$; $\ln(P_t/P_0) = -kt$
 $\ln(0.10 P_0/P_0) = -kt$, $\ln(0.10) = -kt$; $-\ln(0.10)/k = t$
 $t = -(-2.303)/4.5 \times 10^{-2} \text{ s}^{-1} = 51.2 = 51$ s

Check. From part (a), the pressure at 60 s is 30 torr, $P_t \sim 0.07 P_0$. In part (b) we calculate the time where $P_t = 0.10 P_0$ to be 51 s. This time should be smaller than 60 s, and it is. Data and results in the two parts are consistent.

- 14.46 (a) Using Equation [14.13] for a first order reaction: $\ln[A]_t = -kt + \ln[A]_0$
 $5.0 \text{ min} = 300 \text{ s}$; $[\text{N}_2\text{O}_5]_0 = (0.0250 \text{ mol}/2.0 \text{ L}) = 0.0125 = 0.013 \text{ M}$
 $\ln[\text{N}_2\text{O}_5]_{300} = -(6.82 \times 10^{-3} \text{ s}^{-1})(300 \text{ s}) + \ln(0.0125)$
 $\ln[\text{N}_2\text{O}_5]_{300} = -2.0460 + (-4.3820) = -6.4280 = -6.43$
 $[\text{N}_2\text{O}_5]_{300} = 1.616 \times 10^{-3} = 1.6 \times 10^{-3} \text{ M}$; mol $\text{N}_2\text{O}_5 = 1.616 \times 10^{-3} \text{ M} \times 2.0 \text{ L}$
 $= 3.2 \times 10^{-3} \text{ mol}$
- (b) $[\text{N}_2\text{O}_5]_t = 0.010 \text{ mol}/2.0 \text{ L} = 0.0050 \text{ M}$; $[\text{N}_2\text{O}_5]_0 = 0.0125 \text{ M}$
 $\ln(0.0050) = -(6.82 \times 10^{-3} \text{ s}^{-1})(t) + \ln(0.0125)$
 $t = \frac{-[\ln(0.0050) - \ln(0.0125)]}{(6.82 \times 10^{-3} \text{ s}^{-1})} = 134.35 = 1.3 \times 10^2 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} = 2.24 = 2.2 \text{ min}$
- (c) $t_{1/2} = 0.693/k = 0.693/6.82 \times 10^{-3} \text{ s}^{-1} = 101.6 = 102 \text{ s}$ or 1.69 min

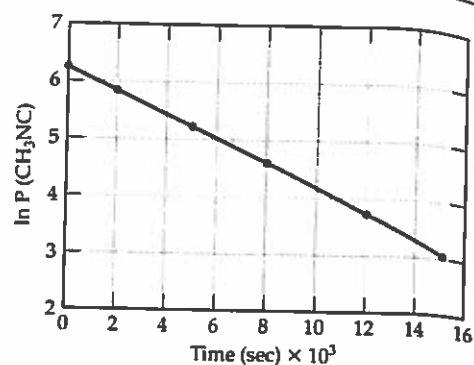
- 14.47 *Analyze/Plan.* Given reaction order, various values for t and P_t , find the rate constant for the reaction at this temperature. For a first-order reaction, a graph of $\ln P$ vs t is linear with a slope of $-k$. *Solve.*

$t(\text{s})$	$P_{\text{SO}_2\text{Cl}_2}$	$\ln P_{\text{SO}_2\text{Cl}_2}$
0	1.000	0
2500	0.947	-0.0545
5000	0.895	-0.111
7500	0.848	-0.165
10000	0.803	-0.219



Graph $\ln P_{\text{SO}_2\text{Cl}_2}$ vs. time. (Pressure is a satisfactory unit for a gas, since the concentration in moles/liter is proportional to P .) The graph is linear with slope $-2.19 \times 10^{-5} \text{ s}^{-1}$ as shown on the figure. The rate constant $k = -\text{slope} = 2.19 \times 10^{-5} \text{ s}^{-1}$.

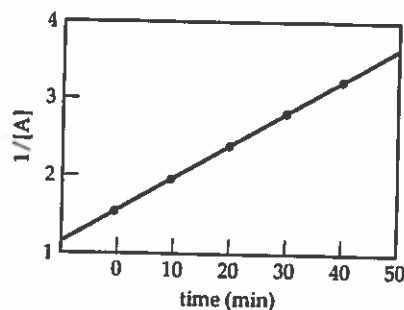
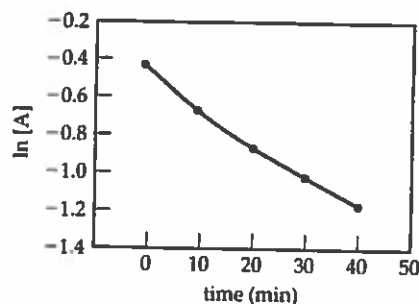
14.48	t(s)	P _{CH₃NC}	ln P _{CH₃NC}
	0	502	6.219
	2000	335	5.814
	5000	180	5.193
	8000	95.5	4.559
	12000	41.7	3.731
	15000	22.4	3.109



A graph of $\ln P$ vs t is linear with a slope of $-2.08 \times 10^{-4} \text{ s}^{-1}$. The rate constant, k , = $-\text{slope} = 2.08 \times 10^{-4} \text{ s}^{-1}$. Half-life = $t_{1/2} = 0.693/k = 3.33 \times 10^3 \text{ s}$.

- 14.49 *Analyze/Plan.* Given: mol A, t . Change mol to M at various times. Make both first- and second-order plots to see which is linear. *Solve.*

(a)	time(min)	mol A	[A] (M)	ln[A]	1/mol A
	0	0.065	0.65	-0.43	1.5
	10	0.051	0.51	-0.67	2.0
	20	0.042	0.42	-0.87	2.4
	30	0.036	0.36	-1.02	2.8
	40	0.031	0.31	-1.17	3.2

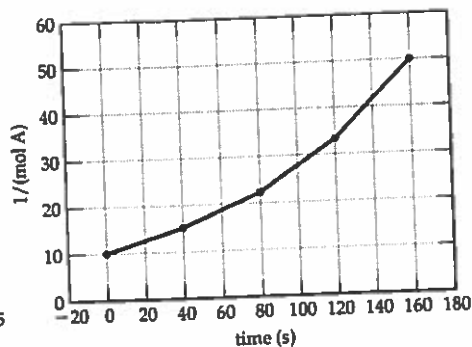
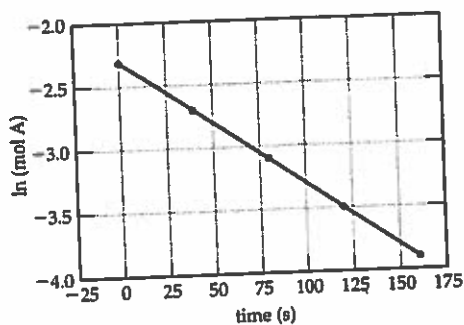


The plot of $1/[A]$ vs time is linear, so the reaction is second-order in $[A]$.

- (b) For a second-order reaction, a plot of $1/[A]$ vs. t is linear with slope k .
 $k = \text{slope} = (3.2 - 2.0) \text{ M}^{-1} / 30 \text{ min} = 0.040 \text{ M}^{-1} \text{ min}^{-1}$
 (The best fit to the line yields slope = $0.042 \text{ M}^{-1} \text{ min}^{-1}$.)
- (c) $t_{1/2} = 1/k[A]_0 = 1/(0.040 \text{ M}^{-1} \text{ min}^{-1})(0.65 \text{ M}) = 38.46 = 38 \text{ min}$
 (Using the "best-fit" slope, $t_{1/2} = 37 \text{ min}$.)

- 14.50 (a) Make both first- and second-order plots to see which is linear. Moles is a satisfactory concentration unit, since volume is constant.

time(s)	mol A	ln (mol A)	1/mol A
0	0.1000	-2.303	10.00
40	0.067	-2.70	14.9
80	0.045	-3.10	22.2
120	0.030	-3.51	33.3
160	0.020	-3.91	50.0



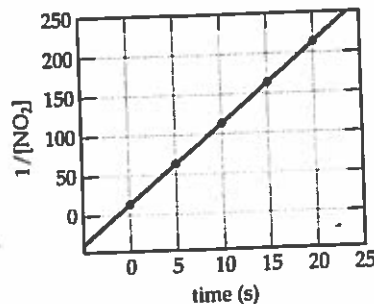
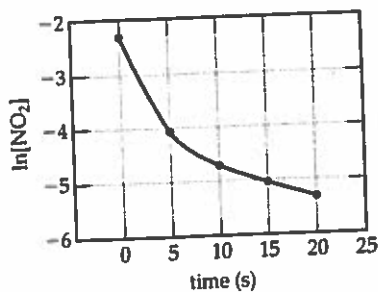
The plot of $\ln(\text{mol A})$ vs time is linear, so the reaction is first-order in A.

(b) $k = -\text{slope} = -[-3.91 - (-2.70)]/120 = 0.010083 = 0.0101 \text{ s}^{-1}$
 (The best fit to this line yields the same value for the slope, $0.01006 = 0.0101 \text{ s}^{-1}$)

(c) $t_{1/2} = 0.693/k = 0.693/0.010083 \text{ s}^{-1} = 68.7 \text{ s}$

14.51 *Analyze/Plan.* Follow the logic in Solution 14.49. Make both first and second order plots to see which is linear. *Solve.*

(a) time(s)	$[\text{NO}_2](M)$	$\ln[\text{NO}_2]$	$1/[\text{NO}_2]$
0.0	0.100	-2.303	10.0
5.0	0.017	-4.08	59
10.0	0.0090	-4.71	110
15.0	0.0062	-5.08	160
20.0	0.0047	-5.36	210



The plot of $1/[\text{NO}_2]$ vs time is linear, so the reaction is second order in NO_2 .

(b) The slope of the line is $(210 - 59) M^{-1} / 15.0 s = 10.07 = 10 M^{-1}s^{-1} = k$. (The slope of the best-fit line is $10.02 = 10 M^{-1}s^{-1}$.)

(c) From the results above, the rate law is: $\text{rate} = k[\text{NO}_2]^2 = 10 M^{-1}s^{-1}[\text{NO}_2]^2$
Using the rate law, calculate the rate at each of the given initial concentrations.

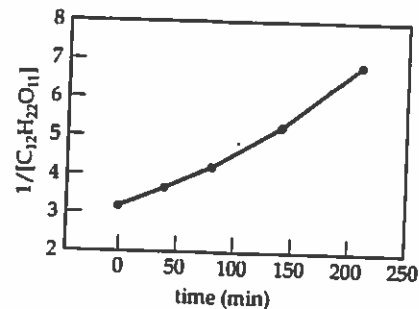
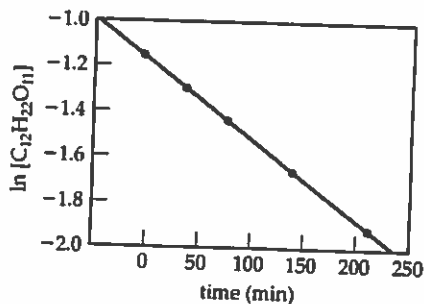
$$\text{Rate @ } 0.200 M = 10 M^{-1}s^{-1}[\text{NO}_2]^2 = 10 M^{-1}s^{-1}[0.200 M]^2 = 0.400 M/s$$

$$\text{Rate @ } 0.100 M = 10 M^{-1}s^{-1}[\text{NO}_2]^2 = 10 M^{-1}s^{-1}[0.100 M]^2 = 0.100 M/s$$

$$\text{Rate @ } 0.050 M = 10 M^{-1}s^{-1}[\text{NO}_2]^2 = 10 M^{-1}s^{-1}[0.050 M]^2 = 0.025 M/s$$

14.52 (a) Make both first- and second-order plots to see which is linear.

time(min)	$[\text{C}_{12}\text{H}_{22}\text{O}_{11}](M)$	$\ln[\text{C}_{12}\text{H}_{22}\text{O}_{11}]$	$1/[\text{C}_{12}\text{H}_{22}\text{O}_{11}]$
0	0.316	-1.152	3.16
39	0.274	-1.295	3.65
80	0.238	-1.435	4.20
140	0.190	-1.661	5.26
210	0.146	-1.924	6.85



The plot of $\ln [\text{C}_{12}\text{H}_{22}\text{O}_{11}]$ is linear, so the reaction is first order in $\text{C}_{12}\text{H}_{22}\text{O}_{11}$.

(b) $k = -\text{slope} = -[-1.924 - (-1.295)] / 171 \text{ min} = 3.68 \times 10^{-3} \text{ min}^{-1}$

(The slope of the best-fit line is $-3.67 \times 10^{-3} \text{ min}^{-1}$.)

(c) For a reaction zero-order in sucrose, the rate does not change as [sucrose] changes. A plot of [sucrose] vs time is linear with negative slope, until all reactant is consumed. $[\text{sucrose}]_t = -kt + [\text{sucrose}]_0$

$$\text{@39 min, } [\text{sucrose}] = -3.68 \times 10^{-3} \text{ min}^{-1}(39 \text{ min}) + 0.316 M = 0.17 M$$

$$\text{@80 min, } [\text{sucrose}] = -3.68 \times 10^{-3} \text{ min}^{-1}(80 \text{ min}) + 0.316 M = 0.022 M$$

$$\text{@140 min, } [\text{sucrose}] = -3.68 \times 10^{-3} \text{ min}^{-1}(140 \text{ min}) + 0.316 M = 0 M$$

$$\text{@210 min, } [\text{sucrose}] = 0 M. \text{ All sucrose is consumed at } (0.316 / 3.68 \times 10^{-3} \text{ min}^{-1}) = 85.9 \text{ min.}$$

Temperature and Rate (section 14.5)

- 14.53 (a) The energy of the collision and the orientation of the molecules when they collide determine whether a reaction will occur.
- (b) According to the kinetic-molecular theory (Chapter 10), the higher the temperature, the greater the speed and kinetic energy of the molecules. Therefore, at a higher temperature, there are more total collisions and each collision is more energetic.
- (c) Assuming other conditions remain the same, the rate and therefore the rate constant usually increase with an increase in reaction temperature.
- 14.54 (a) The orientation factor is less important in $\text{H} + \text{Cl} \rightarrow \text{HCl}$, because the reactants are monatomic and spherical (nondirectional); all collision orientations are equally effective.
- (b) The kinetic-molecular theory tells us that at some temperature T , there will be a distribution of molecular speeds and kinetic energies, and that the average kinetic energy of the sample is proportional to temperature. That is, as temperature of the sample increases, the average speed and kinetic energy of the molecules increases. At higher temperatures, there will be more molecular collisions (owing to greater speeds) and more energetic collisions (owing to greater kinetic energies). Overall there will be more collisions that have sufficient energy to form an activated complex, and the reaction rate will be greater.

- 14.55 *Analyze/Plan.* Given the temperature and energy, use Equation [14.18] to calculate the fraction of Ar atoms that have at least this energy. *Solve.*

$$f = e^{-E_a/RT} \quad E_a = 10.0 \text{ kJ/mol} = 1.00 \times 10^4 \text{ J/mol}; \quad T = 400 \text{ K} (127^\circ\text{C})$$

$$-E_a/RT = -\frac{1.00 \times 10^4 \text{ J/mol}}{400 \text{ K}} \times \frac{\text{mol} \cdot \text{K}}{8.314 \text{ J}} = -3.0070 = -3.01$$

$$f = e^{-3.0070} = 4.9 \times 10^{-2}$$

At 400 K, approximately 1 out of 20 molecules has this kinetic energy.

- 14.56 (a) $f = e^{-E_a/RT} \quad E_a = 160 \text{ kJ/mol} = 1.60 \times 10^5 \text{ J/mol}, \quad T = 500 \text{ K}$

$$-E_a/RT = -\frac{1.60 \times 10^5 \text{ J/mol}}{500 \text{ K}} \times \frac{\text{mol} \cdot \text{K}}{8.314 \text{ J}} = -38.489 = -38.5$$

$$f = e^{-38.489} = 1.924 \times 10^{-17} = 2 \times 10^{-17}$$

- (b) $-E_a/RT = -\frac{1.60 \times 10^5 \text{ J/mol}}{520 \text{ K}} \times \frac{\text{mol} \cdot \text{K}}{8.314 \text{ J}} = -37.009 = -37.0$

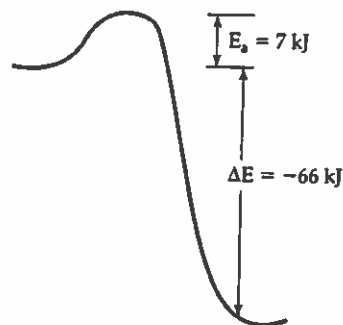
$$f = e^{-37.009} = 8.45712 \times 10^{-17} = 8.46 \times 10^{-17}$$

$$\frac{f \text{ at } 520 \text{ K}}{f \text{ at } 500 \text{ K}} = \frac{8.46 \times 10^{-17}}{1.92 \times 10^{-17}} = 4.41$$

An increase of 20 K means that 4.41 times more molecules have this energy.

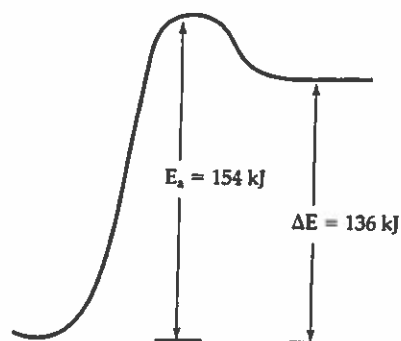
- 14.57 *Analyze/Plan.* Use the definitions of activation energy ($E_{\max} - E_{\text{react}}$) and ΔE ($E_{\text{prod}} - E_{\text{react}}$) to sketch the graph and calculate E_a for the reverse reaction. *Solve.*

(a)

(b) $E_a(\text{reverse}) = 73 \text{ kJ}$

- 14.58 *Analyze/Plan.* Use the definitions of activation energy ($E_{\max} - E_{\text{react}}$) and ΔE ($E_{\text{prod}} - E_{\text{react}}$) to sketch the graph and calculate E_a for the reverse reaction. *Solve.*

(a)

(b) $E_a(\text{reverse}) = 18 \text{ kJ}$

- 14.59 (a) False. If you compare two reactions with similar collision factors, the one with the larger activation energy will be *slower*.
 (b) False. A reaction that has a small rate constant will have either a small frequency factor (A), a large activation energy (E_a), or both.
 (c) True.
- 14.60 (a) False. If you measure the rate constant for a reaction at different temperatures, you can calculate the overall activation energy, E_a , for the reaction.
 (b) False. Exothermic reactions are not necessarily faster than endothermic reactions. (The rate of a reaction is not determined by the overall enthalpy change going from reactants to products.)
 (c) False. If you double the temperature for a reaction, there is no change to the activation energy, E_a .
- 14.61 Assuming all collision factors (A) to be the same, reaction rate depends only on E_a ; it is independent of ΔE . Based on the magnitude of E_a , reaction (b) is fastest and reaction (c) is slowest.

14.62 E_a for the reverse reaction is:

$$(a) 45 - (-25) = 70 \text{ kJ} \quad (b) 35 - (-10) = 45 \text{ kJ} \quad (c) 55 - 10 = 45 \text{ kJ}$$

Based on the magnitude of E_a , the reverse of reactions (b) and (c) occur at the same rate, which is faster than the reverse of reaction (a).

14.63 *Analyze/Plan.* Given k_1 , at T_1 , calculate k_2 at T_2 . Change T to Kelvins, then use the Equation [14.21] to calculate k_2 . *Solve.*

$$T_1 = 20^\circ\text{C} + 273 = 293 \text{ K}; \quad T_2 = 60^\circ\text{C} + 273 = 333 \text{ K}; \quad k_1 = 2.75 \times 10^{-2} \text{ s}^{-1}$$

$$(a) \quad \ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \left(\frac{1}{333} - \frac{1}{293}\right) = \frac{75.5 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol}} (-4.1 \times 10^{-4})$$

$$\ln(k_1/k_2) = -3.7229 = -3.7; \quad k_1/k_2 = 0.0242 = 0.02; \quad k_2 = \frac{0.0275 \text{ s}^{-1}}{0.0242} = 1.14 = 1 \text{ s}^{-1}$$

$$(b) \quad \ln\left(\frac{k_1}{k_2}\right) = \frac{125 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol}} \left(\frac{1}{333} - \frac{1}{293}\right) = -6.1638 = -6.2$$

$$k_1/k_2 = 2.104 \times 10^{-3} = 2 \times 10^{-3}; \quad k_2 = \frac{0.0275 \text{ s}^{-1}}{2.104 \times 10^{-3}} = 13.07 = 1 \times 10 \text{ s}^{-1}$$

(c) The method in parts (a) and (b) assumes that the collision model and thus the Arrhenius equation describe the kinetics of the reactions. That is, activation energy is constant over the temperature range under consideration. There is no assumption about temperature dependence of the frequency factor, because it drops out of the difference equation by subtraction.

$$14.64 \quad T_1 = 737^\circ\text{C} + 273 = 1010 \text{ K}, \quad k_1 = 0.0796 \text{ M}^{-1}\text{s}^{-1};$$

$$T_2 = 947^\circ\text{C} + 273 = 1220 \text{ K}, \quad k_2 = 0.0815 \text{ M}^{-1}\text{s}^{-1}$$

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

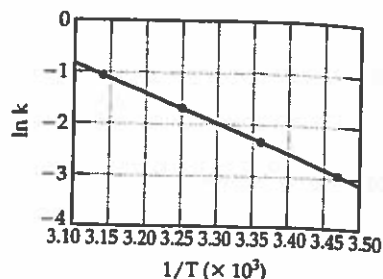
$$\ln\left(\frac{0.0796}{0.0815}\right) = \frac{E_a}{8.314 \text{ J/mol}} \left(\frac{1}{1220} - \frac{1}{1010}\right)$$

$$-0.023589 = \frac{E_a (-1.704 \times 10^{-4})}{8.314 \text{ J/mol}}$$

$$E_a = \frac{8.314 (-0.023589) \text{ J/mol}}{(-1.704 \times 10^{-4})} = 1.151 \times 10^3 \text{ J/mol} = 1.15 \text{ kJ/mol}$$

14.65 *Analyze/Plan.* Follow the logic in Sample Exercise 14.11. *Solve.*

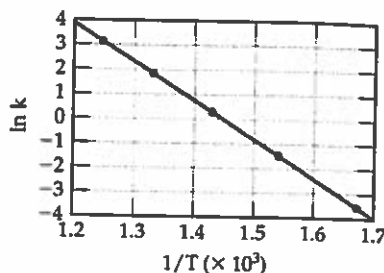
k	ln k	T(K)	1/T ($\times 10^3$)
0.0521	-2.955	288	3.47
0.101	-2.293	298	3.36
0.184	-1.693	308	3.25
0.332	-1.103	318	3.14



The slope, -5.71×10^3 , equals $-E_a/R$. Thus,
 $E_a = 5.71 \times 10^3 \times 8.314 \text{ J/mol} = 47.5 \text{ kJ/mol}$.

14.66

k	ln k	T(K)	1/T ($\times 10^3$)
0.028	-3.58	600	1.67
0.22	-1.51	650	1.54
1.3	0.26	700	1.43
6.0	1.79	750	1.33
23	3.14	800	1.25



Using the relationship $\ln k = \ln A - E_a/RT$, the slope, $-15.94 \times 10^3 = -16 \times 10^3$, is $-E_a/R$.
 $E_a = 15.94 \times 10^3 \times 8.314 \text{ J/mol} = 1.3 \times 10^2 \text{ kJ/mol}$. To calculate A, we will use the rate data at 700 K. From the equation given above, $0.262 = \ln A - 15.94 \times 10^3/700$;
 $\ln A = 0.262 + 22.771$. $A = 1.0 \times 10^{10}$.

14.67 *Analyze/Plan.* Given E_a , find the ratio of rates for a reaction at two temperatures. Assuming initial concentrations are the same at the two temperatures, the ratio of rates will be the ratio of rate constants, k_1/k_2 . Use Equation [14.21] to calculate this ratio. *Solve.*

$$T_1 = 50^\circ\text{C} + 273 = 323 \text{ K}; T_2 = 0^\circ\text{C} + 273 = 273 \text{ K}$$

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] = \frac{65.7 \text{ kJ/mol}}{8.314 \text{ J/mol}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} \left[\frac{1}{273} - \frac{1}{323} \right]$$

$$\ln(k_1/k_2) = 7.902 \times 10^3 (5.670 \times 10^{-4}) = 4.481 = 4.5; k_1/k_2 = 88.3 = 9 \times 10^1$$

The reaction will occur 90 times faster at 50°C , assuming equal initial concentrations and Arrhenius kinetics.

14.68 (a) $T_1 = 77^\circ\text{F}; ^\circ\text{C} = 5/9 (^\circ\text{F} - 32) = 5/9 (77 - 32) = 25^\circ\text{C} = 298 \text{ K}$

$$T_2 = 59^\circ\text{F}; ^\circ\text{C} = 5/9 (59 - 32) = 15^\circ\text{C} = 288 \text{ K}; k_1/k_2 = 6$$

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]; \ln(6) = \frac{E_a}{8.314 \text{ J/mol}} \left[\frac{1}{288} - \frac{1}{298} \right]$$

$$E_a = \frac{\ln(6)(8.314 \text{ J/mol})}{1.165 \times 10^{-4}} = 1.28 \times 10^5 \text{ J} = 1.3 \times 10^2 \text{ kJ/mol}$$

$$T_1 = 77^\circ\text{F} = 25^\circ\text{C} = 298 \text{ K}; T_2 = 41^\circ\text{F} = 5^\circ\text{C} = 278 \text{ K}, k_1/k_2 = 40$$

$$\ln(40) = \frac{E_a}{8.314 \text{ J/mol}} \left[\frac{1}{278} - \frac{1}{296} \right]; E_a = \frac{\ln(40)(8.314 \text{ J/mol})}{2.414 \times 10^{-4}}$$

$$E_a = 1.27 \times 10^5 \text{ J} = 1.3 \times 10^2 \text{ kJ/mol}$$

The values are amazingly consistent, considering the precision of the data.

- (b) For a first order reaction, $t_{1/2} = 0.693/k$, $k = 0.693/t_{1/2}$

$$k_1 \text{ at } 298 \text{ K} = 0.693/2.7 \text{ yr} = 0.257 = 0.26 \text{ yr}^{-1}$$

$$T_1 = 298 \text{ K}, T_2 = 273 - 15^\circ\text{C} = 258 \text{ K}$$

$$\ln\left(\frac{0.257}{k_2}\right) = \frac{1.27 \times 10^5 \text{ J}}{8.314 \text{ J/mol}} \left[\frac{1}{258} - \frac{1}{298} \right] = 7.9497$$

$$0.257/k_2 = e^{7.9497} = 2.835 \times 10^3; k_2 = 0.257/2.835 \times 10^3 = 9.066 \times 10^{-5} = 9.1 \times 10^{-5} \text{ yr}^{-1}$$

$$t_{1/2} = 0.693/k = 0.693/9.066 \times 10^{-5} = 7.64 \times 10^3 \text{ yr} = 7.6 \times 10^3 \text{ yr}$$

Reaction Mechanisms (section 14.6)

- 14.69 (a) An *elementary reaction* is a process that occurs in a single event; the order is given by the coefficients in the balanced equation for the reaction.
- (b) A *unimolecular* elementary reaction involves only one reactant molecule; the activated complex is derived from a single molecule. A *bimolecular* elementary reaction involves two reactant molecules in the activated complex and the overall process.
- (c) A *reaction mechanism* is a series of elementary reactions that describe how an overall reaction occurs and explain the experimentally determined rate law.
- 14.70 (a) The *molecularity* of a process indicates the number of molecules that participate as reactants in the process. A unimolecular process has one reactant molecule, a bimolecular process has two reactant molecules and a termolecular process has three reactant molecules.
- (b) Termolecular processes are rare because it is highly unlikely that three molecules will simultaneously collide with the correct energy and orientation to form an activated complex.
- (c) An *intermediate* is a substance that is produced and then consumed during a chemical reaction. It does not appear in the balanced equation for the overall reaction.
- 14.71 A *transition state* is a high energy complex formed when one or more reactants collide and distort in a way that can lead to formation of product(s). An *intermediate* is the product of an early elementary reaction in a multistep reaction mechanism. A transition state occurs at an energy maximum or peak of a reaction profile such as Figure 14.20. An intermediate exists at an energy minimum or trough of a reaction profile. Every reaction, single- or multi-step, has a transition state. Only multistep reactions have intermediates.

- 14.72 A *rate-determining step* is the slow step in a reaction mechanism. It limits the overall reaction rate.
- 14.73 *Analyze/Plan.* Elementary reactions occur as a single step, so the molecularity is determined by the number of reactant molecules; the rate law reflects reactant stoichiometry. *Solve.*
- (a) unimolecular, rate = $k[\text{Cl}_2]$
 (b) bimolecular, rate = $k[\text{OCl}^-][\text{H}_2\text{O}]$
 (c) bimolecular, rate = $k[\text{NO}][\text{Cl}_2]$
- 14.74 (a) bimolecular, rate = $k[\text{NO}]^2$
 (b) unimolecular, rate = $k[\text{C}_3\text{H}_6]$
 (c) unimolecular, rate = $k[\text{SO}_3]$
- 14.75 *Analyze/Plan.* Use the definitions of the terms 'intermediate' and 'exothermic', along with the characteristics of reaction profiles, to answer the questions. *Solve.*
- This is a three-step mechanism, $\text{A} \rightarrow \text{B}$, $\text{B} \rightarrow \text{C}$, and $\text{C} \rightarrow \text{D}$.
- (a) There are 2 intermediates, B and C.
 (b) There are 3 energy maxima in the reaction profile, so there are 3 transition states.
 (c) Step $\text{C} \rightarrow \text{D}$ has the lowest activation energy, so it is fastest.
 (d) The energy of D is slightly greater than the energy of A, so the overall reaction is endothermic.
- 14.76 (a) Two elementary reactions; two energy maxima
 (b) One intermediate; one energy minimum between reactants and products
 (c) The second step is rate-limiting; second energy maximum and E_a is larger.
 (d) Overall reaction is exothermic; energy of products is lower than energy of reactants.
- 14.77 *Analyze/Plan.* Follow the logic in Sample Exercise 14.14. *Solve.*
- (a) $\text{H}_2(\text{g}) + \text{ICl}(\text{g}) \rightarrow \text{HI}(\text{g}) + \text{HCl}(\text{g})$
 $\text{HI}(\text{g}) + \text{ICl}(\text{g}) \rightarrow \text{I}_2(\text{g}) + \text{HCl}(\text{g})$
 $\text{H}_2(\text{g}) + 2\text{ICl}(\text{g}) \rightarrow \text{I}_2(\text{g}) + 2\text{HCl}(\text{g})$
- (b) Intermediates are produced and consumed during reaction. HI is the intermediate.
 (c) The slow step determines the rate law for the overall reaction. If the first step is slow, the observed rate law is: rate = $k[\text{H}_2][\text{ICl}]$.
- 14.78 (a) $2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$
 (b) $\text{IO}^-(\text{aq})$ is the intermediate.
 (c) rate = $k[\text{H}_2\text{O}_2][\text{I}^-]$

14.79

Analyze. Given data on concentration of a reactant vs time, determine whether the proposed reaction mechanism is consistent with the data. *Plan.* Based on the graph, decide the order of reaction with respect to [NO]. Write the two possible rate laws, depending on which step is rate-determining. Decide if one of the rate laws, and thus the mechanism, is consistent with the rate data. *Solve.*

The graph of $1/[\text{NO}]$ vs time is linear with positive slope, indicating that the reaction is second order in [NO]. The rate law will include $[\text{NO}]^2$. We have no information about reaction order with respect to $[\text{Cl}_2]$.

If the first step is slow, the observed rate law is the rate law for this step: $\text{rate} = k[\text{NO}][\text{Cl}_2]$. Since the observed rate law is second-order in [NO], the second step must be slow relative to the first step. Follow the logic in Sample Exercise 14.15 for determining the rate law of a mechanism with a fast initial step.

From the rate-determining second step, $\text{rate} = k[\text{NOCl}_2][\text{NO}]$.

Assuming the first step is a fast equilibrium, $k_1[\text{NO}][\text{Cl}_2] = k_{-1}[\text{NOCl}_2]$.

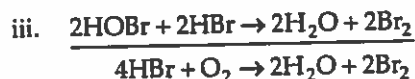
Solving for $[\text{NOCl}_2]$ in terms of $[\text{NO}][\text{Cl}_2]$, $[\text{NOCl}_2] = \frac{k_1}{k_{-1}}[\text{NO}][\text{Cl}_2]$

$$\text{rate} = \frac{k_2 k_1}{k_{-1}} [\text{NO}][\text{Cl}_2][\text{NO}] = [\text{NO}]^2 [\text{Cl}_2]$$

This rate law is second order in [NO]. It is consistent with the observed data.

[The graph of $1/[\text{NO}]$ vs time is linear with positive slope, indicating that the reaction is second order in [NO]. The rate law obtained by assuming the second step is rate determining is: $\text{rate} = [\text{NO}]^2 [\text{Cl}_2]$. The two step mechanism is consistent with the data.]

14.80



- (b) The observed rate law is: $\text{rate} = k[\text{HBr}][\text{O}_2]$, the rate law for the first elementary step. The first step must be rate-determining.
- (c) HOBr and HBr are both intermediates; HOBr is produced in i and consumed in ii and HBr is produced in ii and consumed in iii.
- (d) Since the first step is rate-determining, it is possible that neither of the intermediates accumulates enough to be detected. This does not disprove the mechanism, but indicates that steps ii and iii are very fast, relative to step i.

Catalysis (section 14.7)

- 14.81 (a) A catalyst is a substance that changes (usually increases) the speed of a chemical reaction without undergoing a permanent chemical change itself.

- (b) A homogeneous catalyst is in the same phase as the reactants; a heterogeneous catalyst is in a different phase and is usually a solid.
- (c) A catalyst has no effect on the overall enthalpy change for a reaction. A catalyst does affect activation energy, E_a , which is one way that it changes reaction rate. It can also affect the frequency factor, A .
- 14.82 (a) The smaller the particle size of a solid catalyst, the greater the surface area. The greater the surface area, the more active sites and the greater the increase in reaction rate.
- (b) Adsorption is the binding of reactants onto the surface of the heterogeneous catalyst. It is usually the first step in the catalyzed reaction.

14.83 *Analyze/Plan.* Use the structure and unit cell edge of Pt, along with the formulas for volume and surface area of a sphere, to calculate the number of Pt atoms in a 2-nm sphere and on the surface of a 2-nm sphere.

- (a) For a Pt sphere with a 2.0 nm diameter, radius = 1.0 nm.

$$V = 4/3\pi r^3 = \frac{4\pi (1.0 \text{ nm})^3}{3} \times \frac{10^3 \text{ \AA}^3}{1^3 \text{ nm}^3} = 4.188879 \times 10^3 = 4.2 \times 10^3 \text{ \AA}^3$$

In a face-centered cubic metal structure, there are 4 metal atoms per unit cell. The volume of the unit cell is $(3.924 \text{ \AA})^3 = 60.42 \text{ \AA}^3$

$$\frac{4 \text{ Pt atoms}}{60.42 \text{ \AA}^3} \times 4.1889 \times 10^3 \text{ \AA}^3 = 277.3 = 2.8 \times 10^2 \text{ Pt atoms in a 2.0-nm sphere}$$

- (b) Assume that the "footprint" of an atom is its cross-sectional area, the area of a circle with the radius of the atom. The area of this circle is πr^2 . The diameter, d , of a Pt atom is 2.8 \AA, so $r = d/2 = 1.4 \text{ \AA}$. The footprint of the Pt atom is then
- $$\pi(1.4 \text{ \AA})^2 = 6.1575 = 6.2 \text{ \AA}^2$$

The surface area of the 2.0-nm sphere is

$$4\pi r^2 = 4\pi (1.0 \text{ nm})^2 \times \frac{10^2 \text{ \AA}^2}{1^2 \text{ nm}^2} = 12.56637 \times 10^2 = 1.3 \times 10^3 \text{ \AA}^2$$

$$\frac{1 \text{ Pt atoms}}{6.1575 \text{ \AA}^2} \times 1.2566 \times 10^3 \text{ \AA}^2 = 204.1 = 2.0 \times 10^2 \text{ surface Pt atoms on a 2.0-nm sphere.}$$

- (c) $\frac{204 \text{ surface Pt atoms}}{277 \text{ total Pt atoms}} \times 100 = 74\% \text{ Pt atoms on the surface}$

- (d) For a 5.0-nm Pt sphere, radius = 2.5 nm

$$V = 4/3\pi r^3 = \frac{4\pi (2.50 \text{ nm})^3}{3} \times \frac{10^3 \text{ \AA}^3}{1^3 \text{ nm}^3} = 65.4498 \times 10^3 = 6.5 \times 10^4 \text{ \AA}^3$$

$$\frac{4 \text{ Pt atoms}}{60.42 \text{ \AA}^3} \times 65.4498 \times 10^3 \text{ \AA}^3 = 4,333 = 4.3 \times 10^3 \text{ Pt atoms in a 5.0-nm sphere}$$

The surface area of the 5.0-nm sphere is

$$4\pi r^2 = 4\pi (2.5 \text{ nm})^2 \times \frac{10^2 \text{ \AA}^2}{1^2 \text{ nm}^2} = 7853.98 = 7.9 \times 10^3 \text{ \AA}^2$$

$$\frac{1 \text{ Pt atoms}}{6.1575 \text{ \AA}^2} \times 7.854 \times 10^3 \text{ \AA}^2 = 1275.5 = 1.3 \times 10^3 \text{ surface Pt atoms on a 5.0-nm sphere}$$

$$\frac{1276 \text{ surface Pt atoms}}{4333 \text{ total Pt atoms}} \times 100 = 29\% \text{ Pt atoms on the surface}$$

The calculations in parts (b) and (d) overestimate the number of Pt atoms on the surface of the sphere, because they do not account for empty space between atoms. For the purpose of comparison, it is most important that we use the same method for both spheres.

[Alternatively, use one face of a face-centered cubic unit cell as a model for the surface area that Pt atoms will occupy. On a face, there is the cross-section of 1 Pt atom in the center and $\frac{1}{4}$ Pt atom at each corner. This amounts to the cross-sections of two Pt atoms in $(3.924 \text{ \AA})^2 = 15.398 = 15.4 \text{ \AA}^2$

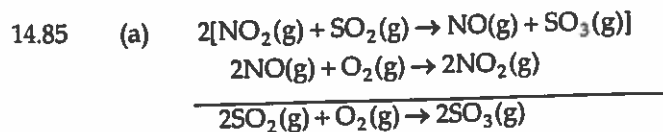
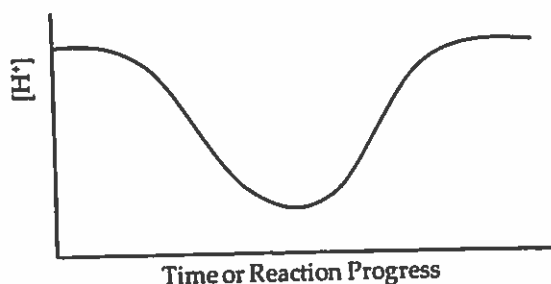
$$\frac{2 \text{ Pt atoms}}{15.40 \text{ \AA}^2} \times 1.2566 \times 10^3 \text{ \AA}^2 = 163.2 = 1.6 \times 10^2 \text{ surface Pt atoms on a 2.0-nm sphere.}$$

$$\frac{163 \text{ surface Pt atoms}}{277 \text{ total Pt atoms}} \times 100 = 59\% \text{ Pt atoms on the surface}$$

Similarly, in a 5.0-nm sphere, there are 1.0×10^3 Pt atoms on the surface, 24% of the total Pt atoms.]

- (e) Both surface models predict that the 2.0-nm sphere will be more catalytically active, because it has a much greater percentage of its atoms on the surface, where they can participate in the chemical reaction.

- 14.84 For an acid-catalyzed reaction in solution, H^+ is a homogeneous catalyst. It is consumed and then regenerated during the reaction. (This assumes that H^+ is present in excess and that H^+ is not a reactant, that the reactants are neither acids nor bases.) The $[\text{H}^+]$ is a maximum at $t = 0$ and when the reaction is complete.



- (b) $\text{NO}_2(\text{g})$ is a catalyst because it is consumed and then reproduced in the reaction sequence. ($\text{NO}(\text{g})$ is an intermediate because it is produced and then consumed.)
- (c) Since NO_2 is in the same state as the other reactants, this is homogeneous catalysis.

- 14.90 Just as the π electrons in C_2H_4 are attracted to the surface of a hydrogenation catalyst, the nonbonding electron density on S causes compounds of S to be attracted to these same surfaces. Strong interactions could cause the sulfur compounds to be permanently attached to the surface, blocking active sites and reducing adsorption of alkenes for hydrogenation.
- 14.91 (a) Living organisms operate efficiently in a very narrow temperature range; heating to increase reaction rate is not an option. Therefore, the role of enzymes as homogeneous catalysts that speed up desirable reactions without heating and undesirable side-effects is crucial for biological systems.
- (b) *catalase*: $2H_2O_2 \rightarrow 2H_2O + O_2$; *nitrogenase*: $N_2 \rightarrow 2NH_3$ (nitrogen fixation)
- (c) This model for enzyme kinetics is similar to the mechanism detailed in Sample Exercise 14.15, where step one is a fast equilibrium and step two is slow and rate-determining. This model assumes that the rate of the bound substrate, ES, being chemically transformed into bound product is slow and rate-determining.
- 14.92 The individual structure of each enzyme molecule leads to a unique coiling and folding pattern. The resulting shape and electronic properties of the active site in each enzyme leads to its substrate specificity.
- 14.93 Let k and E_a equal the rate constant and activation energy without the enzyme (uncatalyzed). Let k_c and E_{ac} equal the rate constant and activation energy with the enzyme (catalyzed). A is the same for the uncatalyzed and catalyzed reactions. The difference in activation energies is $E_{ac} - E_a$, $k_c = 1.0 \times 10^6 s^{-1}$, $k = 0.039 s^{-1}$, $T = 25^\circ C = 298 K$.

According to Equation [14.20], $\ln k = E_a/RT + \ln A$. Subtracting $\ln k$ from $\ln k_c$

$$\ln k_c - \ln k = \left[\frac{-E_{ac}}{RT} \right] + \ln A - \left[\frac{-E_a}{RT} \right] - \ln A$$

$$\ln(k_c/k) = \frac{E_a - E_{ac}}{RT}; \quad E_a - E_{ac} = RT \ln(k_c/k)$$

$$E_a - E_{ac} = \frac{8.314 J}{mol \cdot K} \times 298 K \times \ln \frac{1.0 \times 10^6}{0.039} = 42,267 J = 42.267 kJ = 42 kJ$$

Carbonic anhydrase lowers the activation energy of the reaction by 42 kJ.

- 14.94 (a) $(NH_2)_2C=O(aq) + H_2O(l) \rightarrow CO_2(g) + 2 NH_3(aq)$
- (b) According to Equation [14.20], $\ln k = E_a/RT + \ln A$. Subtracting $\ln k$ from $\ln k_c$

$$\ln k_c - \ln k = \left[\frac{-E_{ac}}{RT_c} \right] + \ln A - \left[\frac{-E_a}{RT} \right] - \ln A; \quad \ln k_c - \ln k = \left[\frac{-E_{ac}}{RT_c} \right] - \left[\frac{-E_a}{RT} \right]$$

$$\ln(3.4 \times 10^4) - \ln(4.15 \times 10^{-5}) = \left[\frac{-E_{ac}}{8.314(294)} \right] - \left[\frac{-E_a}{8.314(373)} \right]$$

$$20.5239(8.314)(294)(373) = 294 E_a - 373 E_{ac}; \text{ Dividing through by 294:}$$

$$20.5239(8.314)(373) = E_a - (1.27)E_{ac}; \quad 63,647 J = 64 kJ = E_a - (1.27)E_{ac}$$

$$\text{Dividing through by 373: } 50,167 J = 50 kJ = (0.788)E_a - E_{ac}$$

$(E_a - E_{ac})$ is somewhere between 50 kJ and 64 kJ. This is a substantial reduction in activation energy for the enzyme-catalyzed reaction.

- 14.95 *Analyze/Plan.* Let k = the rate constant for the uncatalyzed reaction,
 k_c = the rate constant for the catalyzed reaction

According to Equation [14.20], $\ln k = -E_a/RT + \ln A$

Subtracting $\ln k$ from $\ln k_c$,

$$\ln k_c - \ln k = - \left[\frac{55 \text{ kJ/mol}}{RT} + \ln A \right] - \left[- \frac{95 \text{ kJ/mol}}{RT} + \ln A \right]. \text{ Solve.}$$

- (a) $RT = 8.314 \text{ J/mol}\cdot\text{K} \times 298 \text{ K} \times 1 \text{ kJ}/1000 \text{ J} = 2.478 \text{ kJ/mol}$; $\ln A$ is the same for both reactions.

$$\ln(k_c/k) = \frac{95 \text{ kJ/mol} - 55 \text{ kJ/mol}}{2.478 \text{ kJ/mol}}; k_c/k = 1.024 \times 10^7 = 1 \times 10^7$$

The catalyzed reaction is approximately 10,000,000 (ten million) times faster at 25°C.

- (b) $RT = 8.314 \text{ J/mol}\cdot\text{K} \times 398 \text{ K} \times 1 \text{ kJ}/1000 \text{ J} = 3.309 \text{ kJ/mol}$

$$\ln(k_c/k) = \frac{40 \text{ kJ/mol}}{3.309 \text{ kJ/mol}}; k_c/k = 1.778 \times 10^5 = 2 \times 10^5$$

The catalyzed reaction is 200,000 times faster at 125°C.

- 14.96 Let k and E_a equal the rate constant and activation energy for the uncatalyzed reaction. Let k_c and E_{ac} equal the rate constant and activation energy of the catalyzed reaction. A is the same for the uncatalyzed and catalyzed reactions. $k_c/k = 1 \times 10^5$, $T = 37^\circ\text{C} = 310 \text{ K}$.

According to Equation [14.20], $\ln k = -E_a/RT + \ln A$. Subtracting $\ln k$ from $\ln k_c$

$$\ln k_c - \ln k = \left[\frac{-E_{ac}}{RT} \right] + \ln A - \left[\frac{-E_a}{RT} \right] - \ln A$$

$$\ln(k_c/k) = \frac{E_a - E_{ac}}{RT}; E_a - E_{ac} = RT \ln(k_c/k)$$

$$E_a - E_{ac} = \frac{8.314 \text{ J}}{\text{mol}\cdot\text{K}} \times 310 \text{ K} \times \ln(1 \times 10^5) = 2.966 \times 10^4 \text{ J} = 29.66 \text{ kJ} = 3 \times 10^1 \text{ kJ}$$

The enzyme must lower the activation energy by 30 kJ in order to achieve a 1×10^5 -fold increase in reaction rate.

Additional Exercises

- 14.97 A balanced chemical equation shows the overall, net change of a chemical reaction. Most reactions occur as a series of (elementary) steps. The rate law contains only those reactants that form the transition state of the rate-determining step. If a reaction occurs in a single step, the rate law can be written directly from the balanced equation for the step.

$$14.98 \quad \text{rate} = \frac{-\Delta[\text{H}_2\text{S}]}{\Delta t} = \frac{\Delta[\text{Cl}^-]}{2\Delta t} = k[\text{H}_2\text{S}][\text{Cl}_2]$$

$$\frac{-\Delta[\text{H}_2\text{S}]}{\Delta t} = (3.5 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1})(2.0 \times 10^{-4} \text{ M})(0.025 \text{ M}) = 1.75 \times 10^{-7} = 1.8 \times 10^{-7} \text{ M/s}$$

$$\frac{\Delta[\text{Cl}^-]}{\Delta t} = \frac{-2\Delta[\text{H}_2\text{S}]}{\Delta t} = 2(1.75 \times 10^{-7} \text{ M/s}) = 3.5 \times 10^{-7} \text{ M/s}$$

$$14.99 \quad (\text{a}) \quad \text{rate} = \frac{-\Delta[\text{NO}]}{2\Delta t} = \frac{-\Delta[\text{O}_2]}{\Delta t} = \frac{9.3 \times 10^{-5} \text{ M/s}}{2} = 4.7 \times 10^{-5} \text{ M/s}$$

$$(\text{b,c}) \quad \text{rate} = k[\text{NO}]^2[\text{O}_2]; \quad k = \text{rate}/[\text{NO}]^2[\text{O}_2]$$

$$k = \frac{4.7 \times 10^{-5} \text{ M/s}}{(0.040 \text{ M})^2(0.035 \text{ M})} = 0.8393 = 0.84 \text{ M}^{-2} \text{ s}^{-1}$$

(d) Since the reaction is second order in NO, if the [NO] is increased by a factor of 1.8, the rate would increase by a factor of 1.8^2 , or $(3.24) = 3.2$.

14.100 (a) The rate increases by a factor of nine when $[\text{C}_2\text{O}_4^{2-}]$ triples (compare experiments 1 and 2). The rate doubles when $[\text{HgCl}_2]$ doubles (compare experiments 2 and 3). The apparent rate law is: $\text{rate} = k[\text{HgCl}_2][\text{C}_2\text{O}_4^{2-}]^2$

$$(\text{b}) \quad k = \frac{\text{rate}}{[\text{HgCl}_2][\text{C}_2\text{O}_4^{2-}]^2} \quad \text{Using the data for Experiment 1,}$$

$$k = \frac{(3.2 \times 10^{-5} \text{ M/s})}{[0.164 \text{ M}][0.15 \text{ M}]^2} = 8.672 \times 10^{-3} = 8.7 \times 10^{-3} \text{ M}^{-2} \text{ s}^{-1}$$

$$(\text{c}) \quad \text{rate} = (8.672 \times 10^{-3} \text{ M}^{-2} \text{ s}^{-1})(0.100 \text{ M})(0.25 \text{ M})^2 = 5.4 \times 10^{-5} \text{ M/s}$$

14.101 The units of rate are M/s. The reaction must be second order overall if the units of the rate constant are $\text{M}^{-1} \text{ s}^{-1}$. If $\text{rate} = k[\text{NO}_2]^x$, then the cumulative units of $[\text{NO}_2]^x$ must be M^2 , and $x = 2$.

If $[\text{NO}_2]_0 = 0.100 \text{ M}$ and $[\text{NO}_2]_t = 0.025 \text{ M}$, use the integrated form of the second order rate equation, $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$, Equation [14.14], to solve for t .

$$\frac{1}{0.025 \text{ M}} = 0.63 \text{ M}^{-1} \text{ s}^{-1} (t) + \frac{1}{0.100 \text{ M}}; \quad \frac{(40 - 10) \text{ M}^{-1}}{0.63 \text{ M}^{-1} \text{ s}^{-1}} = t = 47.62 = 48 \text{ s.}$$

14.102 For a first order reaction, $t_{1/2} = 0.693/k$. For a second order reaction, $t_{1/2} = 1/k[A]_0$. Half-life is constant over the course of the reaction for first order reactions. Although second order half-life does not appear to depend on t , the value of " $[A]_0$ " does change over the course of the reaction, and $t_{1/2}$ increases with time. (For a zero reaction, $t_{1/2}$ decreases with time.)

The rate law for reaction (1) must be first order, because that is the only reaction type that has a constant half-life. Reaction (2), where $t_{1/2}$ increases with time, is second order.

14.103 (a) $[A]_0$ has been halved four times after four half-lives. That is, $[A]_t = (1/2)^4[A]_0 = (1/16)[A]_0$. Monitor $[A]$; when it reaches 1/16 of the initial concentration, the reaction has proceeded for four half-lives.