Pearson

Exercises

Review Questions

1. Explain why lizards become sluggish in cold weather. How is this phenomenon related to chemistry?

2. Why are reaction rates important (both practically and theoretically)?

3. Using the idea that reactions occur as a result of collisions between particles, explain why reaction rates depend on the concentration of the reactants.

4. Using the idea that reactions occur as a result of collisions between particles, explain why reaction rates depend on the temperature of the reaction mixture.

5. What units are typically used to express the rate of a reaction?

6. Why is the reaction rate for reactants defined as the *negative* of the change in reactant concentration with respect to time, whereas for products it is defined as the change in reactant concentration with respect to time (with a positive sign)?

7. Explain the difference between the average rate of reaction and the instantaneous rate of reaction.

8. Consider a simple reaction in which a reactant A forms products:

$$\text{A} \rightarrow \text{products}$$

What is the rate law if the reaction is zero order with respect to A? First order? Second order? For each case, explain how a doubling of the concentration of A would affect the rate of reaction.

9. How is the order of a reaction generally determined?

10. For a reaction with multiple reactants, how is the overall order of the reaction defined?

11. Explain the difference between the rate law for a reaction and the integrated rate law for a reaction. What relationship does each kind of rate law express?

12. Write integrated rate laws for zero-order, first-order, and second-order reactions of the form $\text{A} \rightarrow \text{products}$.

13. What does the term *half-life* mean? Write the expressions for the half-lives of zero-order, first-order, and second-order reactions.

14. How do reaction rates typically depend on temperature? What part of the rate law is temperature dependent?

15. Explain the meaning of each term within the Arrhenius equation: activation energy, frequency factor, and exponential factor. Use these terms and the Arrhenius equation to explain why small changes in temperature can result in large changes in reaction rates.

16. What is an Arrhenius plot? Explain the significance of the slope and intercept of an Arrhenius plot.

17. Explain the meaning of the orientation factor in the collision model.

18. Explain the difference between a normal chemical equation for a chemical reaction and the mechanism of that reaction.

19. In a reaction mechanism, what is an elementary step? Write down the three most common elementary steps and the corresponding rate law for each one.

20. What are the two requirements for a proposed mechanism to be valid for a given reaction?

21. What is an intermediate within a reaction mechanism?

22. What is a catalyst? How does a catalyst increase the rate of a chemical reaction?

23. Explain the difference between homogeneous catalysis and heterogeneous catalysis.

24. What are the four basic steps involved in heterogeneous catalysis?

25. What are enzymes? What is the active site of an enzyme? What is a substrate?

26. What is the general two-step mechanism by which most enzymes work?

Problems by Topic

Note: Answers to all odd-numbered Problems can be found in Appendix III. Exercises in the Problems by Topic section *are paired, with each odd-numbered problem followed by a similar even-numbered problem. Exercises in the Cumulative Problems section are also paired but more loosely. Because of their nature, Challenge Problems and Conceptual Problems are unpaired.*

Reaction Rates

27. Consider the reaction.

$$2\ HBr(g) \rightarrow H_2(g) + Br_2(g)$$

a. Express the rate of the reaction in terms of the change in concentration of each of the reactants and products.

b. In the first 25.0 s of this reaction, the concentration of HBr drops from 0.600 M to 0.512 M. Calculate the average rate of the reaction during this time interval.

c. If the volume of the reaction vessel in part b is 1.50 L, what amount of Br_2 (in moles) forms during the first 15.0 s of the reaction?

28. Consider the reaction.

$$2\ N_2O(g) \rightarrow 2\ N_2(g) + O_2(g)$$

a. Express the rate of the reaction in terms of the change in concentration of each of the reactants and products.

b. In the first 15.0 s of the reaction, 0.015 mol of O_2 is produced in a reaction vessel with a volume of 0.500 L. What is the average rate of the reaction during this time interval?

c. Predict the rate of change in the concentration of N_2O during this time interval. In other words, what is $\Delta[N_2O]/\Delta t$?

29. For the reaction $2\ A(g) + B(g) \rightarrow 3\ C(g)$,

a. determine the expression for the rate of the reaction in terms of the change in concentration of each of the reactants and products.

b. when A is decreasing at a rate of 0.100 M/s, how fast is B decreasing? How fast is C increasing?

30. For the reaction $A(g) + \frac{1}{2}B(g) \rightarrow 2\ C(g)$,

a. determine the expression for the rate of the reaction in terms of the change in concentration of each of the reactants and products.

b. when C is increasing at a rate of 0.0025 M/s, how fast is B decreasing? How fast is A decreasing?

31. Consider the reaction.

$$Cl_2(g) + 3\ F_2(g) \rightarrow 2\ ClF_3(g)$$

Complete the table.

$\Delta[Cl_2]/\Delta t$	$\Delta[F_2]/\Delta t$	$\Delta[ClF_3]/\Delta t$	Rate
−0.012 M/s			

32. Consider the reaction.

$$8\ H_2S(g) + 4\ O_2(g) \rightarrow 8\ H_2O(g) + S_8(g)$$

Complete the table.

$\Delta[H_2S]/\Delta t$	$\Delta[O_2]/\Delta t$	$\Delta[H_2O]/\Delta t$	$\Delta[S_8]/\Delta t$	Rate
−0.080 M/s				

33. Consider the reaction:

$$C_4H_8(g) \rightarrow 2\ C_2H_4(g)$$

The tabulated data were collected for the concentration of C_4H_8 as a function of time.

Time (s)	C_4H_8 (M)
0	1.000
10	0.913
20	0.835
30	0.763
40	0.697
50	0.637

a. What is the average rate of the reaction between 0 and 10 s? Between 40 and 50 s?

b. What is the rate of formation of C_2H_4 between 20 and 30 s?

34. Consider the reaction.

$$NO_2(g) \rightarrow NO(g) + \frac{1}{2}O_2(g)$$

The tabulated data were collected for the concentration of NO_2 as a function of time.

Time (s)	$[NO_2]$ (M)
0	1.000
10	0.951
20	0.904
30	0.860
40	0.818
50	0.778
60	0.740
70	0.704
80	0.670
90	0.637
100	0.606

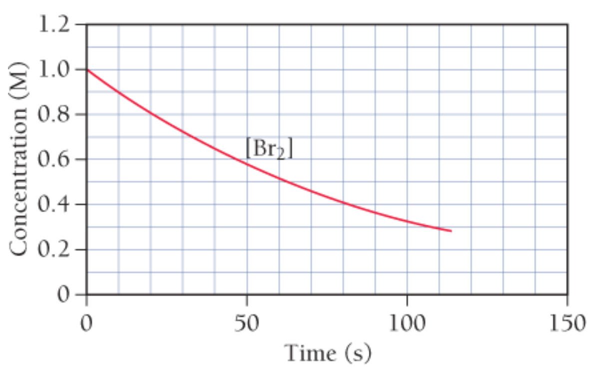
a. What is the average rate of the reaction between 10 and 20 s? Between 50 and 60 s?

b. What is the rate of formation of O_2 between 50 and 60 s?

35. Consider the reaction.

$$H_2(g) + Br_2(g) \rightarrow 2\ HBr(g)$$

The graph shows the concentration of Br_2 as a function of time.



a. Use the graph to calculate each quantity.

i. the average rate of the reaction between 0 and 25 s

ii. the instantaneous rate of the reaction at 25 s

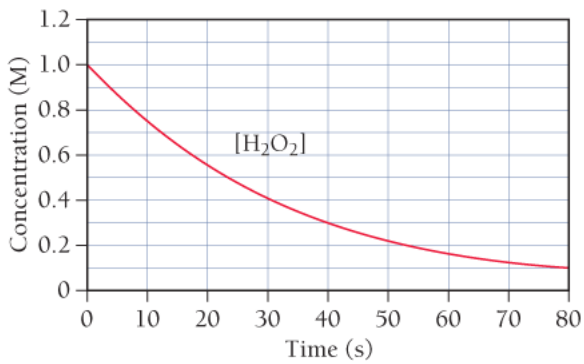
iii. the instantaneous rate of formation of HBr at 50 s

b. Make a rough sketch of a curve representing the concentration of HBr as a function of time. Assume that the initial concentration of HBr is zero.

36. Consider the reaction.

$$2\ H_2O_2(aq) \rightarrow 2\ H_2O(l) + O_2(g)$$

The graph shows the concentration of H_2O_2 as a function of time.



a. Use the graph to calculate each quantity.

i. the average rate of the reaction between 10 and 20 s

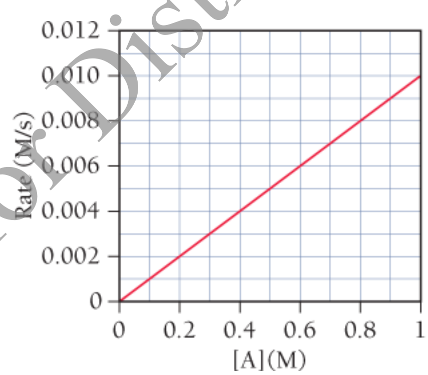
ii. the instantaneous rate of the reaction at 30 s

iii. the instantaneous rate of formation of O_2 at 50 s

b. If the initial volume of the H_2O_2 is 1.5 L, what total amount of O_2 (in moles) is formed in the first 50 s of reaction?

The Rate Law and Reaction Orders

37. This graph shows a plot of the rate of a reaction versus the concentration of the reactant A for the reaction A → products.

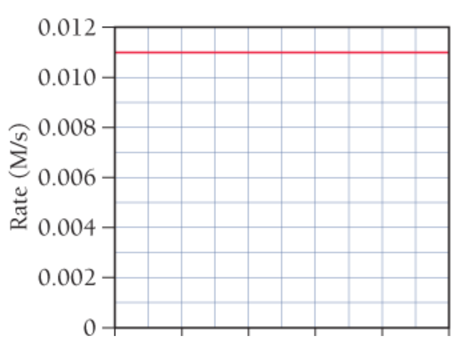


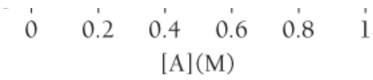
a. What is the order of the reaction with respect to A?

b. Make a rough sketch of a plot of [A] versus *time*.

c. Write a rate law for the reaction including an estimate for the value of k.

38. This graph shows a plot of the rate of a reaction versus the concentration of the reactant.





a. What is the order of the reaction with respect to A?

b. Make a rough sketch of a plot of [A] versus *time*.

c. Write a rate law for the reaction including the value of k.

39. What are the units of k for each type of reaction?

a. first-order reaction

b. second-order reaction

c. zero-order reaction

40. This reaction is first order in N_2O_5:

$$N_2O_5(g) \rightarrow NO_3(g) + NO_2(g)$$

The rate constant for the reaction at a certain temperature is 0.053/s.

a. Calculate the rate of the reaction when $[N_2O_5] = 0.055\ M$.

b. What is the rate of the reaction at the concentration indicated in part a if the reaction is second order? Zero order? (Assume the same *numerical* value for the rate constant with the appropriate units.)

41. A reaction in which A, B, and C react to form products is first order in A, second order in B, and zero order in C.

a. Write a rate law for the reaction.

b. What is the overall order of the reaction?

c. By what factor does the reaction rate change if [A] is doubled (and the other reactant concentrations are held constant)?

d. By what factor does the reaction rate change if [B] is doubled (and the other reactant concentrations are held constant)?

e. By what factor does the reaction rate change if [C] is doubled (and the other reactant concentrations are held constant)?

f. By what factor does the reaction rate change if the concentrations of all three reactants are doubled?

42. A reaction in which A, B, and C react to form products is zero order in A, one-half order in B, and second order in C.

a. Write a rate law for the reaction.

b. What is the overall order of the reaction?

c. By what factor does the reaction rate change if [A] is doubled (and the other reactant concentrations are held constant)?

d. By what factor does the reaction rate change if [B] is doubled (and the other reactant concentrations are held constant)?

e. By what factor does the reaction rate change if [C] is doubled (and the other reactant concentrations are held constant)?

f. By what factor does the reaction rate change if the concentrations of all three reactants are doubled?

43. Consider the tabulated data showing the initial rate of a reaction $(A \rightarrow \text{products})$ at several different concentrations of A. What is the order of the reaction? Write a rate law for the reaction including the value of the rate constant, k.

[A] (M)	Initial Rate (M/s)
0.100	0.053
0.200	0.210
0.300	0.473

44. Consider the tabulated data showing the initial rate of a reaction $(A \rightarrow \text{products})$ at several different concentrations of A. What is the order of the reaction? Write a rate law for the reaction including the value of the rate constant, k.

[A] (M)	Initial Rate (M/s)

0.15	0.008
0.30	0.016
0.60	0.032

45. The tabulated data were collected for this reaction:

$$2\ NO_2(g) + F_2(g) \rightarrow 2\ NO_2F(g)$$

$[NO_2]$ (M)	$[F_2]$ (M)	Initial Rate (M/s)
0.100	0.100	0.026
0.200	0.100	0.051
0.200	0.200	0.103
0.400	0.400	0.411

Write an expression for the reaction rate law and calculate the value of the rate constant, *k*. What is the overall order of the reaction?

46. The tabulated data were collected for this reaction:

$$CH_3Cl(g) + 3\ Cl_2(g) \rightarrow CCl_4(g) + 3\ HCl(g)$$

$[CH_3Cl]$ [M]	$[Cl_2]$ [M]	Initial Rate (M/s)
0.050	0.050	0.014
0.100	0.050	0.029
0.100	0.100	0.041
0.200	0.200	0.115

Write an expression for the reaction rate law and calculate the value of the rate constant, *k*. What is the overall order of the reaction?

The Integrated Rate Law and Half-Life

47. Indicate the order of reaction consistent with each observation.

a. A plot of the concentration of the reactant versus time yields a straight line.

b. The reaction has a half-life that is independent of initial concentration.

c. A plot of the inverse of the concentration versus time yields a straight line.

48. Indicate the order of reaction consistent with each observation.

a. The half-life of the reaction gets shorter as the initial concentration is increased.

b. A plot of the natural log of the concentration of the reactant versus time yields a straight line.

c. The half-life of the reaction gets longer as the initial concentration is increased.

49. The tabulated data show the concentration of AB versus time for this reaction:

$$AB(g) \rightarrow A(g) + B(g)$$

Time (s)	[AB] (M)
0	0.950
50	0.459
100	0.302
150	0.225
200	0.180

250	0.149
300	0.128
350	0.112
400	0.0994
450	0.0894
500	0.0812

Determine the order of the reaction and the value of the rate constant. Predict the concentration of AB at 25 s.

50. The tabulated data show the concentration of N_2O_5 versus time for this reaction:

$$N_2O_5(g) \rightarrow NO_3(g) + NO_2(g)$$

Time (s)	$[N_2O_5]$ (M)
0	1.000
25	0.822
50	0.677
75	0.557
100	0.458
125	0.377
150	0.310
175	0.255
200	0.210

Determine the order of the reaction and the value of the rate constant. Predict the concentration of N_2O_5 at 250 s.

51. The tabulated data show the concentration of cyclobutane $\left(C_4H_8\right)$ versus time for this reaction:

$$C_4H_8 \rightarrow 2\,C_2H_4(g)$$

Time (s)	$[C_4H_8]$ (M)
0	1.000
10	0.894
20	0.799
30	0.714
40	0.638
50	0.571
60	0.510
70	0.456
80	0.408
90	0.364
100	0.326

Determine the order of the reaction and the value of the rate constant. What is the rate of reaction when $\left[C_4H_8\right] = 0.25\ \text{M}$?

52. A reaction in which $A \rightarrow \text{products}$ is monitored as a function of time. The results are tabulated here.

Time (s)	[A] (M)
0	1.000
25	0.914
50	0.829
75	0.744

75	0.744
100	0.659
125	0.573
150	0.488
175	0.403
200	0.318

Determine the order of the reaction and the value of the rate constant. What is the rate of reaction when $[A] = 0.10\ M$?

53. This reaction was monitored as a function of time:

$$A \rightarrow B + C$$

A plot of ln[A] versus time yields a straight line with slope −0.0045/s.

a. What is the value of the rate constant (k) for this reaction at this temperature?

b. Write the rate law for the reaction.

c. What is the half-life?

d. If the initial concentration of A is 0.250 M, what is the concentration after 225 s?

54. This reaction was monitored as a function of time:

$$AB \rightarrow A + B$$

A plot of 1/[AB] versus time yields a straight line with slope −0.055/M · s.

a. What is the value of the rate constant (k) for this reaction at this temperature?

b. Write the rate law for the reaction.

c. What is the half-life when the initial concentration is 0.55 M?

d. If the initial concentration of AB is 0.250 M, and the reaction mixture initially contains no products, what are the concentrations of A and B after 75 s?

55. The decomposition of SO_2Cl_2 is first order in SO_2Cl_2 and has a rate constant of $1.45 \times 10^{-4}\ s^{-1}$ at a certain temperature.

a. What is the half-life for this reaction?

b. How long will it take for the concentration of SO_2Cl_2 to decrease to 25% of its initial concentration?

c. If the initial concentration of SO_2Cl_2 is 1.00 M, how long will it take for the concentration to decrease to 0.78 M?

d. If the initial concentration of SO_2Cl_2 is 0.150 M, what is the concentration of SO_2Cl_2 after 2.00×10^{2} s? After 5.00×10^{2} s?

56. The decomposition of XY is second order in XY and has a rate constant of $7.02 \times 10^{-3}\ M^{-1} \cdot s^{-1}$ at a certain temperature.

a. What is the half-life for this reaction at an initial concentration of 0.100 M?

b. How long will it take for the concentration of XY to decrease to 12.5% of its initial concentration when the initial concentration is 0.100 M? When the initial concentration is 0.200 M?

c. If the initial concentration of XY is 0.150 M, how long will it take for the concentration to decrease to 0.062 M?

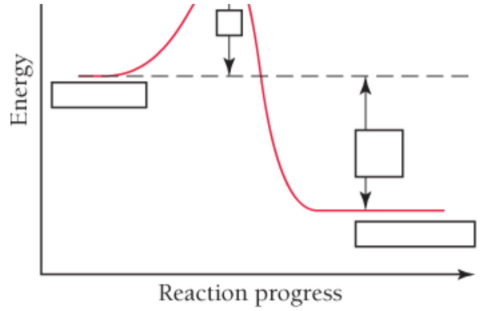
d. If the initial concentration of XY is 0.050 M, what is the concentration of XY after 5.0×10^{1} s? After 5.50×10^{2} s?

57. The half-life for the radioactive decay of U-238 is 4.5 billion years and is independent of initial concentration. How long will it take for 10% of the U-238 atoms in a sample of U-238 to decay? If a sample of U-238 initially contained 1.5×10^{18} atoms when the universe was formed 13.8 billion years ago, how many U-238 atoms does it contain today?

58. The half-life for the radioactive decay of C-14 is 5730 years and is independent of the initial concentration. How long does it take for 25% of the C-14 atoms in a sample of C-14 to decay? If a sample of C-14 initially contains 1.5 mmol of C-14, how many millimoles are left after 2255 years?

The Effect of Temperature and the Collision Model

59. The diagram shows the energy of a reaction as the reaction progresses. Label each blank box in the diagram.



a. reactants

b. products

c. activation energy (E_a)

d. enthalpy of reaction (ΔH_{rxn})

60. A chemical reaction is endothermic and has an activation energy that is twice the value of the enthalpy change of the reaction. Draw a diagram depicting the energy of the reaction as it progresses. Label the position of the reactants and products and indicate the activation energy and enthalpy of reaction.

61. The activation energy of a reaction is 56.8 kJ/mol and the frequency factor is $1.5 \times 10^{11}/\text{s}$. Calculate the rate constant of the reaction at 25 °C.

62. The rate constant of a reaction at 32 °C is 0.055/s. If the frequency factor is $1.2 \times 10^{13}/\text{s}$, what is the activation barrier?

63. The rate constant (k) for a reaction is measured as a function of temperature. A plot of ln k versus $1/T$ (in K) is linear and has a slope of −7445 K. Calculate the activation energy for the reaction.

64. The rate constant (k) for a reaction is measured as a function of temperature. A plot of ln k versus $1/T$ (in K) is linear and has a slope of -1.01×10^4 K. Calculate the activation energy for the reaction.

65. The tabulated data shown here were collected for the first-order reaction:

$$N_2O(g) \rightarrow N_2(g) + O(g)$$

Use an Arrhenius plot to determine the activation barrier and frequency factor for the reaction.

Temperature (K)	Rate Constant (s^{-1})
800	3.24×10^{-5}
900	0.00214
1000	0.0614
1100	0.955

66. The tabulated data show the rate constant of a reaction measured at several different temperatures. Use an Arrhenius plot to determine the activation barrier and frequency factor for the reaction.

Temperature (K)	Rate Constant (s^{-1})
300	0.0134
310	0.0407
320	0.114
330	0.303
340	0.757

67. The tabulated data were collected for the second-order reaction:

$$Cl(g) + H_2(g) \rightarrow HCl(g) + H(g)$$

Use an Arrhenius plot to determine the activation barrier and frequency factor for the reaction.

Temperature (K)	Rate Constant (L/mol · s)
90	0.00357
100	0.0773
110	0.956
120	7.781

68. The tabulated data show the rate constant of a reaction measured at several different temperatures. Use an Arrhenius plot to determine the activation barrier and frequency factor for the reaction.

Temperature (K)	Rate Constant (s^{-1})
310	0.00434
320	0.0140
330	0.0421
340	0.118
350	0.316

69. A reaction has a rate constant of 0.0117/s at 400.0 K and 0.689/s at 450.0 K.

a. Determine the activation barrier for the reaction.

b. What is the value of the rate constant at 425 K?

70. A reaction has a rate constant of 0.000122/s at 27 °C and 0.228/s at 77 °C.

a. Determine the activation barrier for the reaction.

b. What is the value of the rate constant at 17 °C?

71. If a temperature increase from 10.0 °C to 20.0 °C doubles the rate constant for a reaction, what is the value of the activation barrier for the reaction?

72. If a temperature increase from 20.0 °C to 35.0 °C triples the rate constant for a reaction, what is the value of the activation barrier for the reaction?

73. Consider these two gas-phase reactions:

a. $AA(g) + BB(g) \rightarrow 2\,AB(g)$

b. $AB(g) + CD(g) \rightarrow AC(g) + BD(g)$

If the reactions have identical activation barriers and are carried out under the same conditions, which one would you expect to have the faster rate?

74. Which of these two reactions would you expect to have the smaller orientation factor? Explain.

a. $O(g) + N_2(g) \rightarrow NO(g) + N(g)$

b. $NO(g) + Cl_2(g) \rightarrow NOCl(g) + Cl(g)$

Reaction Mechanisms

75. Consider this overall reaction, which is experimentally observed to be second order in AB and zero order in C:

$$AB + C \rightarrow A + BC$$

Is the following mechanism valid for this reaction?

$$\begin{array}{llll} AB + AB & \xrightarrow{k_1} & AB_2 + A & \text{Slow} \\ AB_2 + C & \xrightarrow{k_2} & AB + BC & \text{Fast} \end{array}$$

76. Consider this overall reaction, which is experimentally observed to be second order in X and first order in Y:

$$X + Y \rightarrow XY$$

a. Does the reaction occur in a single step in which X and Y collide?

b. Is this two-step mechanism valid?

$$2\,X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} X_2 \quad \text{Fast}$$
$$X_2 + Y \xrightarrow{k_2} XY + X \quad \text{Slow}$$

77. Consider this three-step mechanism for a reaction:

$$Cl_2(g) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2\,Cl(g) \quad \text{Fast}$$
$$Cl(g) + CHCl_3(g) \xrightarrow{k_3} HCl(g) + CCl_3(g) \quad \text{Slow}$$
$$Cl(g) + CCl_3(g) \xrightarrow{k_4} CCl_4(g) \quad \text{Fast}$$

a. What is the overall reaction?

b. Identify the intermediates in the mechanism.

c. What is the predicted rate law?

78. Consider this two-step mechanism for a reaction:

$$NO_2(g) + Cl_2(g) \xrightarrow{k_1} ClNO_2(g) + Cl(g) \quad \text{Slow}$$
$$NO_2(g) + Cl(g) \xrightarrow{k_2} ClNO_2(g) \quad \text{Fast}$$

a. What is the overall reaction?

b. Identify the intermediates in the mechanism.

c. What is the predicted rate law?

Catalysis

79. Many heterogeneous catalysts are deposited on high surface-area supports. Why?

80. Suppose that the reaction $A \rightarrow \text{products}$ is exothermic and has an activation barrier of 75 kJ/mol. Sketch an energy diagram showing the energy of the reaction as a function of the progress of the reaction. Draw a second energy curve showing the effect of a catalyst.

81. Suppose that a catalyst lowers the activation barrier of a reaction from 125 kJ/mol to 55 kJ/mol. By what factor would you expect the reaction rate to increase at 25 °C? (Assume that the frequency factors for the catalyzed and uncatalyzed reactions are identical.)

82. The activation barrier for the hydrolysis of sucrose into glucose and fructose is 108 kJ/mol. If an enzyme increases the rate of the hydrolysis reaction by a factor of 1 million, how much lower must the activation barrier be when sucrose is in the active site of the enzyme? (Assume that the frequency factors for the catalyzed and uncatalyzed reactions are identical and a temperature of 25 °C.)

Cumulative Problems

83. The tabulated data were collected for this reaction at 500 °C:

$$CH_3CN(g) \rightarrow CH_3NC(g)$$

Time (h)	$[CH_3CN]$ (M)
0.0	1.000
5.0	0.794
10.0	0.631
15.0	0.501
20.0	0.398
25.0	0.316

a. Determine the order of the reaction and the value of the rate constant at this temperature.

b. What is the half-life for this reaction (at the initial concentration)?

c. How long will it take for 90% of the CH_3CN to convert to CH_3NC?

84. The tabulated data were collected for this reaction at a certain temperature:

$$X_2Y \leftarrow 2\,X + Y$$

Time (h)	$[X_2Y]$ (M)
0.0	0.100
1.0	0.0856
2.0	0.0748
3.0	0.0664
4.0	0.0598
5.0	0.0543

a. Determine the order of the reaction and the value of the rate constant at this temperature.

b. What is the half-life for this reaction (at the initial concentration)?

c. What is the concentration of X after 10.0 hours?

85. Consider the reaction:

$$A + B + C \rightarrow D$$

The rate law for this reaction is:

$$\text{rate} = k\frac{[A][C]^2}{[B]^{1/2}}$$

Suppose the rate of the reaction at certain initial concentrations of A, B, and C is 0.0115 M/s. What is the rate of the reaction if the concentrations of A and C are doubled and the concentration of B is tripled?

86. Consider the reaction:

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

The rate law for this reaction is:

$$\text{rate} = k\frac{[O_3]^2}{[O_2]}$$

Suppose that a 1.0 L reaction vessel initially contains 1.0 mol of O_3 and 1.0 mol of O_2. What fraction of the O_3 has reacted when the rate falls to one-half of its initial value?

87. At 700 K acetaldehyde decomposes in the gas phase to methane and carbon monoxide. The reaction is:

$$CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$$

A sample of CH_3CHO is heated to 700 K, and the pressure is measured as 0.22 atm before any reaction takes place. The kinetics of the reaction are followed by measurements of total pressure, and these data are obtained:

t(s)	0	1000	3000	7000
P_{Total}(atm)	0.22	0.24	0.27	0.31

Determine the rate law, the rate constant, and the total pressure after 2.00×10^4s.

88. At 400 K oxalic acid decomposes according to the reaction:

$$H_2C_2O_4(g) \rightarrow CO_2(g) + HCOOH(g)$$

In three separate experiments, the initial pressure of oxalic acid and the final total pressure after 20,000 s are measured.

Experiment	1	2	3
$P_{H_2C_2O_4}$ at $t = 0$	65.8	92.1	111
P_{Total} at $t = 20{,}000$ s	94.6	132	160

Find the rate law of the reaction and its specific rate constant.

89. Dinitrogen pentoxide decomposes in the gas phase to form nitrogen dioxide and oxygen gas. The reaction is first order in dinitrogen pentoxide and has a half-life of 2.81 h at 25 °C. If a 1.5 L reaction vessel initially contains 745 torr of N_2O_5 at 25 °C, what partial pressure of O_2 is present in the vessel after 215 minutes?

90. Cyclopropane $\left(C_3H_6\right)$ reacts to form propene $\left(C_3H_6\right)$ in the gas phase. The reaction is first order in cyclopropane and has a rate constant of $5.87 \times 10^{-4}/s$ at 485 °C. If a 2.5 L reaction vessel initially contains 722 torr of cyclopropane at 485 °C, how long will it take for the partial pressure of cyclopropane to drop to below 1.00×10^2 torr?

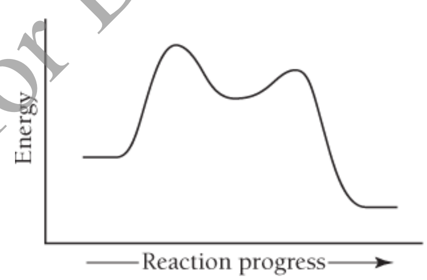
91. Iodine atoms combine to form I_2 in liquid hexane solvent with a rate constant of 1.5×10^{10} L/mol · s. The reaction is second order in I. Since the reaction occurs so quickly, the only way to study the reaction is to create iodine atoms almost instantaneously, usually by photochemical decomposition of I_2. Suppose a flash of light creates an initial [I] concentration of 0.0100 M. How long will it take for 95% of the newly created iodine atoms to recombine to form I_2?

92. The hydrolysis of sucrose $\left(C_{12}H_{22}O_{11}\right)$ into glucose and fructose in acidic water has a rate constant of $1.8 \times 10^{-4}\ s^{-1}$ at 25 °C. Assuming the reaction is first order in sucrose, determine the mass of sucrose that is hydrolyzed when 2.55 L of a 0.150 M sucrose solution is allowed to react for 195 minutes.

93. The reaction $AB(aq) \rightarrow A(g) + B(g)$ is second order in AB and has a rate constant of $0.0118\ M^{-1} \cdot s^{-1}$ at 25.0 °C. A reaction vessel initially contains 250.0 mL of 0.100 M AB that is allowed to react to form the gaseous product. The product is collected over water at 25.0 °C. How much time is required to produce 200.0 mL of the products at a barometric pressure of 755.1 mmHg? (The vapor pressure of water at this temperature is 23.8 mmHg.)

94. The reaction $2\ H_2O_2(aq) \rightarrow 2\ H_2O(l) + O_2(g)$ is first order in H_2O_2 and under certain conditions has a rate constant of $0.00752\ s^{-1}$ at 20.0 °C. A reaction vessel initially contains 150.0 mL of 30.0% H_2O_2 by mass solution (the density of the solution is 1.11 g/mL). The gaseous oxygen is collected over water at 20.0 °C as it forms. What volume of O_2 forms in 85.0 seconds at a barometric pressure of 742.5 mmHg? (The vapor pressure of water at this temperature is 17.5 mmHg.)

95. Consider this energy diagram:



a. How many elementary steps are involved in this reaction?

b. Label the reactants, products, and intermediates.

c. Which step is rate limiting?

d. Is the overall reaction endothermic or exothermic?

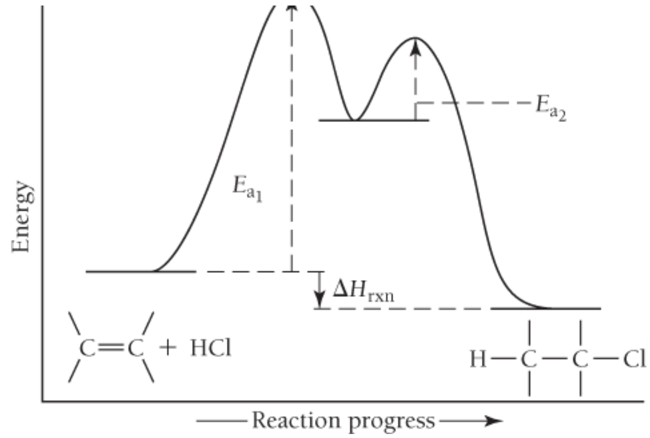
96. Consider the reaction in which HCl adds across the double bond of ethene:

$$HCL + H_2C{=}CH_2 \rightarrow H_3C{-}CH_2Cl$$

The following mechanism, with the accompanying energy diagram, has been suggested for this reaction:

$$\textit{Step 1}\quad HCL + H_2C{=}CH_2 \rightarrow H_3C{=}CH_2^+ + Cl^-$$

$$\textit{Step 2}\quad H_3C{=}CH_2^+ + Cl^- \rightarrow H_3C{-}CH_2Cl$$



a. Based on the energy diagram, determine which step is rate limiting.

b. What is the expected order of the reaction based on the proposed mechanism?

c. Is the overall reaction exothermic or endothermic?

97. The desorption of a single molecular layer of *n*-butane from a single crystal of aluminum oxide is found to be first order with a rate constant of 0.128/s at 150 K.

a. What is the half-life of the desorption reaction?

b. If the surface is initially completely covered with *n*-butane at 150 K, how long will it take for 25% of the molecules to desorb? For 50% to desorb?

c. If the surface is initially completely covered, what fraction will remain covered after 10 s? After 20 s?

98. The evaporation of a 120-nm film of *n*-pentane from a single crystal of aluminum oxide is zero order with a rate constant of 1.92×10^{13} molecules/cm$^2 \cdot$ s at 120 K.

a. If the initial surface coverage is 8.9×10^{16} molecules/cm^2, how long will it take for one-half of the film to evaporate?

b. What fraction of the film is left after 10 s? Assume the same initial coverage as in part a.

99. The kinetics of this reaction were studied as a function of temperature. (The reaction is first order in each reactant and second order overall.)

$$C_2H_5Br(aq) + OH^-(aq) \rightarrow C_2H_5OH(l) + Br^-(aq)$$

Temperature (°C)	k(L/mol · s)
25	8.81×10^{-5}
35	0.000285
45	0.000854
55	0.00239
65	0.00633

a. Determine the activation energy and frequency factor for the reaction.

b. Determine the rate constant at 15 °C.

c. If a reaction mixture is 0.155 M in C_2H_5Br and 0.250 M in OH^-, what is the initial rate of the reaction at 75 °C?

100. The reaction $2\,N_2O_5 \rightarrow 2\,N_2O_4 + O_2$ takes place at around room temperature in solvents such as CCl_4. The rate constant at 293 K is $2.35 \times 10^{-4}\,s^{-1}$, and at 303 K the rate constant is $9.15 \times 10^{-4}\,s^{-1}$. Calculate the frequency factor for the reaction.

101. This reaction has an activation energy of zero in the gas phase:

$$CH_3 + CH_3 \rightarrow C_2H_6$$

a. Would you expect the rate of this reaction to change very much with temperature?

b. Why might the activation energy be zero?

c. What other types of reactions would you expect to have little or no activation energy?

102. Consider the two reactions:

$$\begin{array}{lclcl} O + N_2 & \rightarrow & NO + N & E_a & = 315\ \text{kJ/mol} \\ Cl + H_2 & \rightarrow & HCl + H & E_a & = 23\ \text{kJ/mol} \end{array}$$

a. Why is the activation barrier for the first reaction so much higher than that for the second?

b. The frequency factors for these two reactions are very close to each other in value. Assuming that they are the same, calculate the ratio of the reaction rate constants for these two reactions at 25 °C.

103. Anthropologists can estimate the age of a bone or other sample of organic matter by its carbon-14 content. The carbon-14 in a living organism is constant until the organism dies, after which carbon-14 decays with first-order kinetics and a half-life of 5730 years. Suppose a bone from an ancient human contains 19.5% of the C-14 found in living organisms. How old is the bone?

104. Geologists can estimate the age of rocks by their uranium-238 content. The uranium is incorporated in the rock as it hardens and then decays with first-order kinetics and a half-life of 4.5 billion years. A rock contains 83.2% of the amount of uranium-238 that it contained when it was formed. (The amount that the rock contained when it was formed can be deduced from the presence of the decay products of U-238.) How old is the rock?

105. Consider the gas-phase reaction:

$$H_2(g) + I_2(g) \rightarrow 2\ HI(g)$$

The reaction was experimentally determined to be first order in H_2 and first order in I_2. Consider the proposed mechanisms.

Proposed mechanism I:

$$H_2(g) + I_2(g) \rightarrow 2\ HI(g)\ \text{Single step}$$

Proposed mechanism II:

$$\begin{array}{lcll} I_2(g) & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & 2\ I(g) & \text{Fast} \\ H_2(g) + 2\ I(g) & \xrightarrow{k_2} & 2\ HI(g) & \text{Slow} \end{array}$$

a. Show that both of the proposed mechanisms are valid.

b. What kind of experimental evidence might lead you to favor mechanism II over mechanism I?

106. Consider the reaction:

$$2\ NH_3(aq) + OCl^-(aq) \rightarrow N_2H_4(aq) + H_2O(l) + Cl^-(aq)$$

This three-step mechanism is proposed:

$$\begin{array}{lcll} NH_3(aq) + OCl^-(aq) & \underset{k_2}{\overset{k_1}{\rightleftharpoons}} & NH_2Cl(aq) + OH^-(aq) & \text{Fast} \\ NH_2Cl(aq) + NH_3(aq) & \xrightarrow{k_3} & N_2H_5^{\,+}(aq) + Cl^-(aq) & \text{Slow} \\ N_2H_5^{+}(aq) + OH^-(aq) & \xrightarrow{k_4} & N_2H_4(aq) + H_2O(l) & \text{Fast} \end{array}$$

a. Show that the mechanism sums to the overall reaction.

b. What is the rate law predicted by this mechanism?

107. The proposed mechanism for the formation of hydrogen bromide can be written in a simplified form as:

$$\begin{array}{lcll} Br_2(g) & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & 2\ Br(g) & \text{Fast} \\ Br\left(g\right) + H_2(g) & \xrightarrow{k_2} & HBr(g) + H(g) & \text{Slow} \\ H(g) + Br_2(g) & \xrightarrow{k_3} & HBr(g) + Br(g) & \text{Fast} \end{array}$$

What rate law corresponds to this mechanism?

108. A proposed mechanism for the formation of hydrogen iodide can be written in simplified form as:

k_1

$$\begin{array}{lccl} I_2 & \underset{k_{-1}}{\rightleftharpoons} & 2\,I & \text{Fast} \\ I + H_2 & \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} & H_2I & \text{Slow} \\ H_2I & \xrightarrow{k_3} & 2\,HI & \text{Fast} \end{array}$$

What rate law corresponds to this mechanism?

109. A certain substance X decomposes. Fifty percent of X remains after 100 minutes. How much X remains after 200 minutes if the reaction order with respect to X is (a) zero order, (b) first order, (c) second order?

110. The half-life for radioactive decay (a first-order process) of plutonium-239 is 24,000 years. How many years does it take for one mole of this radioactive material to decay until just one atom remains?

111. The energy of activation for the decomposition of 2 mol of HI to H_2 and I_2 in the gas phase is 185 kJ. The heat of formation of HI(g) from $H_2(g)$ and $I_2(g)$ is $-5.68\ \text{kJ/mol}$. Find the energy of activation for the reaction of 1 mol of H_2 and 1 mol of I_2 to form 2 mol of HI in the gas phase.

112. Ethyl chloride vapor decomposes by the first-order reaction:

$$C_2H_5Cl \rightarrow C_2H_4 + HCl$$

The activation energy is 249 kJ/mol, and the frequency factor is $1.6 \times 10^{14}\ s^{-1}$. Find the value of the specific rate constant at 710 K. What fraction of the ethyl chloride decomposes in 15 minutes at this temperature? Find the temperature at which the rate of the reaction would be twice as fast.

Challenge Problems

113. In this chapter we have seen a number of reactions in which a single reactant forms products. For example, consider the following first-order reaction:

$$CH_3NC(g) \rightarrow CH_3CN(g)$$

However, we also learned that gas-phase reactions occur through collisions.

a. One possible explanation is that two molecules of CH_3NC collide with each other and form two molecules of the product in a single elementary step. If that is the case, what reaction order would you expect?

b. Another possibility is that the reaction occurs through more than one step. For example, a possible mechanism involves one step in which the two CH_3NC molecules collide, resulting in the "activation" of one of them. In a second step, the activated molecule goes on to form the product. Write down this mechanism and determine which step must be rate determining in order for the kinetics of the reaction to be first order. Show explicitly how the mechanism predicts first-order kinetics.

114. The first-order *integrated* rate law for a reaction $A \rightarrow \text{products}$ is derived from the rate law using calculus:

$$\begin{aligned} \text{rate} &= k[A] \quad \text{(first-order rate law)} \\ \text{rate} &= \frac{d[A]}{dt} \\ \frac{d[A]}{dt} &= -k[A] \end{aligned}$$

The equation just given is a first-order, separable differential equation that can be solved by separating the variables and integrating:

$$\begin{aligned} \frac{d[A]}{[A]} &= -kdt \\ \int_{[A]_0}^{[A]} \frac{d[A]}{[A]} &= -\int_0^t kdt \end{aligned}$$

In the integral just given, $[A]_0$ is the initial concentration of A. We then evaluate the integral:

$$\begin{aligned} [\ln [A]]_{[A]_0}^{[A]} &= -k[t]_0^t \\ \ln [A] - \ln [A]_0 &= -kt \\ \ln [A] &= -kt + \ln [A]_0 \ \text{(integrated rate law)} \end{aligned}$$

a. Use a procedure similar to the one just shown to derive an integrated rate law for a reaction $A \rightarrow \text{products}$, which is one-half-order in the concentration of A (that is, $\text{Rate} = k[A]^{1/2}$).

b. Use the result from part a to derive an expression for the half-life of a one-half-order reaction.

115. The previous exercise shows how the first-order integrated rate law is derived from the first-order differential rate law. Begin with the second-order differential rate law and derive the second-order integrated rate law.

116. The rate constant for the first-order decomposition of $N_2O_5(g)$ to $NO_2(g)$ and $O_2(g)$ is $7.48 \times 10^{-3}\ s^{-1}$ at a given temperature.

a. Find the length of time required for the total pressure in a system containing N_2O_5 at an initial pressure of 0.100 atm to rise to 0.145 atm.

b. Find the length of time required for the total pressure in a system containing N_2O_5 at an initial pressure of 0.100 atm to rise to 0.200 atm.

c. Find the total pressure after 100 s of reaction.

117. Phosgene $\left(Cl_2CO\right)$, a poison gas used in World War I, is formed by the reaction of Cl_2 and CO. The proposed mechanism for the reaction is:

$$\begin{array}{cccl} Cl_2 & \rightleftharpoons & 2\ Cl & \text{Fast, equilibrium} \\ Cl + CO & \rightleftharpoons & ClCO & \text{Fast, equilibrium} \\ ClCO + Cl_2 & \rightarrow & Cl_2CO + Cl & \text{Slow} \end{array}$$

What rate law is consistent with this mechanism?

118. The rate of decomposition of $N_2O_3(g)$ to $NO_2(g)$ and $NO(g)$ is monitored by measuring $\left[NO_2\right]$ at different times. The following tabulated data are obtained.

$[NO_2]$(mol/L)	0	0.193	0.316	0.427	0.784
t(s)	0	884	1610	2460	50,000

The reaction follows a first-order rate law. Calculate the rate constant. Assume that after 50,000 s all the $N_2O_3(g)$ had decomposed.

119. At 473 K, for the elementary reaction $2\ NOCl(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\ NO(g) + Cl_2(g)$

$$\begin{aligned} k_1 &= 7.8 \times 10^{-2}\ L/\text{mol s and} \\ k_{-1} &= 4.7 \times 10^{2}\ L^2/\text{mol}^2\ s \end{aligned}$$

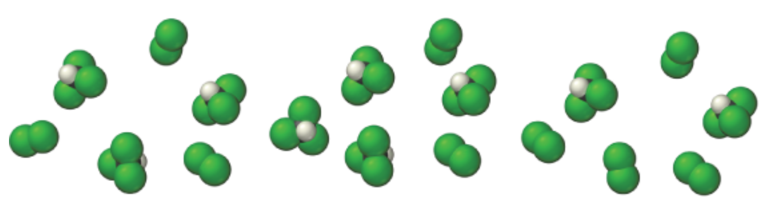
A sample of NOCl is placed in a container and heated to 473 K. When the system comes to equilibrium, [NOCl] is found to be 0.12 mol/L. What are the concentrations of NO and Cl_2?

Conceptual Problems

120. Consider the reaction:

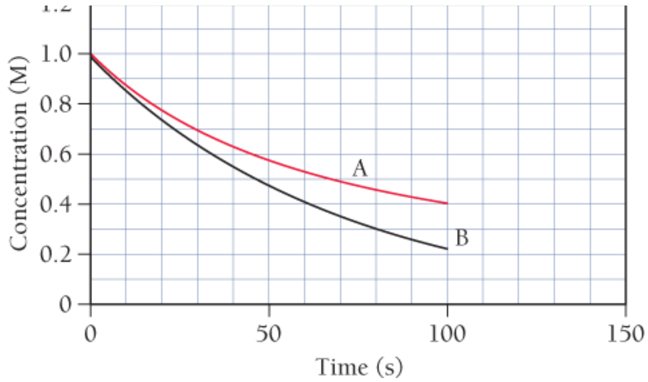
$$CHCl_3(g) + Cl_2\left(g\right) \rightarrow CCl_4(g) + HCl(g)$$

The reaction is first order in $CHCl_3$ and one-half order in Cl_2. Which reaction mixture would you expect to have the fastest initial rate?



a. b. c.

121. The accompanying graph shows the concentration of a reactant as a function of time for two different reactions. One of the reactions is first order and the other is second order. Which of the two reactions is first order? Second order? How would you change each plot to make it linear?



122. A particular reaction, A → products, has a rate that slows down as the reaction proceeds. The half-life of the reaction is found to depend on the initial concentration of A. Determine whether each statement is likely to be true or false for this reaction.

a. A doubling of the concentration of A doubles the rate of the reaction.

b. A plot of 1/[A] versus time is linear.

c. The half-life of the reaction gets longer as the initial concentration of A increases.

d. A plot of the concentration of A versus time has a constant slope.

Questions for Group Work

Active Classroom Learning

Discuss these questions with the group and record your consensus answer.

123. A student says, "The initial concentration of a reactant was doubled, and the rate doubled. Therefore, the reaction is second order in that reactant." Why might the student say that? What is wrong with the statement? What is the actual order with respect to the reactant? Explain your reasoning clearly.

124. A certain compound, A, reacts to form products according to the reaction A → P. The amount of A is measured as a function of time under a variety of different conditions and the tabulated results are shown here:

Time (s)	25.0 °C [A] (M)	35.0 °C [A] (M)	45.0 °C [A] (M)
0	1.000	1.000	1.000
10	0.779	0.662	0.561
20	0.591	0.461	0.312
30	0.453	0.306	0.177
40	0.338	0.208	0.100
50	0.259	0.136	0.057
60	0.200	0.093	0.032

Have one group member make a graph of [A] versus t, one group member make a graph of ln[A] versus t, and one group member make a graph of 1/[A] versus t using the data for 25 °C. Additional group members can make similar graphs for the other temperatures. What is the order of the reaction with respect to A? Explain your answer.

a. Use the data to determine the rate constant at each temperature.

b. What is the activation energy for this reaction?

c. The same reaction is conducted in the presence of a catalyst, and the following data are obtained:

Time (s)	25.0 °C [A] (M)	35.0 °C [A] (M)	45.0 °C [A] (M)
0	1.000	1.000	1.000

0.1	0.724	0.668	0.598
0.2	0.511	0.433	0.341
0.3	0.375	0.291	0.202
0.4	0.275	0.190	0.119
0.5	0.198	0.122	0.071
0.6	0.141	0.080	0.043

What effect does a catalyst have on the rate of the reaction? What is the activation energy for this reaction in the presence of the catalyst? How does it compare with the activation energy for the reaction when the catalyst isn't present?

Data Interpretation and Analysis

125. Methane (CH_4) is a greenhouse gas emitted by industry, agriculture, and waste systems. It is the second most prevalent greenhouse gas (after carbon dioxide). Methane plays an important role in climate change because it absorbs infrared radiation more efficiently than carbon dioxide. Methane is broken down in the atmosphere by ozone (O_3), making its atmospheric lifetime shorter than that of carbon dioxide.

$$CH_4(g) + O_3(g) \rightarrow \text{products}$$

A research group studied the rate of the reaction by which methane reacts with ozone and gets the data shown in the tables shown here. Study the data and answer the questions that follow.

Initial Rate versus Initial Concentrations

$[CH_4]$	$[O_3]$	Initial Rate (M/s)
0.010	0.010	3.94×10^{-7}
0.020	0.010	7.88×10^{-7}
0.020	0.020	1.58×10^{-6}

Rate Constant versus Temperature

Temperature (K)	$k(M^{-1} \cdot s^{-1})$
260	2.26×10^{-5}
265	3.65×10^{-5}
270	6.76×10^{-5}
275	0.000114
280	0.000187
285	0.000303
290	0.000483
295	0.000758
300	0.001171
305	0.001783

a. Use the data in the first table to determine the order of the reaction with respect to each reactant.

b. Use the data in the second table to determine the activation barrier and pre-exponential factor for the reaction.

c. Atmospheric concentrations of methane and ozone can vary depending on the location and altitude. Calculate the rate of the reaction at 273 K for a methane concentration of 1.8 ppm (by volume) and an ozone concentration of 5.0 ppm (by volume). Note that 1 ppm of CH_4 by volume means 1 L $CH_4/10^6$ L air. Assume STP (standard temperature and pressure) so that 1 mol gas occupies 22.4 L.

d. What is the half-life of methane in the atmosphere in years at 323 K? (Assume that $\left[CH_4\right] = \left[O_3\right] = [A]_0 = 5.0 \times 10^{-7} M$.)

Answers to Conceptual Connections

Cc 14.1 **(b)** Increasing the temperature increases the number of collisions that can occur with enough energy for the reaction to occur.

Cc 14.2 **(c)** The rate at which B changes is twice the rate of the reaction because its coefficient is 2, and it is negative because B is a reactant.

Cc 14.3 **(d)** Because the reaction is second order, increasing the concentration of A by a factor of 5 causes the rate to increase by 5^2or 25.

Cc 14.4 **(c)** All three mixtures have the same total number of molecules, but mixture **(c)** has the greatest number of NO molecules. Since the reaction is second order in NO and only first order in O_2, mixture **(c)** has the fastest initial rate.

Cc 14.5 **(c)** The reaction is most likely second order because its rate depends on the concentration (therefore, it cannot be zero order), and its half-life depends on the initial concentration (therefore, it cannot be first order). For a second-order reaction, a doubling of the initial concentration results in the quadrupling of the rate.

Cc 14.6 Reaction A has a faster rate because it has a lower activation energy; therefore, the exponential factor is larger at a given temperature, making the rate constant larger. (With a larger rate constant and the same initial concentration, the rate will be faster.)

Cc 14.7 **(c)** Since the reactants in part **(a)** are atoms, the orientation factor should be about one. The reactants in parts **(b)** and **(c)** are both molecules, so we expect orientation factors of less than one. Since the reactants in **(b)** are symmetrical, we would not expect the collision to have as specific an orientation requirement as in **(c)**, where the reactants are asymmetrical and must therefore collide in such way that a hydrogen atom is in close proximity to another hydrogen atom. Therefore, we expect **(c)** to have the smallest orientation factor.